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ABSTRACTS OF PAPERS
ON
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JOURNAL

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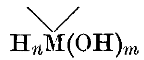
THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Catalytic Reduction of Unsaturated Organic Compounds. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1074—1077).—In the hydrogenation of unsaturated compounds by hydrogen in the presence of metallic hydroxides, complex intermediate compounds are formed of the type



$$\begin{array}{c} R^1\cdot CH\cdot CH\cdot R^2 \\ \diagdown\diagup \\ H_nM(OH)_m \end{array}$$

. These complex compounds yield colloidal solutions, and owing to their continuous formation and decomposition into $R^1CH_2\cdot CH_2R^2 + M(OH)_m$, they constitute the true carriers of the active hydrogen. Z. K.

The Systems Aluminium Bromide and Ethylene Dibromide. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1308—1310).—Aluminium bromide dissolves readily in ethylene bromide, the saturated solution depositing small crystals. The solubility curve is characteristic for the case where the components form no chemical compound. The eutectic point lies at 2° at the approximate composition $AlBr_3,3\cdot37C_2H_4Br_2$. Z. K.

***n*-Butylhexylcarbinol.** SERGIUS BYRTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 876—879).—n-*Butylhexylcarbinol*, $C_{11}H_{24}O$, was obtained by Grignard's reaction by the action of magnesium butyl iodide on heptaldehyde. It is a colourless liquid with an odour something like that of the juice of *Conium maculatum*. It has b. p. 223·5—225°/750·7 mm., 229·1—230·6° (corr.), D_0^0 0·8378, $D_0^{17\cdot5}$ 0·8300, and solidifies at –3·5°. The *acetyl* derivative, $C_{13}H_{26}O_2$, b. p. 232·5—234°/747·7 mm., 239·3—240·8° (corr.), D_0^0 0·8677, $D_0^{17\cdot5}$ 0·8562, has a faint pleasant odour, and solidifies at –1·5°. When oxidised with chromic mixture, the carbinol forms acids and n-*butyl hexyl ketone*, $C_{11}H_{22}O$, b. p. 218—221°/742 mm., 223·9—226·9° (corr.), D_0^0 0·8401, $D_0^{17\cdot5}$ 0·8320, which is a liquid of pleasant odour and forms a *semicarbazone*, $C_{12}H_{25}ON_3$, m. p. 64·5°. Z. K.

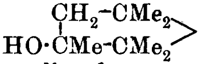
Action of Magnesium Amalgam on Acetone. βγε-Trimethylhexan-βγε-triol and Some of its Derivatives. LOUIS BOUVEAULT and RENÉ LOCQUIN (*Ann. Chim. Phys.*, 1910, [viii], 21, 407—419, 425—432).—A more detailed account of the results published already by Richard and Langlais (Abstr., 1910, i, 455), with further particulars regarding the course of the reaction. The products resulting from the treatment of acetone with magnesium amalgam are of two kinds: (1) those derived from 2 mols. of acetone, namely, pinacone, mesityl oxide, β-methylpentan-β-ol-δ-one (see below), and the glycol corresponding with the last-mentioned alcohol; and (2) those derived from 3 mols. of acetone, namely, *iso*phorone and βγε-trimethylhexan-βγε-triol. Of these, the third appears to be the most important intermediate product, since from it pinacone, the chief final product, and mesityl oxide appear to be formed by decomposition in the course of the reaction (compare Couturier and Meunier, Abstr., 1902, i, 335; 1905, i, 326).

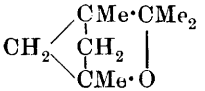
The dihydric alcohol, $C_6H_{14}O_2$, b. p. 102—103°/17 mm. or 188—190°/760 mm., previously referred to (Abstr., 1910, i, 456), furnishes a *diacetate*, b. p. 97—104°/17 mm., and when heated with pyruvic acid yields a *product*, $C_9H_{14}O_3$, m. p. 66°, b. p. 125—130°/17 mm., which crystallises in slender needles, and is provisionally regarded as a "dehydrated pyruvate." These reactions indicate that the dihydric alcohol is β-methylpentan-βδ-diol, and this is confirmed by its preparation by the reduction of β-methylpentan-β-ol-δ-one,

$$HO\cdot CMe_2\cdot CH_2\cdot COMe$$

(Heintz, this Journ., 1876, i, 365), which also occurs in the products of the action of magnesium amalgam on acetone; it has b. p. 75—80°/17 mm., and is readily decomposed on heating, especially in presence of an alkali. Dilute sulphuric acid converts it into mesityl oxide.

βγε-Trimethylhexan-βγε-triol, $OH\cdot CMe_2\cdot CMe(OH)\cdot CH_2\cdot CMe_2\cdot OH$, already described (succeeding abstract, and Abstr., 1910, i, 456), is dealt with in detail in the second paper. On treatment with chromic acid, it is decomposed, yielding 1 mol. each of acetone and β-methylpentan-β-ol-δ-one (see above). When heated alone or with acids, the trihydric alcohol undergoes dehydration, and in the case of acetic anhydride or pyruvic acid furnishes an ester of the dehydrated product.

When heated alone, the alcohol loses $1H_2O$, giving a *substance* (*a*), , m. p. 77°, b. p. 75°/10 mm., which crystallises in needles from a mixture of light petroleum and ether, and this on boiling with 20% sulphuric acid is transformed into a *cyclic oxide* (*b*) (annexed formula), b. p. 126—127°, D^{25} 0·826, a mobile oil having a terpene-like odour. Both these products are formed when the trihydric alcohol is boiled with 20% hydrochloric acid, and (*b*) almost entirely when 20% sulphuric acid is used, although in this case a minute amount of an *isomeride* (?) of (*a*) is produced. This has b. p. 168°/760 mm. With a boiling saturated solution of oxalic acid, substance (*a*) only is formed. Boiling acetic anhydride converts the trihydric alcohol into a *dehydrated monoacetate,* $C_{11}H_{20}O_3$, b. p. 89°/17 mm., D_4^0 0·989, which appears to be the acetyl derivative of substance (*a*), since it is also formed by the acetylation of the latter.



Pyruvic acid heated with the alcohol yields a substance (*b*) in small quantity, and in addition a *dehydrated pyruvate,* $C_{12}H_{18}O_3$, m. p. 122°, b. p. 140°/13 mm., which crystallises in needles, and is probably the pyruvate of substance (*a*), since it is also produced from this by the action of pyruvic acid. T. A. H.

Synthesis of βζ-Dimethylheptan-βδζ-triol and of βγε-Trimethylhexan-βγε-triol. II. LOUIS BOUVEAULT and FERDINAND LEVALLOIS (*Ann. Chim. Phys.*, 1910, [viii], 21, 419—425).—This work was undertaken with a view to the determination of the constitution of the trihydric alcohol obtained by the action of magnesium amalgam on acetone (preceding abstract, and Richard and Langlais, Abstr., 1910, i, 455), which was at one time thought to be the first, but is now known to be the second, of the two substances synthesised.

βζ-Dimethylheptan-βδζ-triol,

$OH\cdot CMe_2\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot CMe_2\cdot OH$,

m. p. 54°, b. p. 155—160°/18 mm., obtained by the interaction of magnesium methyl iodide with methyl β-hydroxyglutarate, is a colourless liquid of sweet taste, and somewhat resembles glycerol.

Methyl citramalate (α-methylmalate), which was used as the starting point for the preparation of the trihydric alcohol, is not easily obtained in good yield by Michael's process (Abstr., 1893, i, 146). For its preparation, ethyl acetoacetate was treated with anhydrous hydrogen cyanide in presence of triethylamine, and the resulting *nitrile,*

$OH\cdot CMe(CN)\cdot CH_2\cdot CO_2Et$,

b. p. 133°/20 mm., saturated with dry hydrogen chloride in presence of excess of methyl alcohol, and the resulting imino-ether hydrochloride poured on ice, treated with potassium carbonate, and the methyl citramalate, b. p. 112°/15 mm., extracted with ether and purified by distillation. With magnesium methyl iodide, it furnished βγε-trimethylhexan-βγε-triol, $OH\cdot CMe_2\cdot CMe(OH)\cdot CH_2\cdot CMe_2\cdot OH$, identical with that described already (preceding abstract, and Richard and Langlais, Abstr., 1910, i, 455). T. A. H.

Aliphatic Nitro-compounds. VIII. α-Nitropropionic Acid. Wilhelm Steinkopf and Alexander Supan (*Ber.*, 1910, 43, 3239—3249. Compare Abstr., 1909, i, 559, 874).—Ethyl α-nitropropionate can be prepared by the action of concentrated alcoholic ammonia on ethyl nitro*iso*succinate; the first product is the ammonium salt of the *aci*-nitro-ester, m. p. 119° (decomp.), but this reacts with dilute sulphuric acid, yielding the free ester.

Ethyl nitro*iso*succinate is best prepared by nitrating ethyl *iso*succinate with a mixture of fuming nitric acid and acetic anhydride (compare Bouveault and Wahl, Abstr., 1904, i, 795). It has b. p. 121—122°/11 mm., whereas Salway gives 108°/13 mm., and Ley and Hantzsch give 126—127°/10 mm. The yields obtained by methylating ethyl nitromalonate by Ulpiani's method (Abstr., 1903, i, 791) or by Purdie's method (Trans., 1899, 75, 157) are poor.

The *ammonium* salt of α-nitropropionamide, $C_3H_9O_3N_3$, formed by heating ethyl α-nitropropionate with concentrated alcoholic ammonia for two hours at 100°, crystallises from a mixture of alcohol and ether, and has m. p. 127—128°. The *amide*, $NO_2\cdot CHMe\cdot CO\cdot NH_2$, is best prepared by converting the ammonium salt into the insoluble lead salt, suspending this in dry ether, and passing in dry hydrogen sulphide at 0°. It crystallises from chloroform or ether in slender, colourless needles, m. p. 68—69°. Chlorine reacts with an ice-cold aqueous solution of the ammonium salt, yielding *α-chloro-α-nitropropionamide*, $NO_2\cdot CClMe\cdot CO\cdot NH_2$, which crystallises from water in glistening, colourless plates, m. p. 82°. The corresponding *bromo*-derivative, $C_3H_5O_3N_2Br$, has m. p. 89°. The *dipotassium* salt of α-nitropropionic acid, $C_3H_3O_4NK_2,EtOH$, is obtained as long needles when the ammonium salt of ethyl *aci*nitropropionate is boiled for fifteen minutes with an alcoholic solution of potassium hydroxide (20%). The corresponding *sodium* salt, $C_3H_3O_4NNa_2$, separates from a mixture of alcohol and water in long needles.

α-Nitropropionic acid, $NO_2\cdot CHMe\cdot CO_2H$, is obtained by suspending the silver salt in a small amount of water, and adding the theoretical amount of *N*-hydrochloric acid and extracting rapidly with ether, or by mixing a concentrated aqueous solution of the sodium salt with much ether, cooling in a freezing mixture, and shaking whilst the theoretical amount of *N*-hydrochloric acid is added. The ethereal solution is dried with phosphoric oxide and the ether removed. It crystallises from carbon disulphide in long, colourless needles, m. p. 61—61·5° (decomp.).

Nitroacetaldehydephenylhydrazone is formed by the action of an aqueous solution of benzenediazonium chloride on a not too dilute solution of sodium α-nitropropionate. It crystallises from alcohol in golden-yellow plates, m. p. 136·5°.

Nitroacetic acid can be obtained from its potassium salt in much the same manner as the nitropropionic acid from its sodium salt.

The conversion of ethyl nitro*iso*succinate into ethyl nitropropionate and then into nitropropionamide by means of ammonia supports Ratz's view regarding the mechanism of the reaction between ethyl nitromalonate and ammonia (compare Abstr., 1904, i, 857). J. J. S.

Ammonium Salts of Fatty Acids (Oleic, Palmitic, Stearic), and the Separation of the Saturated Fatty Acids (Palmitic and Stearic) from Oleic Acid. I. Pietro Falciola (*Gazzetta*, 1910, **40**, ii, 217—229).—The author has studied the composition and the solubilities (in some cases quantitatively) of the ammonium salts of the fatty acids mentioned, and has found that the oleate is soluble in cold alcohol, whilst the palmitate and stearate are not. The quantitative separation is effected by dissolving the mixture of acids in warm ether, passing ammonia through the solution, and allowing it to cool to the ordinary temperature. When almost all the ether has evaporated, the pasty residue is extracted with cold ammoniacal alcohol (at about 0°), filtered at the pump, and washed with a further portion of this solvent. From precipitate and filtrate the separated free fatty acids can be liberated by treatment with dilute hydrochloric acid. The methods gives results sufficiently accurate for technical analysis.

When concentrated aqueous ammonia is added to a warm alcoholic solution of stearic acid, *ammonium stearate*, $C_{18}H_{35}O_2{\cdot}NH_4$, separates as a crystalline precipitate on cooling. When heated, it undergoes change at 90°, and is completely melted at about 110° (with evolution of gas). It loses ammonia on keeping, and, after treatment with water, the crystals have the composition of the *acid* salt,

$$C_{18}H_{36}O_2,C_{18}H_{35}O_2{\cdot}NH_4.$$

The *palmitate*, $C_{16}H_{31}O_2{\cdot}NH_4$, is similarly prepared, and has similar properties. It softens towards 90°, and melts completely above 100° (with evolution of gas). Treatment with water converts it into the *acid* salt, $C_{16}H_{32}O_2,C_{16}H_{31}O_2{\cdot}NH_4$. The *oleate*, $C_{18}H_{33}O_2{\cdot}NH_4$, is prepared by passing ammonia into an ethereal solution of oleic acid. It loses ammonia when kept in the air. With water, it yields a gelatinous colloidal solution. R. V. S.

The Elaidin Reaction. Sergius Fokin (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1068—1073).—From theoretical reasoning it seems probable that the elaidin reaction given with oleic acid by sulphurous and nitrous acids would also be given by many other substances, capable like these of internal re-grouping and existence in at least two forms of different configuration. Phosphoric and phosphorous acids both give the elaidin reaction with oleic acid when heated at 170—180° in a slow current of hydrogen and then in a sealed tube, the former acid reacting more rapidly than the latter. In the presence of phosphorus trichloride, the reaction is still slower.

Tetranitromethane and ethyl nitrite both convert oleic acid into elaidic acid, an additive compound of the nitromethane and unsaturated acid being formed, and gases also evolved in the former case. Elaidic acid when heated with phosphoric acid for thirty to forty hours at 180°, yields an oleic acid, which does not react with ethyl nitrite, is more stable than elaidic or ordinary oleic acid, and seems to be identical with the oleic acid obtained by the prolonged action of sunlight on the ordinary acid. Z. K.

The Optical Behaviour of Lactic Acid in a Meat Preparation. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1910, **69**, 471—473). —In an American meat-juice it was noticed that in time the sarcolactic acid passes more and more into an inactive modification of the acid. In the course of a year the change was almost complete. It is suggested that the cause is the presence of a large amount of potassium dihydrogen phosphate. W. D. H.

New Method for Preparation of Glycidic Esters. GEORGES DARZENS (*Compt. rend.*, 1910, **151**, 883—884).—Ethyl α-chloro-β-hydroxy*iso*valerate is conveniently prepared by adding magnesium amalgam to a mixture in molecular proportions of acetone and ethyl dichloroacetate dissolved in benzene, the product being then treated with water. Esters of this type are readily converted into the corresponding glycidic esters; thus, on treating the foregoing compound with sodium ethoxide, a theoretical yield of ethyl $\beta\beta$-dimethylglycidate is obtained. Although the condensation of ethyl dichloroacetate with ketones other than acetone has not been successful, yet this method of synthesising glycidic esters appears to be general, inasmuch as the required hydroxy-ester can always be obtained through the action of hypochlorous acid on the corresponding unsaturated acid. W. O. W.

Pinacolin Derivatives. A. RICHARD (*Ann. Chim. Phys.*, 1910, [viii], **21**, 323—406. Compare Abstr., 1910, i, 455, 458, 462).—This work was undertaken in order to ascertain what influence the ψ-butyl group has on the stability of the compounds in which it occurs, and particularly whether the unsymmetrical character of substances containing this group gives rise to any peculiar form of isomerism. The results obtained show that the alkyl chlorides containing this group allow of ready molecular transformation when they contain a hydrogen atom attached to the carbon, which carries the chlorine atom, but in no case was any isomerism noticed among the acids containing this group.

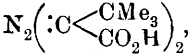
Methyl pivalate has D_4^0 0·891. The ethyl ester has D_4^0 0·875, and on reduction by Bouveault and Blanc's method (Abstr., 1903, i, 597) furnishes $\beta\beta$-dimethylpropyl alcohol, $CMe_3{\cdot}CH_2{\cdot}OH$ (Tissier, Abstr., 1893, i, 542), m. p. 50°, b. p. 113—115°/760 mm. or 64°/100 mm., which yields a *phenylurethane*, m. p. 114°, and a *pyruvate*, b. p. 78—80°/23 mm., the *semicarbazone* of which is crystalline and melts at 166°. On saturation with dry hydrogen chloride, the alcohol yields the corresponding chloride, b. p. 87—90°, but this dissociates when heated into β-methyl-Δ^{β}-butylene and hydrogen chloride, and the former, when re-combined with hydrogen chloride and then transformed into the acetate and the latter hydrolysed, yields the isomeric *tert.*-alcohol, $CMe_2(OH){\cdot}CH_2Me$ (compare Tissier, *loc. cit.*). Magnesium $\beta\beta$-dimethylpropyl chloride on treatment with oxygen furnishes an *alcohol*, m. p. $-12°$, b. p. 101—103°, D_4^0 0·827, possessing a camphoraceous odour, which on heating with pyruvic acid is not esterified, but is dehydrated, yielding β-methyl-Δ^{β}-butylene. Bouveault has shown that this reaction is characteristic of tertiary alcohols (Abstr., 1904, i, 465). With phenylcarbimide, dehydration also occurs. With carbon dioxide, magnesium ββ-dimethylpropyl chloride gives rise to ββ-dimethylbutyric acid.

Pinacolin may be reduced by sodium in alcohol, potassium hydroxide in alcohol, or sodium in moist ether, giving in all cases good yields of pinacolyl alcohol (compare Friedel and Silva, this Journ., 1873, **26**, 488). The latter furnishes a *pyruvate*, b. p. 78—80°/17 mm., and the *semicarbazone* of this is crystalline and melts at 175°. The magnesium derivative of the chloride of this alcohol on treatment with oxygen yields dimethyl*iso*propylcarbinol, which confirms Couturier's observation that the chloride is unstable and on heating yields βγ-dimethyl-Δ^{β}-butylene. The present transformation may be represented thus :

$$CMe_3 \cdot CMeHCl \longrightarrow CMe_2{:}CMe_2 \longrightarrow CMe_2Cl \cdot CHMe_2 \longrightarrow OH \cdot CMe_2 \cdot CHMe_2.$$

With carbon dioxide, magnesium pinacolyl chloride furnishes *ααβ-trimethylbutyric acid*, m. p. 50°, b. p. 106°/15 mm.

ααββ-Tetramethylpropyl chloride (Henry, Abstr., 1906, i, 477) reacts with magnesium methyl iodide, forming a product which on treatment with carbon dioxide gives ββγγ-tetramethylbutane (*loc. cit.*, p. 473) and ααββ-tetramethylbutyric acid, $CMe_3 \cdot CMe_2 \cdot CO_2H$. This chloride is therefore much less liable to undergo intramolecular transformation than those described above, due to the fact that it contains no free hydrogen atom associated with the carbon carrying the chlorine atom.

Trimethylpyruvic acid, $CMe_3 \cdot CO \cdot CO_2H$, prepared by Glücksmann's method (Abstr., 1890, i, 237), crystallises in the absence of moisture, and then melts at 125°. In moist air it absorbs $\frac{1}{2}H_2O$, and then has m. p. 90°. The *oxime*, m. p. 85°, crystallises in colourless spangles ; the *hydrazone*,  $N_2\left({:}C{<}\begin{matrix}CMe_3\\CO_2H\end{matrix}\right)_2$, m. p. 207°, forms sulphur-yellow needles, and the *semicarbazone* has m. p. 195° (decomp.). The *methyl* ester, b. p. 69—70°/20 mm. or 160—162°/760 mm., D_4^0 0·994, is a colourless, mobile oil, and furnishes a *semicarbazone*, m. p. 125°, and an *oxime*, m. p. 66°, b. p. 125°/20 mm. The *ethyl* ester, b. p. 76—77°/20 mm., yields a *semicarbazone*, m. p. 115°, and an *oxime*, m. p. 22—23°, b. p. 131—133°/20 mm., which reacts with phenylcarbimide to give a *phenylurethane*, m. p. 123—124°, crystallising in long, brilliant needles. On reduction, the oxime yields *ethyl α-amino-ββ-dimethylbutyrate*, $CMe_3 \cdot CH(NH_2) \cdot CO_2Et$, b. p. 83°/15 mm., D_4^0 0·952, which with phenylcarbimide yields the corresponding *phenylcarbamide*, m. p. 78°, with benzoyl chloride gives *ethyl ψ-butylhippurate*, m. p. 64°, b. p. 198—200°/15 mm., and also yields a *picrate*, m. p. 134°.

Trimethylpyruvic acid condenses with aniline to form a product which, on distillation, yields αα-dimethylpropaldehyde (compare Bouveault, Abstr., 1896, i, 649) and some *ββ-dimethylpropylideneaniline*, $CMe_3 \cdot CH{:}NPh$, b. p. 101—102°/20 mm., D_4^0 0·941. αα-Dimethylbutaldehyde yields an *oxime*, m. p. 41°, b. p. 65°/20 mm., and an *azine*, m. p. 79°. Ethyl trimethylpyruvate combines with anhydrous hydrogen cyanide in presence of trimethylamine, forming the cyanohydrin (Carlinfanti, Abstr., 1899, i, 671), and this, on hydrolysis with sulphuric acid at − 15°, is converted into the *amide* of *ethyl ψ butyltartronate*, $CMe_3\cdot C(OH)(CO\cdot NH_2)\cdot CO_2Et$, m. p. 60°, b. p. 162—164°/15 mm. With ammonia in alcohol, ethyl trimethylpyruvate forms a *substance*, $C_{12}H_{21}O_2N_3$, m. p. 225°, which is crystalline.

When methyl or ethyl trimethylpyruvate is treated with magnesium methyl iodide or magnesium methyl bromide, α-hydroxy-αββ-trimethylbutyric acid or its ester is formed, with a small amount of the aldehyde corresponding with this acid. Pinacolin combines with hydrogen cyanide to form α-hydroxy-αββ-trimethylbutyronitrile (Carlinfanti, Abstr., 1898, i, 234), m. p. 113°, b. p. 90°/12 mm., and this on treatment with sulphuric acid at 0° is hydrolysed to the *amide*, m. p. 140—141°, b. p. 170°/10 mm. (decomp.), which is converted by boiling with hydrochloric acid into *α-hydroxy-αββ-trimethylbutyric acid*, $CMe_3\cdot CMe(OH)\cdot CO_2H$, m. p. 141°, b. p. 130°/14 mm. The *methyl* ester, b. p. 65·5°/12 mm., D_4^0 1·002, and the *ethyl* ester, b. p. 74°/12 mm., D_4^0 0·975, are oils, the latter having a camphoraceous odour. The acid condenses with chloral to form a *chloralide*, m. p. 85°, b. p. 126—127°/14 mm.

When methyl hydroxytrimethylbutyrate is treated with magnesium methyl iodide, it yields (1) *α-hydroxy-αββ-trimethylbutaldehyde*, b. p. 82—84°/16 mm., which gives an *oxime*, m.p. 65°, b.p. 126—127°/15 mm., that regenerates the nitrile on treatment with acetic anhydride, and (2) *ββγδ-tetramethylamylene βγ-glycol*, $HO\cdot CMe_2\cdot CMe(OH)\cdot CMe_3$, m. p. 22°, b. p. 96—98°/16 mm., and this, when boiled with 20% sulphuric acid, furnishes the hexamethylacetone described by Haller and Bauer (Abstr., 1910, i, 219).

α-Hydroxy-ββ-dimethylbutyric acid yields a *chloralide*, m. p. 63°, b. p. 130°/15 mm., and, when heated at 240°, gives αα-dimethylpropaldehyde (see above) and a less volatile material, which, on distillation under reduced pressure, furnishes (1) *trimeric αα-dimethylpropaldehyde*, b. p. 104—105°/18 mm., D_4^0 0·979, and (2) the *dilactide* of *α-hydroxy-ββ-dimethylbutyric acid*, m. p. 84°, b. p. 148°/13 mm., a substance crystallising in brilliant spangles. αα-Dimethylpropaldehyde combines with hydrogen cyanide in presence of pyridine, forming *α-hydroxy-ββ-dimethylbutyronitrile*, b. p. 100°/100 mm., D_4^0 0·911, and this, on hydrolysis by sulphuric acid at 0°, gives the corresponding *amide*, m. p. 135°, which, when boiled with hydrochloric acid, furnishes the corresponding acid; the *methyl* ester of the latter has b. p. 69—70/16 mm., D_4^0 1·044, and the *ethyl* ester has b. p. 79—80°/16 mm. and D_4^0 0·987. The acid, on treatment with phosphorus pentachloride, followed by methyl alcohol, furnishes (1) a *liquid*, $C_9H_{19}O_6P$, b. p. 165—170°/23 mm., D_4^0 1·437, which is neutral to litmus, and possesses an alliaceous odour; (2) dimethyl hydrogen phosphate; (3) methyl hydroxydimethylbutyrate; (4) an *acid*, b. p. 75—90°/22 mm., and (5) a second *acid*, b. p. 150—155°/22 mm. The first substance probably has the constitution

$$PO(OMe)_2\cdot O\cdot CH(CMe_3)\cdot CO_2Me.$$

Under like conditions with phosphorus pentabromide, a neutral substance, $C_7H_{13}O_2Br$, b. p. 115—125°/23 mm., is formed. Phosphorus tribromide reacts with ethyl hydroxydimethylbutyrate to give two products, *one* having b. p. 85—90°/20 mm., and the *other*, 190—215°/20 mm. With phosphorus tri-iodide the methyl ester yields an *iodo*-compound, having b. p. 102—105°/18 mm., and a *substance*, b. p. 200°/18 mm. (approx.), which contains phosphorus.

T. A. H.

The Photo-chemical Inversion of Maleic Acid. Ludwik Bruner and M. Królikowski (*Bull. Acad. Sci. Cracow*, 1910, 192—208).—As a preliminary step in the investigation of the photo-chemical transformation of maleic into fumaric acid in presence of a small quantity of bromine, the authors have measured the rates at which the two acids take up bromine with the formation of dibromosuccinic acid. The experiments were made in dilute aqueous solntion at 25° in the dark, the reacting substances being present in equimolar proportions. The values obtained for the velocity constant, on the assumption that the reaction is bimolecular, decrease as the reaction proceeds, and this is found to be due to the increasing acidity of the solution as a consequence of the formation of bromomalic acid and hydrobromic acid by hydrolysis of the dibromosuccinic acid formed in the primary reaction. In support of this view, it is found that the addition of mineral acids diminishes the rate of the reaction, but if these are present in considerable excess, the progress of the reaction is in agreement with the equation for a bimolecular change. Under these conditions it is found that the rate at which bromine is taken up by maleic acid is fifteen times as great as for fumaric acid.

In connexion with the photo-chemical inversion, two methods have been worked out for the quantitative estimation of fumaric and maleic acids in their mixed solutions. These depend respectively on measurements of the electrical conductivity and of the solubility of fumaric acid in the solutions.

The rate of transformation of maleic acid into fumaric in presence of a trace of bromine and in sunlight shows that the reaction is unimolecular. If the light is removed whilst the reaction is in progress, the inversion process ceases, and there appears to be no after effect. The active rays are those at the blue end of the spectrum, the reaction ceasing when a 2 cm. layer of 7·5% potassium dichromate or of 5% bromine solution is interposed.

Between 16° and 32° the velocity of the inversion is practically independent of the temperature. The proportion of maleic acid, which is transformed when the reaction comes to an end, increases with the amount of bromine present in the solution. For small concentrations of bromine, the percentage of fumaric acid in the equilibrium mixture is approximately proportional to the quantity of bromine present.

For a definite amount of bromine the proportion of fumaric acid in the final mixture diminishes as the concentration of the maleic acid increases. If fumaric acid is added to the original solution, the proportion of maleic acid which is inverted diminishes. On the other hand, addition of other acids, such as nitric and sulphuric acids, increases the proportion of the maleic acid which is finally transformed.

H. M. D.

Action of Zinc and Magnesium Organic Compounds on Ortho-formic Ester. M. L. SHDANOVITSCH (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1279—1297).—When zinc reacts on a mixture of ethyl ortho-formate and ethyl α-bromo*iso*butyrate in the absence of any solvent, the following products are obtained: (1) *Ethyl ββ-diethoxy-αα-dimethylpropionate*, $CH(OEt)_2{\cdot}CMe_2{\cdot}CO_2Et$, b. p. 211—212°/748·2 mm., D^{19}_{19} 0·9520, n_{19} 1·41886, which when heated with nitric acid readily yields dimethylmalonic acid, m. p. 184—185·5° (decomp.). (2) Ethyl tetramethylacetoacetate, $CHMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$, which when hydrolysed with hydrochloric acid yields di*iso*propyl ketone, the semicarbazone of which has m. p. 153—154·5° (Blaise gives 150—151°). (3) *Ethyl γ-keto-ααββδδ-hexamethyladipate*,

$$CO_2Et{\cdot}CMe_2{\cdot}CMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et,$$

b. p. 303—309°/760 mm. (4) An *unsaturated keto*-ester, probably $CH_2{:}CMe{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$, which on hydrolysis yields methacrylic acid, $CH_2{:}CMe{\cdot}CO_2H$, of which the silver salt was analysed. (5) The resinous product obtained after the distillation of the crude product yields, on hydrolysis, a quantity of cubic crystals, possibly tetramethylsuccinic acid. The *silver* salt, $C_{13}H_{19}O_6Ag_3$ or $C_8H_{12}O_4Ag_2$, was analysed; some butaldehydes were also found amongst the products. When magnesium is substituted for zinc, the chief products of the reaction are: (1) ethyl tetramethylacetoacetate; (2) *ethyl β-keto-δδ-diethoxy-ααγγ-tetramethylvalerate*,

$$CH(OEt)_2{\cdot}CMe_2{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et,$$

b. p. 160—161°/23 mm., 272—273°/760 mm., a yellow liquid with a pleasant sweet odour; (3) ethyl β-hydroxytetramethylglutarate,

$$CO_2Et{\cdot}CMe_2{\cdot}CH(OH){\cdot}CMe_2{\cdot}CO_2Et,$$

which is separated from the acetal with great difficulty. Z. K.

Cholic Acid. II. MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1910, **69**, 383—389).—Reductodehydrocholic acid (Abstr., 1910, i, 10) is now found to have m. p. 190—192° (not sharp), and is dextrorotatory, $[\alpha]_D = +29°$, when dissolved in alcohol. It appears to be identical with the acid obtained by Hammarsten by reducing dehydrocholic acid with sodium amalgam.

A modified method is given for obtaining cholic acid from ox gall and for preparing some of its known derivatives; for this the original paper must be consulted. An examination of cholanic acid, $C_{24}H_{36}O_7$, showed that six of the oxygen atoms are in three carboxyl groups, while the seventh is in a keto-group. The author has succeeded in preparing an oxime, $C_{24}H_{36}O_6{:}N{\cdot}OH$, crystallising in plates or needles from acetone, which begins to decompose at 160°, and is completely decomposed at 197°. E. J. R.

Complex Derivatives of Molybdic Acid. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 439—445. Compare Abstr., 1910, i, 657, 708).—Determinations of the rotatory power of solutions of tartaric acid and molybdates are complicated by the variations in the acidity and ionisation with the composition of the solution, and it is preferable to examine solutions containing only tartaric and molybdic acids. The addition of other acids to such a solution lowers the rotatory power, hydrochloric acid having a greater effect than acetic, and the rotatory power tends to a limit when the quantity of hydrochloric acid is increased. The conclusion is drawn that the exaltation observed on adding further quantities of molybdic acid to molybdotartaric acid is specific, and is due to the formation of complexes. Cryoscopic determinations show that the group $C_4H_4O_6,MoO_3$, is largely polymerised in solution. On the other hand, sodium molybdo-oxalate has a normal molecular weight. C. H. D.

Complexes of Permolybdic and Pertungstic Acids with Active Organic Acids. ARRIGO MAZZUCCHELLI and MARIO BORGHI (*Gazzetta*, 1910, 40, ii, 241—261).—The rotatory power of the *ammonium molybdotartrate*, $(NH_4)_2C_4H_4O_6,MoO_3$, at different concentrations agrees fairly well with those observed by Rosenheim and Itzig (Abstr., 1900, i, 135, 272) for the potassium and sodium salts of this composition, so that it may be considered to produce the same active ion. To solutions of this salt containing in combination 1·646% of tartaric acid (by volume), hydrogen peroxide was added in the quantity required by the ratio $MoO_3 : 2H_2O_2$. The specific rotatory power of the tartaric acid is thereby reduced from +528° to +203°. It rises again when the solution is kept, owing to catalytic decomposition of the hydrogen peroxide, and if this decomposition is accelerated by the addition of amyl alcohol (compare Brode, Abstr., 1901, ii, 433) the specific rotatory power reaches its initial value in the course of some hours. The change of specific rotatory power caused by hydrogen peroxide is not due to scission of the molybdotartaric ion into ozomolybdate and tartaric acid, because when more hydrogen peroxide is added, making the ratio $MoO_3 : 3H_2O_2$, no further change in rotatory power occurs. The specific rotatory power in a solution containing hydrogen peroxide in the ratio $MoO_3 : 3H_2O_2$ diminishes on dilution.

The authors have made experiments to ascertain whether complex ozo-salts exist corresponding with the molybdotartrates containing other numbers of molybdenum trioxide groups, the method adopted being to mix hydrogen peroxide with solutions of tartaric acid and of the yellow acid, $MoO_3,2H_2O$ (compare Rosenheim, Abstr., 1906, ii, 762). The rotatory power attains a maximum when the solution contains $C_4H_4O_6,4MoO_3,4H_2O_2$, so that the existence of a complex of this composition is probable, although for other reasons not certain.

Rosenheim has shown (Abstr., 1904, ii, 128) that white molybdic acid, MoO_3,H_2O, differs from the yellow dehydrated acid, $MoO_3,2H_2O$, even in solution. White α-molybdic acid is readily obtained by treating methyl molybdate with water. Its behaviour with tartaric acid and hydrogen peroxide is analogous to that of the yellow acid, but the rotatory powers of solutions of the same composition are different, and the maximum corresponds with the existence of a compound $C_4H_4O_6,5(MoO_3,H_2O_2)$, thus affording a further proof of the difference between the two acids.

Solutions of sodium molybdomalate, obtained by mixing equimolecular quantities of sodium molybdate and malic acid, containing 1 mol. of hydrogen peroxide, rapidly decompose, and the specific rotatory power of the malic acid returns to the value +151° due to the molybdomalate. When an excess of hydrogen peroxide is taken, the specific rotation at first is about $-140°$, but eventually it becomes $+151°$. It is considered that the hydrogen peroxide in the undecomposed solution forms the complex $Na_2C_4H_4O_5,MoO_4$.

Similar experiments with solutions of sodium tungstotartrate, $Na_2C_4H_4O_6.WO_2$, indicate the formation of a complete ozotungstotartrate, which contains probably equimolecular quantities of tungsten trioxide and hydrogen peroxide (compare Mazzucchelli and Inghilleri, Abstr., 1908, i, 755). The rotatory power does not alter when the solution is kept, so that the decomposition of the hydrogen peroxide is slower in presence of tungsten trioxide than in the presence of molybdenum trioxide (compare Brode, *loc. cit.*). R. V. S.

Resolution of Pentane-ββδ-tricarboxylic Acid and of a *s*-Dimethylglutaric Acid into Optically Active Components.

Elof Möller (*Ber.*, 1910, **43**, 3250—3251).—Pentane-ββδ-tricarboxylic acid, $CMe(CO_2H)_2\cdot CH_2\cdot CHMe\cdot CO_2H$, obtained by condensing ethyl α-bromo*iso*butyrate with the sodio-derivative of ethyl *iso*succinate and hydrolysing the resulting ester, separates from water in slender crystals, and has $K = 0{\cdot}220$ at 25°. The *potassium* salt, $C_8H_{11}O_6K$, forms readily soluble prisms, and the *normal* salt, $C_8H_9O_6K_3,H_2O$, transparent, deliquescent crystals. It can be resolved by means of strychnine; the salt of the *d*-acid is sparingly soluble, and crystallises in long, pointed needles, whereas the salt of the *l*-acid forms long, transparent prisms. The *d*-acid has $[\alpha]_D^{20}$ $+16{\cdot}3°$, and the *l*-acid $[\alpha]_D^{20}$ $-15{\cdot}6°$, in aqueous solution. The *d*-acid evolves carbon dioxide at 140°, and yields a dimethylglutaric acid with $[\alpha]_D^{20}$ $+16{\cdot}2°$; the *l*-acid under similar conditions yields a dibasic acid with $[\alpha]_D^{20}$ $-15{\cdot}7°$. The inactive acid evolves carbon dioxide at 135°, and at 140° yields a mixture of the two *s*-dimethylglutaric acids. These can be separated by means of their calcium hydrogen salts, and the acid with m. p. 140—141° can be resolved by means of strychnine into its active constituents. The salt of the *d*-acid crystallises, first, in large prisms, and then the salt of the *l*-acid in small, felted needles.

The *d*-acid has $[\alpha]_D^{20}$ $+41{\cdot}9°$, and the *l*-acid, $[\alpha]_D^{20}$ $-24{\cdot}3°$. The acid melting at 141° is thus the racemic form, and the acid with m. p. 128° the meso-form. J. J. S.

Glucodeconic Acids.

L. H. Philippe (*Compt. rend.*, 1910, **151**, 986—988).—The preparation of α-glucodeconic acid, $C_{10}H_{20}O_{11}$, from gluconose by Fischer's method is described. The acid could not be isolated in a pure state, since on concentrating its aqueous solutions, crystals were deposited consisting of an hydrated *lactone*,

$$C_{10}H_{18}O_{10},H_2O,$$

m. p. 168° (anhydrous, m. p. 214°), $[\alpha]_D^{20}$ $-37{\cdot}2°$, together with an *anhydride*, $(OH\cdot CH_2\cdot[CH(OH)]_8\cdot CO)_2O$, m. p. 250°. These were separated by taking advantage of the much greater solubility of the former compound. Both substances after hydrolysis yield the same *phenylhydrazide*, crystallising in rectangular lamellæ, m. p. 268°. The acid forms an ill-defined *amide*, $C_{10}H_{21}O_{10}N$, m. p. about 250°. The *sodium*, *barium*, *zinc*, *copper*, *lead*, and *cadmium* salts are sparingly soluble;

the *brucine*, *quinine*, *morphine*, and *strychnine* salts have been prepared. W. O. W.

The Oxidation of Aldehydes in Alkaline Solution. GEORGE W. HEIMROD and PHŒBUS A. LEVENE (*Biochem. Zeitsch.*, 1910, **29**, 31—59).—The authors studied the oxidation of various substances in alkaline solution, using principally hydrogen peroxide as the oxidising agent, and, by means of a specially constructed apparatus which is figured, estimated the hydrogen evolved, and also estimated the carbon dioxide and formic acid formed. They confirmed the observations of previous observers that formaldehyde yields on treatment with hydrogen peroxide, hydrogen gas, and assumed that the evolution of this gas is evidence of the formation of formaldehyde as an intermediate product of oxidation when it is obtained from other substances. Ethylene glycol, under the conditions of oxidation chosen, evolved no hydrogen, whereas glycerol did, and the authors give equations to represent what they consider to be the mechanism of oxidation of this substance. They also investigated the oxidation of acetaldehyde, and its possible intermediate oxidation products, glycollaldehyde, glyoxal, glycollic acid, and glyoxylic acid, estimating in each case the carbon dioxide and formic acids formed, and give equations showing the various courses of oxidation possible. As a result of their experiment, they draw the conclusion that acetaldehyde oxidises through the following stages: acetaldehyde (vinyl alcohol) —> glycollaldehyde —> glyoxal —> formic acid —> carbon dioxide. There is no evidence of the formation of formaldehyde as an intermediate product. The reaction rates of the oxidation of acetaldehyde under various conditions were also investigated. S. B. S.

Preparation of Aldehyde Diacetates. ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1910, **43**, 3291—3295. Compare Mannich and Hâncu, Abstr., 1908, i, 245; Semmler, Abstr., 1909, i, 239, 312, 364, 594; Wohl and Berthold, Abstr., 1910, i, 620; Blanksma, Abstr., 1909, i, 779; Wegscheider and Späth, Abstr., 1910, i, 155).—It is pointed out that the formation of a monoacetate of the type $R\cdot CH:CH\cdot OAc$ does not necessarily mean that the aldehyde exists in the tautomeric enolic form, as the monoacetates are formed at high temperatures only, whereas diacetates of the type $R\cdot CH_2\cdot CH(OAc)_2$ are formed at moderate temperatures, and it is highly probable that the monoacetates are formed by the decomposition of diacetates at the high temperature used:

$$R\cdot CH_2\cdot CH(OAc)_2 = R\cdot CH:CH\cdot OAc + AcOH.$$

It is shown that Wegscheider's yields can be materially improved if an excess of acetic anhydride is avoided; thus a 90% yield of acetaldehyde diacetate is formed when 1·25 mols. of aldehyde are used for 1 mol. of anhydride, and a 70% yield when equimolecular quantities are taken.

α-Keto-γ-acetoxyvaleric acid, $OAc\cdot CHMe\cdot CH_2\cdot CO\cdot CO_2H$, obtained by heating a mixture of molecular quantities of pyruvic acid, acetaldehyde, and acetic anhydride for five hours at 100° and distilling under reduced pressure, is a colourless oil, b. p. 100—103°/12 mm. and does not decolorise bromine. Ethylidene diacetate is formed at the same time. A good yield of the latter can be obtained by heating paraldehyde with acetic anhydride and a few drops of concentrated sulphuric acid for an hour at 100°.

Acraldehyde diacetate, 64% yield, is best prepared at the ordinary temperature.

Phenylacetaldehyde diacetate, $CH_2Ph\cdot CH(OAc)_2$, has b.p. 147°/15 mm., and the monoacetate of the enolic form does not appear to be formed. A less volatile fraction, however, yields a small amount of glistening plates, $C_{20}H_{22}O_5$, probably $(CH_2Ph\cdot CH\cdot OAc)_2O$. J. J. S.

The History of Chemical Fermentation Hypotheses. WALTHER LÖB (*Biochem. Zeitsch.*, 1910, **29**, 311—315).—A theoretical paper, in which the author, as a result of data obtained from his investigations on the action of the silent discharge on sugar solutions, etc., suggests that one molecule of sugar may first undergo scission into two molecules (glyceraldehyde or dihydroxyacetone), which themselves can undergo further scission into glycollaldehyde and formaldehyde, and, finally, into formaldehyde only. Ethyl alcohol can be formed by reaction between glycollaldehyde and formaldehyde, carbon dioxide being formed at the same time. Equations are given to explain the phenomena. S. B. S.

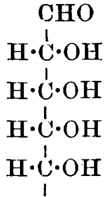
Mutarotation and Electrical Conductivity of Carbohydrates. I. Dextrose. PAUL RABE and CHARLES ROY (*Ber.*, 1910, **43**, 2964—2971).—*N*/10-Solutions of dextrose show no change in conductivity after twenty-four hours at 20°, during which the rotation falls from $[\alpha]_D^{20}$ $+97\cdot5°$ to $+50°$. No change was observed even with the most delicate instruments after five months' further keeping. E. F. A.

β-Dextrose. ROBERT BEHREND (*Annalen*, 1910, **377**, 220—223).—The separation of β-dextrose by cooling a hot solution of α-dextrose in pyridine (Abstr., 1907, i, 481) can only be explained if the β-dextrose crystallises with pyridine. If the β dextrose separates as such, it is possible by selecting two suitable solvents at the same temperature and pressure to create a system in which perpetual motion must occur. It is shown that the β-dextrose does separate in crystals, which rapidly weather and lose pyridine in amount corresponding approximately with 1 molecule of pyridine of crystallisation.

The author arrives at the same result as Dimroth (compare this vol., ii, 31), namely, that the same substance must always separate from solutions, at the same temperature and pressure, of two mutually interconvertible isomerides in any solvent, provided that by-products are not formed. C. S.

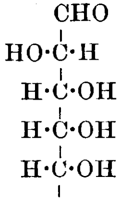
Hexoses from *d*-Ribose. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, **43**, 3141—3147).—The four unknown aldohexoses are theoretically to be derived from the isomeric riboses, but the lack of these pentoses, has hitherto prevented the synthesis of the hexoses.

Nucleic acids now afford a relatively simple means of obtaining *d*-ribose in some quantity, and by the application of the cyanohydrin synthesis, d-*allose* and d-*altrose* have been obtained. They have the annexed configuration.



$$\begin{array}{c} CHO \\ | \\ H\cdot C\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ CH_2\cdot OH \end{array}$$

d-Allose.



$$\begin{array}{c} CHO \\ | \\ HO\cdot C\cdot H \\ | \\ H\cdot C\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ H\cdot C\cdot OH \\ | \\ CH_2\cdot OH \end{array}$$

d-Altrose.

Both are syrups insoluble in alcohol, and have not been obtained free from impurities. They yield the same phenylosazone, and *d*-altronic acid yields talomucic acid on oxidation.

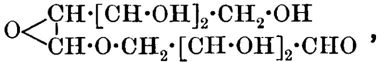
Calcium d-*altronate* is obtained by the addition of hydrogen cyanide to *d*-ribose and hydrolysis of the nitrile formed with barium hydroxide. The solution is rendered slightly acid, and treated in turn with lead carbonate, hydrogen sulphide, and calcium carbonate. It crystallises in thick crusts of cauliflower-like aggregates of needles. The free *acid* is a colourless syrup; the specific rotatory power increases in solution, $[\alpha]_D^{30}$ $+35\cdot14°$.

On reduction, *d*-altrose is obtained as a syrup. The *phenylbenzylhydrazone* crystallises in well formed, yellow, lustrous plates, which sinter at 145°, m. p. 148—150° (corr.). d-*Altrosephenylosazone*, crystallises in long, thin, matted needles or stellate aggregates of platelets, which sinter at 175°, m. p. 183—185° (corr.). It is lævorotatory in pyridine solution.

The mother liquors from the calcium altronate contain calcium allonate. d-*Allonolactone*, $C_6H_{10}O_6$, forms long, colourless prisms, which sinter at 97° and are completely melted to a clear liquid at 120°, and have $[\alpha]_D^{20}$ $-6\cdot79°$ ($\pm0\cdot2°$). d-*Allose*-p-*bromophenylhydrazone* crystallises in lustrous plates, which sinter at 143°, m. p. 145—147° (corr.), $[\alpha]_D^{30}$ $-6\cdot7°$.

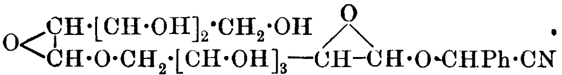
E. F. A.

Constitution of Vicianose and of Vicianin. Gabriel Bertrand and Gustave Weisweiller (*Compt. rend.*, 1910, 151, 884—886. Compare Abstr., 1906, i, 68; 1908, i, 817; Abstr., 1910, i, 156).—The new sugar vicianose, prepared from vicianin, a glucoside occurring in the vetch, has been oxidised by bromine water in presence of calcium carbonate. A calcium vicianobionate was thus obtained, which on hydrolysis gave calcium gluconate and *l*-arabinose. Vicianose, therefore, appears to have the constitution:



$$O\begin{cases} CH\cdot[CH\cdot OH]_2\cdot CH_2\cdot OH \\ | \\ CH\cdot O\cdot CH_2\cdot[CH\cdot OH]_2\cdot CHO \end{cases},$$

whilst the glucoside is represented as:



The other properties of the substances described previously are in agreement with these representations.

W. O. W.

The Degradation of the Sugar Group. Adolf Jolles (*Biochem. Zeitsch.*, 1910, 29, 152—201).—It is shown that the majority of the sugars undergo chemical change at 37° when treated with *N*/100-

alkali hydroxide, the optical rotation of the solution decreasing and the acidity increasing. The latter change continues after the former change has ceased. In certain cases, as, for example, that of sucrose, the change is small. The rate of acid formation is increased by the addition of hydrogen peroxide and silver oxide, although the addition of oxidising reagents does not affect the rate of change in optical activity. Ferments exert but slight influence. If sugars be kept in alkaline medium, the estimation by polariscope becomes, owing to the above-mentioned changes, untrustworthy, although they do not affect the reducing powers. Formic acid and, in case of certain sugars, acetaldehyde were detected as reaction products. Polyhydroxy-acids were not found. The author gives a large number of data showing the rate of the changes in various sugars. S. B. S.

Mutarotation of Maltose. GERHARD SCHLIEPHACKE (*Annalen*, 1910, **377**, 164—188).—The theory that the mutarotation of a sugar in solution is due to the equilibrium of the two stereoisomeric lactone forms of the sugar with one another, and probably also with the aldehydic form, is supported by the relations which have been shown to exist between dextroses of different rotatory powers and their penta-acetates (Behrend and Roth, Abstr., 1904, i, 716), and between galactoses of different rotatory powers and their penta-acetates (Heikel, Abstr., 1905, i, 173). The author has now examined a biose, maltose, with regard to its mutarotation and its acetates. Dissolved in pyridine, the sugar has $[\alpha]_D^{20}$ +97·7° forty minutes after solution, and 122·2° after fourteen days; after being warmed to 50° for ten minutes, the solution attains a constant rotatory power, $[\alpha]_D^{20}$ +123·5°. After being boiled for three minutes and then cooled, the solution attains its maximum rotation, having $[\alpha]_D^{20}$ +128·8°, which falls to 124·0° after one hundred and thirty-two hours.

Ordinary maltose belongs probably to the β-series, since it yields, when acetylated under suitable conditions, chiefly the only known crystalline acetate, Herzfeld's maltose octa-acetate, m. p. 155—156°, which belongs to the β-series, having been converted into β-methylglucoside by Königs and Knorr. When solid maltose in the presence of pyridine at 0° is treated with acetic anhydride, it yields a crude acetate, from which 73·9% of crystallised β-octa-acetate has been obtained together with a syrup which has the composition of an octa-acetate and $[\alpha]_D$ +101·3° in benzene. When a solution of maltose in pyridine, of constant rotation, is acetylated at 0°, 36·1% of the crystallised β-octa-acetate and a syrup having $[\alpha]_D$ +107·4° in benzene are obtained. Finally, when the pyridine solution of maximum rotation obtained by boiling is acetylated at 0°, only 18·8% of the crystallised β-octa-acetate is obtained, together with a syrup having $[\alpha]_D$ +110·6°. These results indicate that the solution of maltose in pyridine contains ordinary β-maltose (which yields the β-octa-acetate) in equilibrium with another or, more probably, two other forms of maltose (which yield the syrup). The rotation of the unknown α-maltose octa-acetate, calculated by Hudson's theory (Abstr., 1909, i, 135), corresponds with $[\alpha]_D$ +131·88° in benzene and +117·51° in chloroform; the values are given with reserve, since it is as yet uncertain whether Hudson's theory is applicable to the acetates of the sugars.

When maltose is acetylated in pyridine there is produced, together with the octa-acetates, about 6% of a *hexa-acetate*, which is an amorphous powder having $[\alpha]_D + 133\cdot96°$ in benzene and $139\cdot96°$ in chloroform; it separates together with the β-octa-acetate from alcoholic solutions, and is separated therefrom mechanically.

By treating β-maltose octa-acetate with liquid hydrogen chloride, Fischer and Armstrong obtained a hepta-acetylchloromaltose having m. p. 66—68° and $[\alpha]_D^{20} + 176\cdot0$—$177\cdot1°$ in benzene. By treating maltose with acetic anhydride and hydrogen chloride, Foerg obtained a hepta-acetylchloromaltose having m. p. 118—120° and $[\alpha]_D\ -159°$ in chloroform. The author hoped to get α-maltose octa-acetate from the latter, but by treatment with glacial acetic acid and anhydrous sodium acetate on the water-bath, it yielded the β-isomeride. The author confirms Foerg's m. p. for the substance, but finds that it has $[\alpha]_D + 158\cdot68°$ in chloroform and $175\cdot66°$ in benzene, the latter value being almost identical with the corresponding value of Fischer and Armstrong's compound. The relation between these two substances, having the same rotatory power but different m. p.'s, has not yet been ascertained; both give the same β-hepta-acetylmethylmaltoside by treatment with methyl alcohol and silver carbonate. C. S.

Carbohydrates Occurring in Seeds. ERNST SCHULZE and URS PFENNINGER (*Zeitsch. physiol. Chem.*, 1910, **69**, 366—382).—A large number of plant seeds contain soluble carbohydrates that give mucic acid on oxidation with nitric acid, and therefore yield galactose on hydrolysis. Raffinose is known to occur in cotton seed, in the embryos of wheat, and of certain leguminous plants; the authors now describe another carbohydrate, *lupeose*, which has not yet been crystallised, but is, they believe, a single substance and not a mixture.

Lupeose has been extracted from seeds of *Lupinus luteus* and *Lupinus angustifolius* by extraction either with hot dilute alcohol or with water; it is then obtained from this solution by precipitation with alcohol. It forms a white powder, readily soluble in water, and does not reduce Fehling's solution until it has been heated with acids. It is dextrorotatory; the different preparations in 4 or 5% solution have given $[\alpha]_D = +138°$ to $+144°$, the differences no doubt arising from the presence of impurities. Oxidation with nitric acid gives rise to 38—40% of mucic acid; presumably, therefore, galactose constitutes half of the products of hydrolysis. Lævulose is also formed on hydrolysis, and there appears to be a third sugar. For this and other reasons lupeose is considered to be more complex than a disaccharide. In several ways lupeose resembles stachyose, but the differences are sufficient to justify the conclusion that the two are distinct. E. J. R.

Mercerised Cellulose. OSWALD MILLER (*Ber.*, 1910, **43**, 3430—3435. Compare Vieweg, Abstr., 1907, i, 893; Schwalbe, *ibid.*, 1909, i, 136, 366).—If cellulose is dried for six hours at 95° both before and after treatment with concentrated sodium hydroxide solution at 10°, there is practically no alteration in weight. The loss in weight of the mercerised product when dried at 95° is the same as when the drying takes place at 22—23° over calcium chloride. Analyses also show that the mercerised and not mercerised compounds have the same percentage composition. That the compounds, however, are not identical has been proved by Wichelhaus and Vieweg (Abstr., 1907, i, 186) by an examination of the products of nitration, and is confirmed by the fact that the amount of water adsorbed by mercerised cellulose is much greater than by ordinary cellulose. The degree of mercerisation can be determined especially by dyeing with rosaniline base; with substantive dyes of the type of geranin-G and chrysophenin an increase in the depth of colour is observed only after the cellulose has been treated with 9% sodium hydroxide solution, and then the colour increases with the concentration of the alkali up to, and probably beyond, 25%. J. J. S.

The Reaction between Humin and Potassium Hypobromite.

ARTUR KONSCHEGG (*Zeitsch. physiol. Chem.*, 1910, **69**, 390—394).—The humin was obtained from dextrose by heating 250 grams for twelve hours with 1 litre of 24% hydrochloric acid; the brown flocks produced were then treated with aqueous potassium hydroxide to dissolve out humic acid. The residual humin forms a viscid, mucilaginous mass, that can only with difficulty be separated by filtration from the alkaline solution of humic acid. When dried at 100° it forms a glassy, brittle mass, that breaks down to a powder much darker than humic acid. It is insoluble in water, acids, alkalis, alcohol, or ether.

When, however, humin is suspended in potassium hydroxide and a little bromine added, it passes into solution. After a time, white crystals of tetrabromomethane separate. Humic acid behaves in the same way.

The author finds that humic acid dissolves in water to form a colloidal solution. If the precipitate obtained by adding hydrochloric acid to the alkaline solution of humic acid is washed with water, the filtrate soon begins to be coloured. The dark liquid on evaporation leaves a black, caseous residue soluble both in water and alcohol.

E. J. R.

Chloro-salts of Osmium.

ALEXANDER GUTBIER [with K. MAISCH] (*Ber.*, 1910, **43**, 3234—3239).—The substituted ammonium osmichlorides described were prepared by the interaction of the respective substituted ammonium chlorides with sodium osmichloride (Abstr., 1910, ii, 45), than which they are much less soluble; they are all anhydrous and stable in the air. In aqueous solution they undergo decomposition, but in hydrochloric acid solution they are stable. In some cases they are readily soluble in alcohol.

Methylammonium osmichloride, $(NH_3Me)_2OsCl_6$, reddish-brown, anisotropic crystals. *Dimethylammonium osmichloride*,

$$(NH_2Me_2)_2OsCl_6,$$

yellowish-red, rhombic prisms, which are pleochroic. *Trimethyl-*

ammonium osmichloride, $(NHMe_3)_2OsCl_6$, light yellowish-red, regular crystals. *Ethylammonium osmichloride*, $(NH_3Et)_2OsCl_6$, scarlet-red, pleochroic leaflets. *Diethylammonium osmichloride*, $(NH_2Et_2)_2OsCl_6$, yellowish-red, monoclinic crystals. *Triethylammonium osmichloride*, $(NHEt_3)_2OsCl_6$, reddish-yellow, monoclinic needles. n-*Propylammonium osmichloride*, $(NH_3Pr^{\alpha})_2OsCl_6$, dark brownish-red, monoclinic crystals. iso*Propylammonium osmichloride*, $(NH_3Pr^{\beta})_2OsCl_6$, brownish-red, pleochroic crystals. *Dipropylammonium osmichloride*, $(NH_2Pr_2)_2OsCl_6$, reddish-yellow, monoclinic prisms. n-*Butylammonium osmichloride*, $(NH_3{\cdot}C_4H_9)_2OsCl_6$. brownish-red, monoclinic crystals. iso*Butylammonium osmichloride*, $(NH_3{\cdot}C_4H_9)_2OsCl_6$, dark brownish-red, monoclinic or rhombic crystals. *Ethylenediammonium osmichloride*, $C_2H_{10}N_2OsCl_6$, dark brown, monoclinic crystals. *Propylenediammonium osmichloride*, $C_3H_{12}N_2OsCl_6$, dark brownish-red, monoclinic crystals.

T. S. P.

Nitrilo-trimethylnitroaminomethylene. ANTOINE P. N. FRANCHIMONT (*Rec. trav. chim.*, 1910, [ii], 14, 355—367.* Compare Abstr., 1910, i, 616, 617; Eschweiler, Abstr., 1894, i, 267).—An investigation (1) of the conditions under which hexamethylenetetra-amine and methylnitroamine react to form nitrilo-trimethylnitroaminomethane, $N(CH_2{\cdot}NMe{\cdot}NO_2)_3$, and (2) of the constitution of the latter. This substance is formed in small quantity when hexamethylenetetra-amine is mixed in aqueous solution with methylnitroamine and boiled for some days, but a better yield is obtained when water is replaced by a solution of formaldehyde, and a quantitative yield when the decomposition products of hexamethylenetetra-amine, namely, formaldehyde and ammonia, are mixed with methylnitroamine and slightly warmed.

Nitrilo-trimethylnitroaminomethane, m. p. 116°, crystallises in colourless, transparent prisms, and gives the nitroamine reaction with zinc and α-naphthylamine. When boiled with alkalis, it decomposes in accordance with the equation $N(CH_2{\cdot}NMe{\cdot}NO_2)_3 + 3H_2O = NH_3 + 3H{\cdot}CHO + 3NHMe{\cdot}NO_2$, whilst with acids the reaction takes place as follows: $N(CH_2{\cdot}NMe{\cdot}NO_2)_3 + 3H_2O = NH_3 + 3H{\cdot}CHO + 3N_2O + 3CH_3OH$. In the former case some of the ammonia combines with the formaldehyde, and the reaction cannot be followed quantitatively, but in the second case ammonia, formaldehyde, and nitrous oxide can be estimated, and the results of these estimations serve to establish the constitution of the substance. When dissolved in chloroform and treated with hydrogen chloride, a crystalline *hydrochloride*,

$$NO_2{\cdot}NMe{\cdot}CH_2{\cdot}NH_2,HCl,$$

is formed, which, on evaporation of its aqueous solution, evolves hydrogen chloride and forms a mixture of ammonium chloride, and a soluble substance giving the nitroamine reaction. T. A. H.

Synthesis of γ-Amino-α-hydroxybutyric Acid and its Trimethyl Derivative. EMIL FISCHER and ALBERT GÖDDERTZ (*Ber.*, 1910, **43**, 3272—3280. Compare Fischer and Zemplén, Abstr., 1910, i, 100).—*γ-Phthalimino-α-hydroxybutyric acid*,

$$C_6H_4(CO)_2{:}N{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H,$$

can be obtained by boiling the corresponding α-bromo-acid (Gabriel and Colman, Abstr., 1908, i, 274) with water and calcium or barium carbonate for about fifteen minutes. The *calcium* salt,

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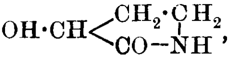
* and *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 527—530.

$$Ca(C_{12}H_{10}O_5N_2)_2,6H_2O,$$

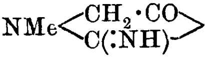
crystallises from water at 0° in colourless crusts of minute prisms. The *barium* salt also crystallises with $6H_2O$, and when treated with a slight excess of dilute sulphuric acid yields the free acid, which crystallises from hot water in long, colourless needles, containing $1H_2O$, and melting at about 100°; when anhydrous it has m. p. 144—145° (corr.). It has a feebly acidic, but strongly astringent, taste. When hydrolysed with concentrated hydrochloric acid in a platinum flask, it yields *γ-amino-α-hydroxybutyric acid hydrochloride* and phthalic acid. The *hydrochloride*, $C_4H_9O_3N,HCl$, crystallises from a mixture of alcohol and ethyl acetate in colourless needles. The *platinichloride* crystallises from warm alcohol in orange-coloured plates; the *acid*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2H$, crystallises from dilute alcohol, and has m. p. 191—192° (corr.). It has no characteristic taste, is not precipitated by phosphotungstic acid, and when heated at 210° for five minutes yields *3-hydroxypyrrolidone*,  $OH{\cdot}CH<\begin{matrix}CH_2{\cdot}CH_2\\ CO{-}NH\end{matrix}$, which crystallises from ethyl acetate at 0° in thin plates, m. p. 85° (corr.). It has a sweet taste, yields a crystalline mercury derivative, and is partly hydrolysed to the amino-acid when boiled with 25% hydrochloric acid. The pyrrolidone is also formed when an alcoholic solution of the amino-acid is saturated with hydrogen chloride.

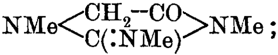
α-Hydroxy-γ-trimethylaminobutyric acid is formed when the amino-acid is exhaustively methylated. The *sulphate* is readily soluble in water; the *aurichloride*, $C_7H_{15}O_3N,HAuCl_4$, crystallises in yellow needles, m. p. 175—176° (corr.) after sintering at 162°. The *hydrochloride* and *platinichloride* are syrups which crystallise slowly. The latter crystallises in long, slender needles, m. p. 216° (decomp.). The methyl derivative is probably identical with *dl*-carnitine. J. J. S.

Preparation of Creatinine from Urine. OTTO FOLIN and FREDERICK C. BLANCK. **Preparation of Creatinine from Creatine.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1910, **8**, 395—397, 399—400).—Details are given of the picric acid procedure in the separation of creatinine from urine. Creatine may be converted into creatinine without the use of any solvent or acid. The water of crystallisation of creatine is sufficient. If creatine is placed in a closed bottle and heat applied until a pressure of 4·5 kilos. per square centimetre is reached, and this is kept up for three hours, the contents contain crystalline creatinine. W. D. H.

Creatinine. ERNST SCHMIDT (*Arch. Pharm.*, 1910, **248**, 568—578).—Mainly an introduction to the two following papers, the object of which is the confirmation of Pommerehne and Toppelius' statement that the creatinines from flesh, from urine, or synthetically produced, are all identical (Abstr., 1897, i, 128), not different as claimed by Johnson (Abstr., 1889, 165).

Neubauer's statement (*Annalen*, 1861, **119**, 49) that creatinine when alkylated behaves as a tertiary base has been denied by

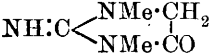
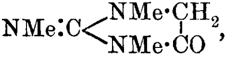
Korndörfer (Abstr., 1904, i, 768), whose results are now confirmed by the fact that creatinine by methylation yields first methylcreatinine,  $NMe<\begin{matrix}CH_2\cdot CO\\ C(:NH)\end{matrix}>NMe$, and then dimethylcreatinine,



$$NMe<\begin{matrix}CH_2-CO\\ C(:NMe)\end{matrix}>NMe;$$

the latter then behaves as a tertiary base. C. S.

Methyl-, Dimethyl-, and Trimethyl-creatinines. GERHARD KUNZE (*Arch. Pharm.*, 1910, **248**, 578—593).—The methylation of creatinines produced synthetically or from flesh yields methylcreatinine hydriodides, which are identical, and from which identical hydrochlorides, aurichlorides, and platinichlorides are obtained. All these compounds are identical with the corresponding substances obtained by Korndörfer (Abstr., 1905, i, 152) from creatinine prepared from urine.

The base liberated from the methylcreatinine hydriodide by potassium carbonate, lead oxide, or silver oxide is hydrolysed by boiling baryta, yielding carbon dioxide, ammonia, methylamine, and sarcosine, and is oxidised by alkaline 5% potassium permanganate at 50—60° to oxalic acid and Schenck's *s*-dimethylguanidine (Abstr., 1910, i, 99); consequently, the methylcreatinine has the constitution  $NH:C<\begin{matrix}NMe\cdot CH_2\\ | \\ NMe\cdot CO\end{matrix}$. By further methylation at 50—70°, it yields dimethylcreatinine hydriodide, m. p. 179—180°; *aurichloride*, m. p. 128—129°; platinichloride, m. p. 177—179° (not 169—170°), the base in which has the constitution  $NMe:C<\begin{matrix}NMe\cdot CH_2\\ | \\ NMe\cdot CO\end{matrix}$, since it is oxidised by alkaline potassium permanganate to oxalic acid and Schenck's trimethylguanidine (*loc. cit.*). C. S.

Ethylcreatinine. CARL HENZERLING (*Arch. Pharm.*, 1910, **248**, 594—608).—The work is very similar to that of Kunze (preceding abstract), and proves that creatinines obtained from different sources are identical. When alkylated by ethyl iodide, creatinine behaves like a secondary base, yielding *ethylcreatinine hydriodide*,

$$C_6H_{11}ON_3,HI,$$

m. p. 217—219° (from which are formed an *aurichloride* and a *platinichloride*, m. p. 197—211°, monoclinic plates, $a:b:c = 0{\cdot}8685:1:0{\cdot}7385$, $\beta = 86°24{\cdot}5'$), and also creatinine hydriodide, m. p. 195°, as a by-product. The ethylcreatinine hydriodide cannot be an ethiodide, as stated by Neubauer, because the chloride prepared from it is decomposed by potassium carbonate, yielding ethylcreatinine, which has not been obtained crystalline. It is oxidised by alkaline potassium permanganate to oxalic acid and methylethylguanidine (*platinichloride*, m. p. 179—181°), and is hydrolysed by boiling barium hydroxide, yielding carbon dioxide, ammonia, ethylamine, and sarcosine. By treatment with ethyl iodide at 100°, ethylcreatinine yields chiefly ethylcreatinine hydriodide, small quantities of ethylamine and diethylcreatinine (*platinichloride*, m. p. 201—202°) also being formed.

When ethylcreatinine is treated with methyl iodide, the chief product is again ethylcreatinine hydriodide, methylamine and a small amount of methylethylcreatinine (*platinichloride,* m. p. 181—182°) also being formed. C. S.

Propiolic Compounds. Cyanoacetylene, C_3HN. CHARLES MOUREU and J. CHARLES BONGRAND (*Compt. rend.*, 1910, **151**, 946—948. Compare Abstr., 1910, i, 159).—*Propiolamide*,

$$CH{:}C{\cdot}CO{\cdot}NH_2,$$

has been obtained by the action of aqueous ammonia at 0° on methyl propiolate. It occurs in lamellæ, m. p. 61—62°; the aqueous solution forms a white precipitate with silver nitrate, and a yellow one with ammoniacal cuprous chloride. When distilled with phosphoric oxide in an atmosphere of carbon dioxide under diminished pressure, cyanoacetylene, $CH{:}C{\cdot}CN$, is obtained as a colourless, mobile liquid, b. p. 42·5°/760 mm., D_4^{17} 0·8159, solidifying to crystals, m. p. 5°. The compound is inflammable, and becomes brown on keeping, even in absence of light and air. The vapour is intensely irritating. With silver nitrate, it forms a white explosive substance, whilst the compound obtained by the action of ammoniacal cuprous chloride is green and deflagrates on heating. The molecular refractions for the *D*-sodium line and for the α-, β-, and γ-hydrogen lines have been determined at 17°: M_D 14·7207; $M_\gamma - M_\alpha$ 0·563. Owing to the presence of the acetylenic linking, the refraction and dispersion are higher than the calculated values.

The action of potassium ferricyanide on cyanoacetylene gives rise to a product, which, when sublimed in an atmosphere of carbon dioxide, yields colourless needles, m. p. 64°. This substance has an irritating odour, and the author believes it to be a new carbon subnitride, C_6N_2. W. O. W.

Catalytic Action. IV. Comparison of the Action of Various Catalytic Agents. II. Acetylation of Carbamide. JACOB BÖESEKEN [with Mlle. J. LANGEZAAL] (*Rec. trav. chim.*, 1910, **29**, 330—339. Compare Abstr., 1910, i, 152).—Geuther first effected the acetylation of carbamide, and showed the formation of only a small amount of cyanuric acid, thus differing from the behaviour of the symmetrical di-substituted products of carbamide. The authors show that the difference in behaviour of carbamide and its derivatives is quantitative rather than qualitative.

Various catalytic agents were used in the acetylation, and the results obtained, showing their relative influence and the amounts of acetylcarbamide and cyanuric acid formed, are tabulated in the original.

Various salts of cyanuric acid were made to try and effect its estimation, and the *strontium* salt is described. It was found more convenient to estimate the acid by titration with dilute potassium hydroxide, the acetylcarbamide not being affected.

It was found that on prolonged heating with the catalytic agents, acetylcarbamide is partly decomposed, the percentage of cyanuric acid present increasing. N. C.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVII. Tetra-alkylthiocarbamides and Tetra-alkyl*iso*thiocarbamides. Marcel Delépine (*Bull. Soc. chim.*, 1910, [iv], 7, 988—993).—Compounds of these two types have been prepared previously, but have not been described in detail, and in this paper an account is given of their preparation, properties, and chief derivatives.

The tetra-alkylthiocarbamides are best obtained by Billeter's method, which consists in treating the appropriate secondary amine in benzene or toluene with thiocarbonyl chloride. The tetramethyl compound may be obtained from von Braun and Stechele's tetramethylthiouram sulphide (Abstr., 1903, i, 618) by the action at 100° of dimethylamine dissolved in benzene, thus: $S(CS{\cdot}NMe_2)_2 + 2NMe_2 = NMe_2{\cdot}CS{\cdot}NMe_2 + NMe_2{\cdot}CS{\cdot}S{\cdot}NH_2Me_2$, dimethylamine dimethyldithiocarbamate being also formed. The same two substances result from the action of dimethylamine on dimethylthiouram disulphide: a method analogous with that used by Fromm (Abstr., 1909, i, 506).

The tetra-alkyl*iso*thiocarbamides are obtained by the action of the necessary alkyl iodide on the trialkylthiocarbamides.

The two series of compounds differ considerably in properties. The tetra-alkylthiocarbamides are usually of higher specific gravity and boiling point than their isomerides, and are not basic, whilst their isomerides are markedly basic up to the tetrapropyl compound, which on titration in presence of the usual indicators appears to be saturated before one equivalent of acid has been added. The members of both groups form additive compounds with one mol. of methyl iodide.

Tetramethylthiocarbamide, $S{:}C(NMe_2)_2$, m. p. 78°, b. p. 245°, is readily soluble in warm, but less so in cold, water (compare Billeter, Abstr., 1910, i, 544). The *methiodide*, $SMeI{:}C(NMe_2)_2$ or

$$SMe{\cdot}CI(NMe_2)_2,H_2O,$$

crystallises from alcohol in colourless prisms. On treatment with silver nitrate followed by ammonia, it yields silver methylmercaptide. *Tetraethylthiocarbamide*, b. p. 130°/12 mm., 264—266°/760 mm., D^0_4 0·9804, D^{18}_4 0·9662, is an oily liquid of pleasant odour. *Tetrapropylthiocarbamide*, b. p. 165°/12 mm., or about 305°/760 mm., D^0_4 0·9430, D^{19}_4 0·9300, is a viscid, almost inodorous liquid.

*Tetramethyl*iso*thiocarbamide*, $NMe{:}C(SMe){\cdot}NMe_2$, b. p. 176°, D^0_4 1·0194, D^{16}_4 1·0061, is a colourless liquid of strong odour. The *picrate*, m. p. 99·5°, crystallises in yellow needles. Tetraethyl*iso*thiocarbamide has b. p. 216°, D^0_4 0·9426, D^{21}_4 0·9252 (Grodzky, Abstr., 1882, 823). *Tetrapropyl*iso*thiocarbamide*, b. p. 154°/15 mm., 270°/760 mm. (decomp.), D^0_4 0·9179, D^{21}_4 0·9014, is a colourless, oily liquid of slight odour. It was prepared by the general method from *tripropylthiocarbamide*, m. p. 33°, which crystallises in colourless needles, and was obtained by the union of dipropylamine with propylthiocarbimide. T. A. H.

Formation of Fulminic Acid from Alcohol. Heinrich Wieland (*Ber.*, 1910, **43**, 3362—3364).—Polemical against Wöhler (Abstr., 1910, i, 231). The following details for the preparation of mercury fulminate from oximinoacetic acid are given. 1·5 Grams of oximinoacetic acid are added to a solution of 1 gram of mercuric nitrate in 3 c.c. of nitric acid (D = 1·34) and 2 c.c. of water. If the reaction is allowed to go on of its own accord, without cooling, 0·1—0·2 gram of mercury fulminate is obtained, whereas when the reaction is moderated no fulminate is formed. Silver fulminate is obtained in a similar manner. T. S. P.

Chloralurethane. II. OTTO DIELS and ARMENAK GUKASSIANZ (*Ber.*, 1910, **43**, 3314—3320. Compare Abstr., 1909, i, 885).—The constitution, $CCl_2{:}C(CN){\cdot}NH{\cdot}CO_2Et$, of the nitrile obtained by boiling the acetyl derivative of chloralurethane with aqueous potassium cyanide has been proved by the behaviour of the substance towards ozone and towards nitric acid. The former converts it into carbonyl chloride and a substance (probably $CN{\cdot}CO{\cdot}NH{\cdot}CO_2Et$) which yields oxalic acid by hydrolysis. Warm concentrated nitric acid converts the nitrile into dichlorodinitromethane and oxalic acid.

The action of ethylamine, aniline, piperidine, and sodium ethoxide on the nitrile also supports the constitution. An ethereal solution of the nitrile and ethylamine at 0° yield the *substance*,

$$C(NHEt)_2{:}C(CN){\cdot}NH{\cdot}CO_2Et,$$

m. p. 104° (corr.), flat plates. The nitrile and aniline, after being heated on the water-bath for one and a-half hours, yield the *substance*, $C(NHPh)_2{:}C(CN){\cdot}NH{\cdot}CO_2Et$, m. p. 166—167° (corr.). The nitrile and piperidine in ether yield a corresponding substance which, however, cannot be isolated, but is converted by concentrated hydrochloric acid into the *piperidide*, $C_5NH_{10}{\cdot}CO{\cdot}C(CN){\cdot}NH{\cdot}CO_2Et$, m. p. 131·5—132·5° (corr.). The nitrile is converted by alcoholic sodium methoxide or sodium ethoxide into the *ortho*-esters,

$$C(OMe)_3{\cdot}CH(CN){\cdot}NH{\cdot}CO_2Et,$$

m. p. 86—87° (corr.), and $C(OEt)_3{\cdot}CH(CN){\cdot}NH{\cdot}CO_2Et$, m. p. 56°; when the former is boiled with glacial acetic acid it is converted into *methyl cyanocarbethoxyglycine*, $CO_2Me{\cdot}CH(CN){\cdot}NH{\cdot}CO_2Et$, m. p. 130·5° (corr), which is easily soluble in alkalis. C. S.

Synthetical Experiments in the Cincholeupone Series. ALFRED WOHL and RUDOLF MAAG (*Ber.*, 1910, **43**, 3280—3291).—Attempts have been made to synthesise cincholeupone derivatives, but, so far, without success. A dimethylpiperidine has been prepared by the following method:

By the addition of ethyl sodiocyanoacetate to the condensation product of aldehyde and acetone, ethyl α-cyano-γ-acetyl-β-methyl butyrate, $CO_2Et{\cdot}CH(CN){\cdot}CHMe{\cdot}CH_2Ac$, is formed, and when this is hydrolysed and reduced, 2 : 4-dimethylpiperidine is formed.

A fairly good yield of ethylideneacetone (Claisen, Abstr., 1893, i, 8) is obtained by saturating a well cooled mixture of paraldehyde and acetone with dry hydrogen chloride and leaving for two days at 0°. The product obtained by distillation contains appreciable amounts of chlorine, but can be obtained pure by distilling twice over diethylaniline. An impure product, b. p. 120—130°, was used for the condensation with ethyl sodiocyanoacetate. The condensation product, $C_{10}H_{15}O_3N$, has b. p. 155—168°/14 mm., and when hydrolysed with 5*N*-sodium hydroxide solution and distilled, gives a 50% yield of *δ-keto-β-methylvaleronitrile*, $COMe{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CN$, b. p. 105°/11 mm.

The *amide*, $COMe{\cdot}CH_2{\cdot}CHMe{\cdot}CH(CN){\cdot}CO{\cdot}NH_2$, obtained by shaking the cyano-ester with ammonium hydroxide solution, crystallises from alcohol or water, and has m. p. 134°.

The nitrile forms a definite compound with hydrogen chloride, $2C_7H_{11}ON,HCl$, in the form of colourless crystals. The nitrile is not affected by zinc dust and acetic acid, zinc dust and ammonia, sodium amalgam and dilute alcohol, but is reduced by sodium and boiling amyl alcohol, yielding small amounts of 2 : 4-*dimethylpiperidine*, $C_7H_{15}N$, which, after careful fractionation, has b. p. 136—138°. The *oxalate*, $C_9H_{17}O_4N,\frac{1}{2}H_2O$, crystallises in nacreous needles, m. p. 134°, after sintering at 130°. A small amount of *ε-hydroxy-γ-methylhexylamine*, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CHMe{\cdot}OH$, is also formed during the reduction; it has b. p. 119—120°/12 mm., and yields an *oxalate*, $C_{10}H_{19}O_5N$, with m. p. 142—145°. The amine reacts at 100—115° with a solution of hydrobromic acid saturated at below 0°, yielding an unsaturated *base* isomeric with dimethylpiperidine. It has b. p. 145—150°, and yields an *oxalate*, m. p. 150°. One of the formulæ $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH{:}CHMe$ or

$$NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH{:}CH_2$$

is suggested.

Acetone does not condense with acraldehyde in the presence of hydrogen chloride; the only product appears to be mesityl oxide. The condensation takes place in the presence of a small amount of potassium cyanide, but the additive product formed polymerises with the greatest readiness. Definite products could not be isolated by condensing acraldehyde with ethyl acetoacetate in the presence of piperidine or potassium cyanide at − 10°.

Ethoxypropaldehydediethylacetal and ethyl acetoacetate condense in the presence of glacial acetic acid and a little concentrated sulphuric acid or zinc chloride, yielding a product,

$$OEt{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CAc{\cdot}CO_2Et,$$

with b. p. 142—144°/11 mm. This product is unsaturated, and readily decolorises solutions of bromine and permanganate.

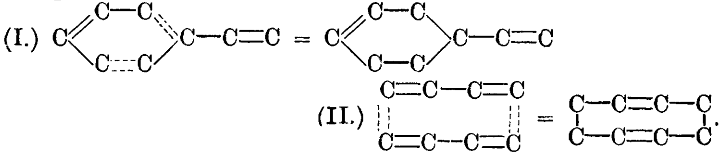
Claisen's β-hydroxypentan-δ-one is formed when one-eighth of the amount of potassium cyanide recommended by Claisen is used for the condensation of aldehyde and acetone. Phosphorus tribromide reacts with an ethereal solution of the hydroxy-compound, yielding *β-bromopentan-δ-one*, $CH_3{\cdot}CHBr{\cdot}CH_2{\cdot}COMe$, with b. p. 50—55°/15 mm. The bromo-derivative is extremely unstable, and when kept for several days is transformed into a dark brown syrup. It condenses with ethyl sodiocyanoacetate, yielding ethyl α-cyano-γ-acetyl-β-methylbutyrate. J. J. S.

Catalytic Reactions at High Temperatures and Pressures. XX. Dehydration of Cyclic Alcohols. WLADIMIR N. IPATIEFF (*Ber.*, 1910, **43**, 3383—3387).—It has been shown previously (Abstr., 1903, i, 593; 1904, ii, 644; 1907, i, 6) that alcohols may be dehydrated in contact with alumina that has been only gently heated, ethers being formed at first, and then olefines.

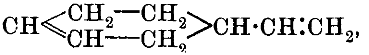
Cyclic polyhydric alcohols may be dehydrated by heating with alumina in an atmosphere of hydrogen under a pressure of 39—40 atmospheres. Quinitol yields *cyclo*hexadiene with a little *cyclo*hexene at 350°, a good yield of the latter compound being obtained from *cyclo*hexanol. 1-Methyl*cyclo*hexan-2-ol yields methyl*cyclo*hexene in a mixture of several isomerides. Decahydro-β-naphthol yields octahydronaphthalene. C. H. D.

Polymerisation of Diethylene Hydrocarbons of the Type C:C·C:C. S. V. Lebedeff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 949—961).—The polymerisation of hydrocarbons with a system of double bonds is so typical that it can be regarded as a general characteristic of these compounds; the temperature, however, greatly influences the velocity of the reaction and the character of the products; the latter, on the other hand, does not depend on the period of heating.

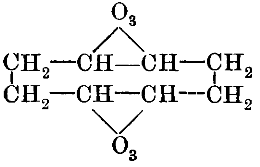
Two processes are possible, thus:

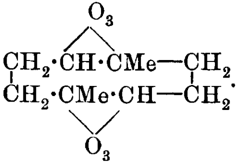


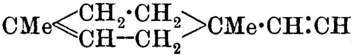
The lower the temperature the more is the 8-membered ring obtained. Light also favours process (II).



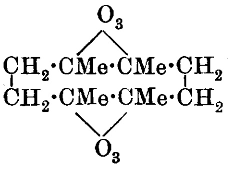
Divinyl heated in a sealed tube at 150° for six or seven days forms: (1) *Ethenyl*cyclo*hexene*, $CH{<}\begin{matrix}CH_2—CH_2\\ CH—CH_2\end{matrix}{>}CH\cdot CH{:}CH_2$, b. p. 66°/100 mm., 131°/760 mm., D_0^{20} 0·8321. When reduced with hydrogen in the presence of platinum-black, it yields ethyl*cyclo*hexane, b. p. 129—130° (Sabatier and Senderens give 128—129°). (2) A resin-like *polymeride*, which yields an explosive *ozonide* (I).

(I.) 

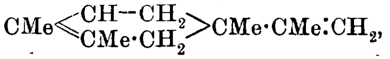
(II.) 



Isoprene under similar conditions yields (1) dipentene. (2) A *hydrocarbon*, b. p. 44°/9 mm., 160—161°/760 mm., D_0^{20} 0·8331, for which the formula $CMe{<}\begin{matrix}CH_2\cdot CH_2\\ CH—CH_2\end{matrix}{>}CMe\cdot CH{:}CH_2$ is proposed; when reduced, it yields a *hydrocarbon*, $C_{10}H_{20}$, b. p. 164—165°/764 mm., D_0^{20} 0·799. (3) A resin-like *polymeride*, the *ozonide* of which has the constitution (II).

(III.) 

Di-isoprene yields the *hydrocarbon*,



$$CMe{<}\begin{matrix}CH—CH_2\\ CMe\cdot CH_2\end{matrix}{>}CMe\cdot CMe{:}CH_2,$$

b. p. 85°/13 mm., D_0^{20} 0·8598, and a resin-like *polymeride*, which yields the *ozonide* (III). Z. K.

Isomorphous Mixtures of Para-dihalogen Derivatives of Benzene. NICOLAI N. NAGORNOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1159—1167).—1 : 4-Dichloro- and 1 : 4-di-iodo-benzene do not form solid solutions; their melting-point curve consists of two branches, with the eutectic point at 45° at the composition of 1·4 mol.% of the iodo-compound.

1 : 4-Dichloro- and 1 : 4-chloroiodo-benzene (m. p. 53°) form continuous isomorphous mixtures; their fusion curve passes through a minimum at 41° at the composition 50 mol.% of each compound.

1 : 4-Di-iodo- and 1 : 4-chloroiodo-benzene form solid solutions in one another. The saturated solution in chloroiodobenzene contains 20 mol.% of di-iodobenzene, whilst the saturated solution in the latter contains 15% of chloroiodobenzene. The curve consists of two branches, the eutetic point lying at 59° at the composition 14 mol.% of di-iodobenzene.

1 : 4-Dibromo- and 1 : 4-bromoiodo-benzene (m. p. 89·9°) form a continuous series of isomorphous mixtures; the minimum of their fusion curve is at 85·1°, corresponding with the composition of 60 mol.% of the dibromide.

1 : 4-Di-iodo- and 1 : 4-bromoiodo-benzene also form a continuous series of isomorphous mixtures, their curve passing through a minimum at about 100·5° at about 30 mol.% of di-iodo-benzene. Curves and tables are given for every pair of substances mentioned. Z. K.

Iodine Derivatives of Toluene. HENRY L. WHEELER (*Amer. Chem. J.*, 1910, **44**, 493—507).—In papers on the action of iodine on *o*-, *m*-, and *p*-toluidines (Abstr., 1910, i, 17, 19, 662), an account has been given of 2 : 3-, 3 : 5-, and 2 : 5-di-iodotoluenes, 3 : 4 : 5-, 2 : 3 : 6-, and 3 : 4 : 6-tri-iodotoluenes, and 2 : 3 : 4 : 6-tetraiodotoluene. The study of the iodotoluenes has now been continued.

[With CHARLES A. BRAUTLECHT.]—5-*Iodo*-3-*nitro*-o-*toluidine*,

$$NO_2{\cdot}C_6H_2MeI{\cdot}NH_2,$$

m. p. 135°, prepared by the action of iodine chloride on 3-nitro-*o*-toluidine in presence of glacial acetic acid, forms orange needles. By the action of potassium iodide on the diazotisation product of this compound, 2 : 5-*di-iodo-3-nitrotoluene*, $NO_2{\cdot}C_6H_2MeI_2$, m. p. 95°, is obtained, which crystallises in colourless prisms, and on reduction with ferrous sulphate and ammonia is converted into 2 : 5-*di-iodo*-m-*toluidine*, m. p. 82°, which forms pale brown prisms. When this substance is diazotised and the product treated with potassium iodide, 3 : 5 : 6-tri-iodotoluene is produced. 2 : 5-*Di-iodoaceto*-m-*toluidide*,

$$C_6H_2MeI_2{\cdot}NHAc,$$

m. p. 198—199°, forms long, colourless needles. When a mixture of 2 : 5-di-iodo-*m*-toluidine and iodine with ether, water, and calcium carbonate is warmed for eighteen hours, 2 : 5 : 6-*tri-iodo*-m-*toluidine*, m. p. 119—120°, and 2 : 4 : 5 : 6-tetraiodo-*m*-toluidine are produced; the former crystallises in colourless needles, and when its diazotisation product is treated with potassium iodide, 2 : 3 : 5 : 6-*tetraiodotoluene*, m. p. 125°, is obtained, which forms colourless needles.

4 : 5-*Di-iodo*-o-*toluidine*, $NH_2\cdot C_6H_2MeI_2$, m. p. 85°, prepared by the action of iodine or iodine chloride on *p*-iodo-*o*-toluidine, forms stout needles or long prisms. When its diazotisation product is treated with potassium iodide, 3 : 4 : 6-tri-iodotoluene (Abstr., 1910, i, 663) is obtained. 5-*Iodo*-4-*nitro*-o-*toluidine*, m. p. 109°, prepared by the action of iodine chloride on *p*-nitro-*o*-toluidine, forms long, bright yellow prisms. When its diazotisation product is treated with potassium iodide, 2 : 5-*di-iodo*-4-*nitrotoluene*, m. p. 117°, is obtained, which crystallises in buff-coloured, prismatic plates. This compound, on reduction with ferrous sulphate and ammonia, yields 2 : 5-*di-iodo*-p-*toluidine*, m. p. 109°, which forms buff-coloured prisms, and when diazotised and treated with potassium iodide is converted into 2 : 4 : 5-tri-iodotoluene, m. p. 118°, which is identical with the compound described by Neumann (Abstr., 1887, 573) as 2 : 4 : 6-tri-iodotoluene. 2 : 4 : 6-*Tri-iodotoluene*, m. p. 105°, prepared by the diazotisation of 2 : 4 : 6-tri-iodo-*m*-toluidine, crystallises in colourless needles.

[With CHARLES HOFFMAN.]—3-*Iodo*-5-*nitro*-o-*toluidine*, m. p. 173°, obtained by the action of iodine chloride on 5-nitro-*o*-toluidine in presence of glacial acetic acid, forms long, brown prisms. By the action of potassium iodide on the diazotisation product of this compound, 2 : 3-*di-iodo*-5-*nitrotoluene*, m. p. 143°, is produced, which crystallises in long, light brown, prismatic needles, and when reduced with ferrous sulphate and ammonia is converted into 5 : 6-*di-iodo*-m-*toluidine*, m. p. 106°, which forms large, brown crystals, but can be obtained in a colourless condition by distillation with steam. 5 : 6-*Di-iodo*-m-*acetotoluidide* has m. p. 208°. 3 : 5 : 6-*Tri-iodotoluene*, m. p. 72—73°, obtained by the action of potassium iodide on the diazotisation product of 5 : 6-di-iodo-*m*-toluidine, forms large, pale orange plates. On warming a mixture of 5 : 6-di-iodo-*m*-toluidine with iodine for several hours in presence of water, ether, and calcium carbonate, 4 : 5 : 6-*tri-iodo*-m-*toluidine*, m. p. 122°, and 2 : 4 : 5 : 6-*tetra-iodo*-m-*toluidine*, m. p. 205°, are produced, which crystallise in small needles. 4 : 5 : 6-*Tri-iodo*-m-*acetotoluidide*, m. p. 265° (decomp.), forms colourless needles. 2 : 3 : 4-*Tri-iodotoluene*, m. p. 92°, obtained by the diazotisation of 4 : 5 : 6-tri-iodo-*m*-toluidine, forms radiating crystals. By the action of potassium iodide on the diazotisation product of 4 : 5 : 6-tri-iodo-*m*-toluidine, 3 : 4 : 5 : 6-*tetraiodotoluene*, m. p. 284—285°, is obtained, which crystallises in straw-coloured needles. *Pentaiodotoluene*, m. p. 340° (decomp.), obtained by the action of potassium iodide on the diazotisation product of 2 : 4 : 5 : 6-tetraiodo-*m*-toluidine, forms small, dull yellow needles. E. G.

Auto-decomposition of Phenylnitromethane. FRIEDRICH HEIM (*Ber.*, 1910, **43**, 3417—3420. Compare Dimroth, Abstr., 1910, i, 831).—In attempting to purify crude phenylnitromethane (Wislicenus and Endres, Abstr., 1902, i, 541) by distilling the crude product under diminished pressures, rapid decomposition ensued in one experiment, nitrous fumes were evolved, and a *product*, $C_{21}H_{17}ON$ (probably triphenyldihydro*iso*oxazole), was obtained. This crystallises from alcohol, and has m. p. 138—139°. Other products were also formed.

In a second experiment, the crude product was subjected to steam distillation, and the phenylnitromethane obtained as a yellow oil; at the same time a small amount of a yellow solid was deposited in the condenser towards the end of the distillation, and dibenzhydroxamic acid was left in the flask.

Decomposition was also noticed when a specimen of phenylnitromethane, which has turned brown after exposure to light, was distilled.

It is suggested that the cause of the rapid decomposition is the presence of small amounts of phenylnitrolic acid in the crude material. J. J. S.

Nitro- and Amino-sulphobenzoic Acids. S. van Dorssen (*Rec. trav. chim.*, 1910, [ii], **14**, 368—393).—In view of Taverne's statement (Abstr., 1906, i, 273) that *m*-sulphobenzoic acid on nitration furnishes 2-nitro-3-sulphobenzoic acid, whereas the symmetrical acid is to be expected, the author has re-investigated Taverne's acid and compared it with aminosulphobenzoic acids prepared in other ways. For the characterisation of the acids, the electrical conductivity and the solubility have been used. The results show that the acid prepared by Taverne is 3-nitro-5-sulphobenzoic acid. The conductivities quoted are for $v = 1200$ unless otherwise stated, and the solubilities are grams of acid in 100 grams of water, saturated at 25°.

4-Amino-2-sulphobenzoic acid, $\mu = 302\cdot4$, solubility 0·2997, crystallises in batons. 5-Amino-2-sulphobenzoic acid, $\mu = 332\cdot4$, solubility 0·1035, crystallises with $1H_2O$, and is unstable in aqueous solution. 4-Amino-3-sulphobenzoic acid, $\mu_{600} = 360\cdot0$, solubility 2·8346, was prepared by Fischer's method (Abstr., 1892, i, 331). Its constitution was established by the fact that aniline-*o*-sulphonic acid is formed with it as a by-product. 5-Nitro-3-sulphobenzoic acid, prepared from *m*-sulphobenzoic acid as described by Taverne, who wrongly assumed it to be the 2 : 3-isomeride, is identical with the acid prepared from *m*-nitrotoluene by sulphonation and subsequent oxidation of the CH_3- group, both acids furnishing *s*-dichlorobenzoic acid on treatment with phosphorus pentachloride. The nitro-acid, on reduction with tin and hydrochloric acid, furnishes the corresponding *amino-acid*, $\mu = 302\cdot4$, solubility 0·5745, and this gives no tribromoaniline with bromine water, a further proof of its symmetrical structure. 6-Amino-3-sulphobenzoic acid could not be obtained by sulphonating *o*-bromobenzoic acid and then replacing the bromine atom by $-NH_2$ by the action of ammonia, this reaction furnishing only aniline-*p*-sulphonic acid, $\mu_{128} = 93\cdot8$, which crystallises with 1 or 2 H_2O. 2-Amino-4-sulphobenzoic acid has $\mu = 356\cdot4$, solubility 1·0482, and shows a blue fluorescence in solution in water. 3-Amino-4-sulphobenzoic acid has $\mu_{1311\cdot2} = 382\cdot9$, solubility 0·0810. Attempts to prepare 2-amino-3-sulphobenzoic and 2-amino-5-sulphobenzoic acids were unsuccessful. The sulphonation of *m*-aminobenzoic acid gives rise to a mixture of 3-amino-4-sulphobenzoic and 5-amino-2-sulphobenzoic acids (compare Griess, this Journ., 1872, 717)

These acids are all considerably ionised in solution, and, as in the case of the aminobenzenesulphonic acids, the ionisation decreases for the isomerides in the order ortho → para → meta (for the relative positions of $-HSO_3$ and $-NH_2$), whilst in the case of the aminobenzoic acids it diminishes in the order meta → ortho → para. The difference is probably due to the tendency to form internal salts in the ortho- and para-compounds in the first case. T. A. H.

Sulphonation of Benzenesulphonic Acid. Julius J. Polak (*Rec. trav. chim.*, 1910, [ii], **14**, 416—446).—It is shown that in the sulphonation of benzenesulphonic acid, both meta- and para-disulphonic acids are formed, the former being the chief product. In sulphonating at high temperatures, some trisulphonic acid is produced.

Benzene-*o*-disulphonic acid was prepared from *o*-chloronitrobenzene by methods described by Blanksma (Abstr., 1900, i, 482) and by Wohlfahrt (Abstr., 1903, i, 203), the orthoanilic acid so obtained being converted into the *o*-disulphonic acid by Leuckart's method (Abstr., 1890, i, 603). The meta- and para-isomerides were prepared by similar processes, but as regards the second of these, a better yield was obtained by Gattermann's process (Abstr., 1899, i, 516), starting from aniline-*p*-sulphonic acid. The method of determining the relative proportions of the two isomerides formed in the sulphonation of benzenesulphonic acid consisted in determining the solidifying point of the mixed sulphonyl chlorides, these being produced quantitatively by a special process from the potassium salts of the mixed acids. For this purpose it was necessary to construct a table showing the solidifying points of mixtures of the two pure sulphonyl chlorides, and this is given in the original. It shows a transition point for the para-isomeride at 71·6°.

The barium salt was used for sulphonation, as this could be obtained dry, and the temperature was controlled by conducting the experiments in vessels surrounded by vapours of substances boiling at the required temperatures.

Tables showing the relative percentages of the two disulphonic acids formed after various intervals, (*a*) with fuming sulphuric acid of known composition, (*b*) with 98% acid, that is, in presence of water, are given. At 183°, sulphonation is incomplete, whilst at 233° some trisulphonic acid is formed, but complete sulphonation to disulphonic acids takes place at 209°. It appears that meta- and para-acids are both formed initially, and that reciprocal transformation of both acids may then go on, the change para → meta being more rapid than the reverse one at 209°, but both are very slow, although they are accelerated by rise of temperature and by the presence of water. T. A. H.

Preparation of Certain Sulphonic Acids in the Free State. Joseph H. Kastle (*Amer. Chem. J.*, 1910, **44**, 483—487).—A simple method is described for the preparation of certain sulphonic acids by precipitating them from concentrated aqueous solutions by the addition of another strong acid, such as hydrochloric or sulphuric acid.

p-Nitro-*o*-toluenesulphonic acid can be prepared in a pure state in the following manner. *p*-Nitrotoluene is treated with fuming sulphuric acid, and the product is poured into an equal volume of water.

On cooling, the sulphonic acid separates in crystals, and is collected, dissolved in a small quantity of water, precipitated by the addition of concentrated hydrochloric acid, and recrystallised several times from water. The acid is thus obtained in pale yellow prisms containing $2H_2O$, and not $2\frac{1}{2}H_2O$ as stated by Jenssen (Abstr., 1874, 479).

In a similar way, a toluenesulphonic acid, probably the para-compound, can be prepared, which forms colourless, prismatic crystals, containing $1H_2O$.

Attempts have been made to isolate benzenesulphonic and *o*-nitrotoluenesulphonic acids by this method, but without success. E. G.

Catalytic Reactions at High Temperatures. XXI. Influence of Foreign Substances on the Activity of Catalysts. WLADIMIR N. IPATIEFF (*Ber.*, 1910, 43, 3387—3393).—Hydroaromatic compounds containing a double linking in the ring are completely reduced when heated with copper and hydrogen in an iron vessel, but when the vessel is of copper or phosphor-bronze, the reduction does not extend to this linking. Further experiments show that amylene is completely reduced at 300° in an iron tube in presence of copper oxide, but that no reduction occurs in the absence of the copper oxide, whilst in presence of copper or copper oxide, enclosed in a copper tube, the reduction is very incomplete, the reaction $C_5H_{10} + H_2 \rightleftarrows C_5H_{12}$ being reversible.

Using copper oxide in an iron tube, octahydronaphthalene is partly reduced to decahydronaphthalene, and partly decomposed, yielding *cyclo*hexane. The copper walls of the vessel may hinder the reaction, or it may be necessary that two catalysts should be simultaneously present. Further experiments are in progress. C. H. D.

Action of Metals on Aromatic Keto-chlorides and the Properties of Compounds of the Type $R_2CCl\cdot CClR_2$. JAMES F. NORRIS, RUTH THOMAS, and B. MARION BROWN (*Ber.*, 1910, 43, 2940—2959. Compare Schmidlin and Escher, Abstr., 1910, i, 369). —In compounds of the type CR_2Cl_2, when the substituting radicle is positive or strongly negative, the halogen atom only reacts with difficulty with metals and certain metallic oxides; but on passing from the positive end of the series to the negative, the reactivity increases until keto-chlorides are obtained which readily part with chlorine. If the negative character of the substituting group is increased from this point, the compounds become stable again; for example, mercury only eliminates one halogen from benzophenone chloride, forming tetraphenylethylene dichloride; 4 : 4′-dichlorobenzophenone chloride and mercury yield a mixture of tetrachlorotetraphenylethylene and tetraphenylethylene; 2 : 4′-dichlorobenzophenone chloride gives exclusively tetrachlorotetraphenylethylene, whilst 2 : 5 : 2′ : 5′-tetrachlorobenzophenone chloride does not interact either with mercury or with zinc. Both zinc and silver act rapidly on benzophenone chloride, forming tetraphenylethylene.

Sulphuryl chloride in presence of small quantities of acetic acid was found to afford an effective means of causing the addition of chlorine to double linkings, and it is possible to obtain tetraphenylethylene dichloride in this manner. This substance forms characteristic additive compounds with carbon tetrachloride and chloroform.

When tetraphenylethylene dichloride is slowly heated (compare Schmidlin and Escher, *loc. cit.*), the chief product is 4-chlorotetraphenylethylene. At higher temperatures, tetraphenylethylene is formed. With magnesium phenyl bromide, 4-phenyltetraphenylethylene is formed in addition to tetraphenylethylene.

Tetraphenylethylene dibromide could not be obtained by the action of metals on benzophenone bromide tetraphenylethylene being the sole product of the reaction. Tetraphenylethylene dichloride when heated with bromobenzene and sodium also yields tetraphenylethylene.

By the action of aluminium chloride on 4 : 4′ : 4″ : 4‴-tetrachlorotetraphenylethylene dichloride, 9 : 10-diphenylphenanthrene and a tetrachloro-substitution product are obtained; the para-hydrogen atoms take no part in the reaction.

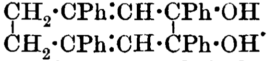
Both triphenylmethyl and pentaphenylethane react with sulphuryl chloride, forming triphenylmethyl chloride in each instance; tetraphenylethane and sulphuryl chloride do not interact. Sulphuryl chloride converts triphenylcarbinol into triphenylmethyl chloride, and its trinitro-derivative into trinitrotriphenylmethyl chloride.

4 : 4′ : 4″ : 4‴-*Tetrachlorotetraphenylethylene* has m. p. 216—217°; the *dichloride* has m. p. 190—191°. Fluorenone chloride crystallises in long, straw-yellow needles, m. p. 101·5—102·5°. Silver converts it into bisdiphenylene ethylene; mercury into *dibiphenylene-ethylene dichloride*, which crystallises in colourless needles, m. p. 228—236°, to a red liquid.

4-*Phenylbenzophenone chloride* forms crystals, m. p. 45—47°. When boiled with diphenylmethane, 4-*phenyltetraphenylethylene* is formed, m. p. 189—190°. A *tetranitro*-derivative forms yellow crystals, m. p. 278—280°.

Convenient methods are described for the preparation of benzophenone, tetraphenylethylene, etc., on a large scale. E. F. A.

Gradual Synthesis of the Benzene Chain. MAURICE DELACRE (*Bull. Soc. chim.*, 1910, [iv], 7, 1041—1046. Compare Abstr., 1910, i, 120, 323).—A paper detailing the steps in the synthesis of triphenylbenzene from acetophenone, through dypnone, CMePh:CHBz, and dypnopinacone,



$\begin{array}{l} CH_2\cdot CPh{:}CH\cdot CPh\cdot OH \\ \vert \qquad\qquad\qquad\quad \vert \\ CH_2\cdot CPh{:}CH\cdot CPh\cdot OH \end{array}$.

The latter, like the members of the homodypnopinacone and *iso*dypnopinacolin groups, furnishes readily the hydrocarbon, $C_{25}H_{22}$, the reduction product of which gives triphenylbenzene, allylbenzene, and ethylbenzene on heating. The remainder of the paper is devoted to discussing the bearing of this and other reactions among pinacolin derivatives, on the general question of the gradual synthesis of the benzene chain. T. A. H.

Bromo-salts of Platinum. ALEXANDER GUTBIER [with FR. BAURIEDEL and C. J. OBERMAIER] *Ber.*, 1910, **43**, 3228—3234. Compare Abstr., 1910, i, 12).—Various substituted ammonium platinibromides have been prepared by adding a solution of the substituted ammonium bromide to a solution of hydrogen platinibromide. The resulting precipitates were purified by recrystallisation from aqueous hydrobromic acid. In some cases there was a tendency for decomposition to take place when aqueous solutions were used, a resin being formed; this tendency could be obviated by using dilute alcoholic solutions of the substituted ammonium bromide and of hydrogen bromide.

Phenylammonium platinibromide, $(NH_3Ph)_2PtBr_6$: yellowish-red, felted crystals, which are still solid at 260°. *Phenylmethylammonium platinibromide*, $(NH_2MePh)_2PtBr_6$: bright red, rhombic needles, m. p. 227—228° (decomp.). *Phenyldimethylammonium platinibromide*,

$$(NHMe_2Ph)_2PtBr_6:$$

red needles. *Phenylethylammonium platinibromide*,

$$(NH_2EtPh)_2PtBr_6:$$

bright red, microscopic needles, m. p. 209—210°. *Phenyldiethylammonium platinibromide*, $(NHEt_2Ph)_2PtBr_6$: bright red, prismatic crystals. o-*Tolylammonium platinibromide*, $(NH_3{\cdot}C_6H_4Me)_2PtBr_6$: bright yellowish-red needles, probably monoclinic, m. p. 225—226° (decomp.). m-*Tolylammonium platinibromide*,

$$(NH_3{\cdot}C_6H_4Me)_2PtBr_6:$$

bright red, shining crystals, m. p. 266° (decomp.). p-*Tolylammonium platinibromide*, $(C_6H_4Me{\cdot}NH_3)_2PtBr_6$: shining, yellowish-red, flat prisms, m. p. 268—269°. 1:2:4-*Xylylammonium platinibromide*,

$$(C_6H_3Me_2{\cdot}NH_3)_2PtBr_6:$$

bright red, felted, rhombic needles, m. p. 262—263°. 1 : 3 : 4-*Xylylammonium platinibromide*: yellowish-red needles and plates, m. p. 256°. 1 : 4 : 5-*Xylylammonium platinibromide*: red, monoclinic needles or rhombic plates, m. p. 241°. *Pyridinium platinibromide*,

$$(PyH)_2PtBr_6:$$

shining, reddish-brown needles, which are still solid at 270°. α-*Picolinium platinibromide*, $(C_5NH_5Me)_2PtBr_6$: red or reddish-brown, rhombic plates, m. p. 211—212°. *Quinolinium platinibromide*, $(C_9NH_8)_2PtBr_6$: bright red, monoclinic prisms, m. p. 254—255° (decomp.). *Benzylammonium platinibromide*, $(NH_3{\cdot}C_7H_7)_2PtBr_6$: yellowish-red, rhombic plates, m. p. 257—259° (decomp.). *Benzylethylammonium platinibromide*, $(NH_2Et{\cdot}C_7H_7)_2PtBr_6$: bright red plates and needles, m. p. 177°. *Benzidinium platinibromide*,

$$[N_2H_6(C_6H_4)_2]PtBr_6:$$

yellowish-red monoclinic, needles, which are strongly pleochroic. o-*Phenylenediammonium platinibromide*, $[C_6H_4(NH_3)_2]PtBr_6$, brownish-yellow, monoclinic, pleochroic needles or plates. m-*Phenylenediammonium platinibromide*: dark red, rhombic needles, which do not melt at 270°. p-*Phenylenediammonium platinibromide*: dark red, monoclinic prisms, slightly pleochroic. α-*Naphthylammonium platinibromide*, $(C_{10}H_7{\cdot}NH_3)_2PtBr_6$: red, monoclinic crystals, which do not melt at 270°. β-*Naphthylammonium platinibromide*, reddish-yellow plates and prisms, which are still solid at 275°.

The above compounds are only very slightly soluble in cold water, giving yellow solutions; they are more soluble in hot water to yellowish-red or red solutions. T. S. P.

Hydroxy- and Dihydroxy-phenylalkylammonium Compounds, and β-Nitrostyrenes. KARL W. ROSENMUND (*Ber.*, 1910, **43**, 3412—3417).—Attempts have been made to synthesise compounds analogous to hordenine alkylhalides (compare Abstr., 1910, i, 241), the method of procedure consisting in the complete methylation of the alkyl ethers of the base, and then removal of the alkyl group of the phenolic ether by means of hydriodic acid. p-*Methoxyphenyl*iso*propyltrimethylammonium iodide*,

$$OMe\cdot C_6H_4\cdot CH_2\cdot CHMe\cdot NMe_3I,$$

obtained by methylating *p*-methoxyphenyl*iso*propylamine, crystallises from water in long, colourless needles, m. p. 215—216°, and when boiled with hydriodic acid yields p-*hydroxyphenyl*iso*propyltrimethylammonium iodide* in the form of colourless needles, m. p. 241—242°. 3 : 4-*Dimethoxyphenyl*iso*propyltrimethylammonium iodide*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot CHMe\cdot NMe_3I,$$

forms colourless crystals, m. p. 187°, and the corresponding *dihydroxy*-derivative crystallises from alcohol in colourless, compact prisms, m. p. 190°, and its aqueous solution gives the catechol reaction with ferric chloride.

A good yield of β-nitromethylenedioxystyrene (Bouveault and Wahl, *Bull. Soc. chim.*, 1903, [iii], **29**, 523; Medinger, *Monatsh.*, 1906, **27**, 244) is obtained by the gradual addition of a methyl-alcoholic solution of potassium hydroxide (1·5 mols.) to an alcoholic solution of piperonal and nitromethane, and then pouring the whole into an excess of ice-cold 10% hydrochloric acid. When reduced with zinc dust and a mixture of alcohol and glacial acetic acid, the nitro-compound yields homopiperonylaldoxime, m. p. 119—120°, and this when reduced with 3% sodium amalgam yields homopiperonylamine, the hydrochloride of which has m. p. 208° (Medinger, Abstr., 1906, i, 421, gives 197°).

β-Nitrodimethoxystyrene, $C_6H_3(OMe)_2\cdot CH:CH\cdot NO_2$, obtained from veratraldehyde and nitromethane, crystallises in yellow plates, m. p. 140°.

Veratraldehyde is easily prepared by methylating vanillin with methyl sulphate at 65—70° in the presence of 10% aqueous potassium hydroxide solution (compare Perkin and Robinson, Trans., 1907, **91**, 1079; Decker and Koch, Abstr., 1908, i, 35). J. J. S.

Action of Cyanogen Bromide on Tertiary Bases containing the Phenylethyl and Phenylpropyl Groups. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 3209—3220. Compare Abstr., 1910, i, 189, 506).—It has been shown previously that groups containing an unsaturated linking in the βγ-position are, in general, more readily removed from amines by the action of cyanogen bromide than saturated groups. In order to ascertain if a similar influence is to be observed in the case of groups containing unsaturated linkings in more remote positions, the author has investigated the behaviour towards cyanogen bromide of tertiary amines of the following types: $CH_2Ph\cdot CH_2\cdot NR_2$ and $CH_2Ph\cdot CH_2\cdot CH_2\cdot NR_2$, and finds that the groups are more firmly attached as the length of the aliphatic chain increases.

Di-β-phenylethyl-dimethylammonium bromide,
$NMe_2(CH_2·CH_2Ph)_2Br$,
soft, fatty leaflets, m. p. 160°, is obtained together with β-phenylethyldimethylamine, $NMe_2·CH_2·CH_2Ph$, b. p. 205°/760 mm. (compare Barger, Trans., 1909, **95**, 2193), by the action of β-phenylethyl bromide on dimethylamine.

Cyanogen bromide reacts vigorously with β-phenylethyldimethylamine, yielding *β-phenylethyltrimethylammonium bromide*,
$CH_2Ph·CH_2·NMe_3Br$,
m. p. 220°, β-phenylethyl bromide, and *β-phenylethylmethylcyanamide*, $CH_2Ph·CH_2·NMe·CN$. The latter has b. p. 164—165°/10 mm., and is hydrolysed by sulphuric acid in aqueous alcoholic solution to *as*-β-phenylethylmethylcarbamide, $C_2H_4Ph·NMe·CO·NH_2$; energetic hydrolysis yields β-phenylethylmethylamine, $NHMe·C_2H_4Ph$ (compare Johnson and Guest, Abstr., 1909, i, 794).

Phenyl-β-phenylethylmethylamine, $NMePh·C_2H_4Ph$, obtained from β-phenylethyl bromide and methylaniline, is a pale yellow liquid, b. p. 198—199°/18 mm., and solidifies in ice to a snow-white mass, m. p. 44°; it yields a *picrate*, m. p. 101°, and a *platinichloride*, m. p. 162—163° (decomp.); when treated with cyanogen bromide, it yields *β-phenylethylphenylcyanamide*, $C_2H_4Ph·NPh·CN$, b. p. 220—225°/11 mm. (slight decomp.), together with methyl bromide and β-phenylethyl bromide.

β-Phenylethyldiethylamine, $NEt_2·C_2H_4Ph$, prepared by heating β-phenylethyl bromide with diethylamine, is a colourless, almost odourless liquid, b. p. 103°/10 mm., and gives a crystalline *picrate*, m. p. 95°, and an oily *platinichloride*, which slowly solidifies, m. p. 140°; when heated with cyanogen bromide, it yields β-phenylethyl bromide and *β-phenylethylethylcyanamide*, $C_2H_4Ph·NEt·CN$, which has b. p. 174°/15 mm., and is hydrolysed by sulphuric acid to *β-phenylethylethylamine*, $NHEt·C_2H_4Ph$, a colourless oil, b. p. 99—100°/13 mm.; the latter gives an oily *platinichloride*, which slowly solidifies, and a crystalline *picrate*, m. p. 130°, a *phenylthiocarbamide*, $C_2H_4Ph·NEt·CS·NHPh$, m. p. 88°, and a *carbamide*,
$C_2H_4Ph·NEt·CO·NH_2$,
m. p. 58°; the *benzoyl* and *benzenesulphonyl* derivatives are oils.

γ-Phenylpropyldimethylamine (Senfter and Tafel, Abstr., 1894, i, 579) is obtained by the interaction of γ-phenylpropyl chloride or bromide with dimethylamine.

The action takes place more readily with the bromide, but is accompanied by the formation of an oily quaternary *bromide*,
$NMe_2(C_3H_6Ph)_2Br$,
which is converted by silver chloride into the corresponding *chloride*, m. p. 88°.

γ-Phenylpropyldimethylamine reacts vigorously with cyanogen bromide, yielding γ-phenylpropylmethylcyanamide and *γ-phenylpropyltrimethylammonium bromide*, $CH_2Ph·CH_2·CH_2·NMe_3Br$, which forms a red, crystalline *platinichloride*, m. p. 205—209°.

γ-Phenylpropylmethylcyanamide, $C_3H_6Ph·NMeCN$, b. p. 187—189°/17 mm., forms a colourless liquid, and is hydrolysed with difficulty. On heating for several hours at 170° with strong hydrochloric acid, it is converted into *γ-phenylpropylmethylamine*, $NHMe\cdot C_3H_6Ph$, a colourless oil, b. p. 110°/17 mm., which gives an oily *picrate* and a crystalline *platinichloride*, m. p. 188°; the *carbamide*, $C_3H_6Ph\cdot NMe\cdot CO\cdot NH_2$, crystallises in leaflets, m. p. 101°.

The direct interaction of γ-phenylpropyl chloride or bromide and methylamine furnishes a very small yield of γ-phenylpropylmethylamine.

γ-Phenylpropyldiethylamine, $NEt_2\cdot C_3H_6Ph$, prepared from γ-phenylpropyl bromide and diethylamine, is a colourless liquid, b. p. 137—139°/22 mm., giving an oily *picrate* and *platinichloride*. It is converted by the action of cyanogen bromide into a mixture of γ-phenylpropyl bromide, diethylcyanamide, and *γ-phenylpropylethylcyanamide*,

$$C_3H_6Ph\cdot NEt\cdot CN.$$

The latter has b. p. 191—192°/14 mm., and is hydrolysed by hydrochloric acid into *γ-phenylpropylethylamine*, a colourless liquid, b. p. 118°/16 mm.

γ-Phenylpropyldipropylamine, $NPr^{\alpha}_2\cdot C_3H_6Ph$, obtained from γ-phenylpropyl bromide and dipropylamine, is a colourless, almost odourless liquid, b. p. 158—160°/17 mm.; the *picrate* is an oil; the *platinichloride* has m. p. 91—93°. It reacts vigorously with cyanogen bromide, yielding propyl bromide, γ-phenylpropyl bromide, and *γ-phenylpropylpropylcyanamide*, $C_3H_6Ph\cdot NPr^{\alpha}\cdot CN$, b. p. 200°/16 mm. The latter is hydrolysed by hydrochloric acid into *γ-phenylpropylpropylamine*, $NHPr^{\alpha}\cdot C_3H_6Ph$, a colourless, odourless liquid, b. p. 134°/17 mm., which forms an orange-yellow, crystalline *picrate*, m. p. 97°, and an oily *platinichloride*. F. B.

Isomerism of Anils (Schiff's Bases). III. WILHELM MANCHOT (*Ber.*, 1910, **43**, 3359—3362).—Reply to Anselmino (Abstr., 1910, i, 462), who has not appreciated the fact that the object of the molecular-weight determinations by Manchot and Furlong (Abstr., 1909, i, 805; 1910, i, 33) is to ascertain whether the entire differences between the two forms of an anil may not be due to differences in molecular magnitude. The existence of a temperature limit, stated by Anselmino, above and below which the two forms of an anil are stable respectively, is disproved by the fact that the yellow form of *p*-bromosalicylaldehydeanil separates from solutions at temperatures much higher than 33°, the limit set by Anselmino. C. S.

Sulphanilide. ALFRED WOHL and FRANZ KOCH (*Ber.*, 1910, **43**, 3295—3307).—A good yield of sulphanilide (W. Traube, Abstr., 1891, 569) can be obtained by dropping a solution of sulphuryl chloride dissolved in dry ether into an excess of aniline dissolved in about three times its volume of dry ether and cooled by a good freezing mixture. The yield is 60% of the theoretical, and the by-product is azobenzene. When chloroform or carbon tetrachloride is used as diluent, Mohr's trianilinobenzene (Abstr., 1890, 614) is formed. The anilide is not readily hydrolysed, and is not affected when heated with sodium ethoxide at 180°.

The *disodium* salt, $C_{12}H_{10}O_2N_2SNa_2$, crystallises on the addition of benzene and light petroleum to its alcoholic solution in slender, glistening needles containing alcohol. The *acetyl* derivative,

$NPhAc\cdot SO_2\cdot NHPh$,

prepared by the action of acetic anhydride and a little sulphuric acid at the ordinary temperature, forms compact, rhombic prisms, m. p. 158—159°, after sintering at 155°, and dissolves in alkalis. The *diacetyl* derivative, $SO_2(NAcPh)_2$, obtained by using a temperature of 45°, crystallises from carbon tetrachloride in prismatic needles, m. p. 164°, after sintering at 159°. This compound is decomposed readily when heated with acetic anhydride, yielding diacetanilide and sulphuric acid, but at the same time the sulphuric acid reacts with the acetylsulphonamic acid, which is an intermediate product, yielding acetylaniline-*p*-sulphonic acid:

$$SO_2(NPhAc)_2 \longrightarrow NPhAc\cdot SO_3H \longrightarrow NHAc\cdot C_6H_4\cdot SO_3H.$$

Diphenyldimethylsulphamide, $SO_2(NPhMe)_2$, obtained by the action of methyl iodide and sodium methoxide at 100°, crystallises in prismatic needles or plates, m. p. 96—97°, and is also formed when silver oxide and methyl iodide are used.

An explosive *dinitroso*-derivative, $SO_2(NPh\cdot NO)_2$, is formed when nitrous fumes are passed into a dry ethereal solution of the anilide. It forms hygroscopic crystals, which explode at 73—74°. Ethereal or chloroform solutions of the nitroso-derivative, and also of the nitroso-derivative of 4 : 4′-dibromosulphanilide, condense with β-naphthol, yielding azo-derivatives and black azo-dyes, which have not been obtained pure.

A solution of sulphanilide in sodium carbonate reacts with an excess of a diazotised solution of *p*-nitroaniline, yielding a brownish-black dye.

2 : 4 : 2′ : 4′-*Tetranitrodiphenylsulphamide*, $SO_2[NH\cdot C_6H_3(NO_2)_2]_2$, prepared by adding the sulphamide or, still better, its mono- or diacetyl derivative to fuming nitric acid cooled to 0°, separates as well developed prisms, m. p. 183°, and is decomposed when boiled with water. Fuming nitric acid reacts with a well cooled sulphuric acid solution of the anilide, yielding *o*-nitroaniline-*p*-sulphonic acid. A chloroform solution of bromine converts the anilide into its 4 : 4′-*dibromo*-derivative, $C_{12}H_{10}O_2N_2Br_2S$, in the form of plates, m. p. 124—125°. The bromo-derivative reacts with sodium acetate and acetic anhydride, yielding *p*-bromoacetanilide. When further brominated, the dibromo-derivative yields 2 : 4 : 4′-*tribromodiphenylsulphamide*, $C_{12}H_9O_2N_2Br_3S$, which crystallises from benzene in tetragonal pyramids, m. p. 143°.

Sulpho-p-*toluidide*, $C_{14}H_{16}O_2N_2S$, obtained when a chloroform solution of sulphonyl chloride is added to a well cooled solution of *p*-toluidine in dry chloroform, crystallises from carbon tetrachloride or light petroleum in colourless, prismatic needles, m. p. 96—97°.

Nitroanilines, acetanilide, and aniline hydrochloride do not react with sulphuryl chloride, and monomethylaniline yields dark brown dyes.

J. J. S.

Comparative Nitration of Mono- and Diacylated Aromatic Amines. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Ber.*, 1910, **43**, 3460—3464; *Compt. rend.*, 1910, **151**, 985. Compare Abstr., 1909, i, 377, 913).—A comparative examination of the nitration of a few acylated and diacylated aromatic amines has been undertaken in order to ascertain what influence is exerted on the stability of the molecule by the second acyl group attached to the nitrogen atom, and what orientating effect it has on the entrant nitro-group. The experimental results are given only in the paper in the *Berichte*.

As already recorded, 2 : 3-dinitro-4-toluenesulphonylaminoanisole is obtained when 1 part of 4-toluenesulphonylaminoanisole in 10 parts of glacial acetic acid is added to 5 parts of nitric acid, D 1·52, between 20—30°; under the same conditions, 4-acetyltoluenesulphonylaminoanisole is unchanged. When, however, using the same proportions, the temperature is allowed to rise to 60°, the first substance behaves as before, whilst the diacylated compound yields 3-*nitro*-4-*acetyltoluenesulphonylaminoanisole*, $OMe\cdot C_6H_3(NO_2)\cdot NAc\cdot SO_2\cdot C_7H_7$, m. p. 197°. Finally, when the monoacylated compound is added to the nitric acid below 20°, and the mixture, after being heated momentarily to 55°, is poured into water, the 2 : 3-dinitro-compound is obtained, together with the 3-nitro-compound. Under the same conditions (except that the temperature can be raised to 65° before gas is evolved), the diacylated compound yields 2 : 5-*dinitro*-4-*acetyltoluenesulphonylaminoanisole*, m. p. 169°, yellow leaflets, and the 2 : 3-dinitro-*isomeride*, m. p. 205°, colourless needles, which are soparated by the greater solubility of the former in hot alcohol.

3-Nitroaceto-*p*-toluidide is formed when aceto-*p*-toluidide in acetic acid is added to nitric acid below 15° and the temperature is then raised gradually to 65°; the same compound is also formed when diaceto-*p*-toluidide is treated similarly, the temperature being raised, however, only to 20° (evolution of gas). When nitrated by nitric acid alone, aceto-*p*-toluidide at 65° (evolution of gas) yields 38% of 3 : 5-dinitroaceto-*p*-toluidide and 62% of 3-nitroaceto-*p*-toluidide, whilst diaceto-*p*-toluidide must be cooled by ice during the nitration, and yields 3-nitro-*p*-toluidine.

When nitrated in acetic acid solution, 4-toluenesulphonylaminotoluene at 70° yields 80% of 3 : 5-*dinitro*-4-*toluenesulphonylaminotoluene*, $C_6H_2Me(NO_2)_2\cdot NH\cdot SO_2\cdot C_7H_7$, m. p. 204° (the same substance is also produced at 40° in the absence of the acetic acid), whilst 4-*acetyltoluenesulphonylaminotoluene*, $C_6H_4Me\cdot NAc\cdot SO_2\cdot C_7H_7$, m. p. 134°, obtained from 4-toluenesulphonylaminotoluene and acetic anhydride, is not nitrated, even at 75°; when, however, the diacylated compound is treated below 15° with nitric acid alone, the temperature being raised subsequently to 40° (evolution of gas), 2-*nitro*-4-*nitrotoluenesulphonylaminotoluene*, $NO_2\cdot C_6H_3Me\cdot NH\cdot SO_2\cdot C_7H_6\cdot NO_2$, m. p. 183°, is obtained, which yields 2-nitro-*p*-toluidine by hydrolysis.

From the preceding experiments, it seems that the presence of the acetyl and the toluenesulphonyl groups increases the stability of the molecule, and, in the case of *p*-toluidine, affects the orientation of the nitro-group and facilitates the introduction of a nitro-group into the toluenesulphonyl nucleus; the presence of two acetyl groups in *p*-toluidine apparently diminishes the stability of the molecule. C. S.

Action of Phenylthiocarbimide on Mono- and Di-*iso*amylaniline. THEODOR ST. WARUNIS (*Ber.*, 1910, **43**, 2972—2976).—By the action of phenylthiocarbimide on mono*iso*amylaniline, *diphenyl*iso*amylthiocarbamide*, $NHPh\cdot CS\cdot NPh\cdot C_5H_{11}$, is formed; the same compound is obtained from crude di*iso*amylaniline, owing to the mono-derivative present as impurity. It crystallises in large, transparent, colourless needles, m. p. 107·5°, and sublimes at 240—250°.

To determine sulphur in organic substances, they are heated with a mixture of potassium hydroxide and sodium peroxide in a silver crucible, at first at 75—85°, and subsequently over a small flame.

E. F. A.

Some Derivatives of 3 : 4 : 5-Trinitro-2-methoxytoluene. Jan J. Blanksma (*Rec. trav. chim.*, 1910, **29**, 410—415).—The 3 : 4 : 5-trinitro-2-methoxytoluene was prepared by the nitration of 4-nitro-2-methoxytoluene (Kaufler and Wenzel, Abstr., 1901, i, 590). When treated with ammonia, it yields chiefly 3 : 5-*dinitro*-2-*methoxy*-p-*toluidine* as yellow crystals, m. p. 130°, the *acetyl* derivative of which melts at 220°.

By the diazotisation of 3 : 5-dinitro-2-methoxy-*p*-toluidine, colourless crystals of 3 : 5-dinitro-2-methoxytoluene are produced; when treated with ammonia, this is transformed into 3 : 5-dinitro-*o*-toluidine. On heating 3 : 4 : 5-trinitro-2-methoxytoluene with ammonia in a sealed tube, dark brown crystals of 3 : 5-dinitro-2 : 4-tolylenediamine, m. p. 254°, are formed; Nietzki and Rösel found 300° as the melting point of this substance (Abstr., 1891, 192); its *acetyl* derivative does not melt below 300°.

3 : 5-*Dinitro*-2 : 4-*di*(*methylnitroamino*)*toluene* forms colourless crystals, m. p. 169°; 2-*chloro*-5-*nitro*-4-*aceto*-p-*toluidide* crystallises in pale yellow crystals, m. p. 112°.

N. C.

Quinol Di*iso*butyl Ether. Rudolf Nietzki and Kesselring (*Ber.*, 1910, **43**, 3459—3460).—Attempts to prepare Schubert's tetranitroquinol di*iso*butyl ether (Abstr., 1883, 60) have resulted in the preparation of only a *trinitro*-compound, $C_{14}H_{19}O_8N_3$, m. p. 96°, even when fuming nitric acid and high temperatures have been employed.

C. S.

Phenols Insoluble in Alkalis. Henry A. Torrey and Roger Adams (*Ber.*, 1910, **43**, 3227—3228. Compare Abstr., 1907, i, 325; 1908, i, 460).—Of the isomeric nitrophenylhydrazones of paenol and bromopaenol, only the para-compounds are soluble in aqueous sodium hydroxide.

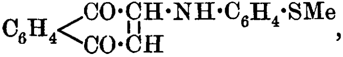
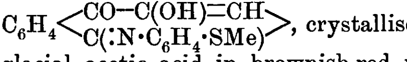
Paeonol-o-*nitrophenylhydrazone*,

$$OH\cdot C_6H_3(OMe)\cdot CMe\colon N\cdot NH\cdot C_6H_9\cdot NO_2,$$

crystallises in deep red, monoclinic prisms, m. p. 217°; the m-*nitro*-derivative in red lamellæ, m. p. 197°, and the p-*nitro*-derivative in red crystals, m. p. 235—236° (decomp.).

Bromopaeonol-o-*nitrophenylhydrazone* forms red needles, m. p. 253—254°; the m-*nitrophenylhydrazone*, brownish-red lamellæ, m. p. 208°, and the p-*nitro*-derivative, orange needles, m. p. 222°. F. B.

***p*-Aminothiophenol [*p*-Aminophenyl Mercaptan]. II.** Theodor Zincke and P. Jörg (*Ber.*, 1910, **43**, 3443—3450. Compare Abstr., 1909, i, 789).—*p*-Methylthiolaniline (*p*-aminophenyl methyl sulphide) resembles aniline in many of its reactions, for example, it reacts with quinones, yielding intensely coloured anilino-derivatives, it condenses with 1-chloro-2 : 4-dinitrobenzene, yielding a substituted diphenylamine derivative, and yields diazonium salts which are readily transformed into corresponding chloro- and cyano-derivatives.

*Dimethylthiolanilino-*p*-benzoquinone,* $C_6H_2O_2(NH\cdot C_6H_4\cdot SMe)_2$, prepared by boiling an alcoholic solution of the aminothiophenol with *p*-benzoquinone for a short time, separates from tetrachloroethane as a finely crystalline powder, and dissolves in concentrated sulphuric acid to a deep bluish-green solution. The *derivative* from *α*-naphthaquinone,  $C_6H_4<\begin{matrix}CO\cdot C(H)\cdot NH\cdot C_6H_4\cdot SMe\\ \| \\ CO\cdot CH\end{matrix}$, crystallises from hot alcohol in dark red, glistening plates with a metallic lustre, and has m. p. 164—165°; when boiled with alkalis it is slowly decomposed, and yields hydroxynaphthaquinone. The isomeric *compound* from *β*-naphthaquinone,  $C_6H_4<\begin{matrix}CO—C(OH)=CH\\ C(:N\cdot C_6H_4\cdot SMe)\end{matrix}>$, crystallises from a mixture of alcohol and glacial acetic acid in brownish-red plates, and needles with a golden-yellow lustre, and has m. p. 242—243°. Its solution in concentrated sulphuric acid has a brownish-violet colour. It is more stable than the corresponding dianilino-derivative of *β*-naphthaquinone, and is not transformed so readily into derivatives of *α*-naphthaquinone.

2 : 4-*Dinitro-4′-methylthioldiphenylamine,* $C_6H_3(NO_2)_2\cdot NH\cdot C_6H_4\cdot SMe$, prepared by boiling an alcoholic solution of the *p*-methylthiolaniline and 1-chloro-2 : 4-dinitrobenzene with potassium acetate, crystallises from glacial acetic acid in dark orange-red needles or stout plates, m. p. 141°, and when reduced with an aqueous alcoholic solution of sodium sulphide yields 4-*nitro-2-amino-4′-methylthioldiphenylamine,* $NO_2\cdot C_6H_3(NH_2)\cdot NH\cdot C_6H_4\cdot SMe$, which crystallises from alcohol in dark reddish-brown needles or plates, m. p. 128°. Its solution in concentrated sulphuric acid has a deep bluish-green colour.

The diazonium chloride from *p*-methylthiolaniline couples with an alkaline solution of *β*-naphthol, yielding a deep red *azo-dye.* The *diazoamino*-compound, $SMe\cdot C_6H_4\cdot N:N\cdot NH\cdot C_6H_4\cdot SMe$, crystallises from light petroleum in pale brown needles, m. p. 99°. p-*Methylthiolbenzonitrile,* $CN\cdot C_6H_4\cdot SMe$, crystallises from dilute methyl alcohol in colourless plates, m. p. 64°, and on hydrolysis yields p-*methylthiolbenzoic acid,* $SMe\cdot C_6H_4\cdot CO_2H$, which crystallises in colourless, flat needles, m. p. 192°. 1-*Methylthiol-4-iodobenzene,* $C_6H_4I\cdot SMe$, crystallises in colourless plates, m. p. 38°; the *dibromide,* $C_6H_4I\cdot SBr_2Me$, crystallises in dark garnet-red needles, and with water yields the *sulphoxide,* $C_6H_4I\cdot SOMe$, which crystallises from light petroleum in needles, m. p. 112°. The *iododichloride,* $ICl_2\cdot C_6H_4\cdot S\cdot CCl_3$, prepared by the action of chlorine on a chloroform solution of the iodo-derivative in the absence of all traces of moisture, crystallises in pale yellow needles, and by the removal of chlorine yields p-*iodophenyl trichloromethyl sulphide,* $C_6H_4I\cdot S\cdot CCl_3$, which crystallises from light petroleum in colourless needles, m. p. 103°. Aniline reacts with the trichloro-derivative, yielding triphenylguanidine and *iodophenyl mercaptan,* $C_6H_4I\cdot SH$, the latter of which crystallises in nacreous plates, m. p. 85°. Other methylthiols react in a similar manner. p-*Nitrophenyl trichloromethyl sulphide*, $NO_2\cdot C_6H_4\cdot S\cdot CCl_3$, has m. p. 94°. *Acetylaminochlorophenyl trichloromethyl sulphide*, $NHAc\cdot C_6H_3Cl\cdot S\cdot CCl_3$, crystallises in plates, m. p. 136°. It reacts with aniline, yielding triphenylguanidine and acetylaminochlorophenyl mercaptan, the *disulphide* of which has m. p. 181°.

When the *p*-iodophenyl methyl sulphide is treated with chlorine in chloroform solution, and then exposed to the air and shaken with potassium iodide solution, Langmuir's *p*-iodobenzenesulphonyl chloride (Abstr., 1895, i, 230) is obtained. The corresponding *anilide*, $C_{12}H_{10}O_2NSI$, forms colourless, fibrous needles, m. p. 143°.

J. J. S.

Action of Bromine on Diphenyl Sulphide, Diphenyl Sulphoxide, and Diphenylsulphone. JACOB BÖESEKEN (*Rec. trav. chim.*, 1910, **29**, 315—329).—Bromine reacts with diphenyl sulphide to give a mixture of 4-bromodiphenyl sulphide and 4 : 4′-dibromodiphenyl sulphide. With chlorine in glacial acetic acid solution, 4 : 4′-dichlorodiphenyl sulphide is produced, but with dilute acetic acid only the sulphone. In the case of diphenylsulphoxide, a direct replacement by bromine does not take place, but in the presence of a little hydrobromic acid, 4 : 4′-dibromodiphenyl sulphide is formed, as in the case of the sulphide; no corresponding chloro-derivative is produced by the action of chlorine. Bromine does not react easily with diphenylsulphone, but at high temperatures the molecule is broken up with the formation of sulphuryl bromide and bromobenzene; a similar change is brought about by the action of chlorine.

N. C.

Electrolytic Oxidation of Aromatic Sulphides. FRITZ FICHTER and PH. SJÖSTEDT (*Ber.*, 1910, **43**, 3422—3429).—The electrolytic oxidation of benzyl sulphide gives three different products according to the conditions. In all cases the benzyl sulphide is dissolved in glacial acetic acid and a platinum anode used; a divided cell is unnecessary, since the products of reaction are only reduced with difficulty at a platinum cathode. If concentrated hydrochloric acid is added to the glacial acetic acid solution, and electrolysis carried out at 25°, using 0·08 ampere per sq. cm., and passing slightly less than the theoretical current, an almost theoretical yield of benzyl sulphoxide is obtained. Excess of current should be avoided, or else benzaldehyde is formed. Benzyl sulphide dichloride is probably first formed, and this is then hydrolysed into benzylsulphoxide and hydrogen chloride. Oxygen acids in place of hydrochloric acid give rise to further oxidation products of benzyl sulphide.

When the oxidation is carried out in hydrochloric-acetic acid solution at 90—95°, benzyldisulphoxide is formed. The benzylsulphoxide first formed is decomposed by the hydrochloric acid, the chief product being benzyldisulphide (compare Smythe, Trans., 1909, **95**, 349); the benzyl disulphide is then oxidised to the disulphoxide. Special experiments proved that benzyldisulphoxide is readily obtained by the electrolytic oxidation of benzyl disulphide.

When sulphuric acid is added to the acetic acid instead of hydrochloric acid, and the electrolysis carried out at 18°, *tribenzylsulphinium sulphate*, $(C_7H_7)_3S\cdot SO_4H$, is formed. The benzyl sulphide is oxidised to a mixture of benzyl alcohol and benzylsulphinic acid,

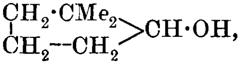
$$(C_7H_7)_2S + 2O + H_2O = C_7H_7\cdot OH + C_7H_7\cdot SO_2H,$$

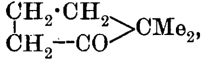
and the former compound, in the presence of sulphuric acid, unites with the excess of benzyl sulphide, forming tribenzylsulphinium sulphate. This is proved by the ready formation of this compound by the interaction of benzyl sulphide and benzyl alcohol in sulphuric-glacial acetic acid solution at 70°. It is also formed by dissolving mono-tribenzylsulphinium ferrichloride in water, precipitation of the iron with ammonium hydroxide, and addition of ammonium sulphate and excess of sulphuric acid to the filtrate.

Tribenzylsulphinium sulphate forms cubes from alcohol, m. p. 170—175° (decomp.).

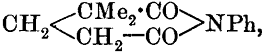
Replacement of hydrochloric and sulphuric acids by hydrobromic, hydrofluoric, nitric or phosphoric acids, addition of cerium salts as oxygen carriers, etc., did not give such good results in the electrolytic oxidation.

Dibenzylsulphone could not be prepared electrolytically either from benzyl sulphide or sulphoxide, but diphenylsulphone is readily obtained from phenyl sulphide at 20—30° in hydrochloric-glacial acetic acid solution. Diphenylsulphoxide prepared electrolytically is always mixed with unchanged phenyl sulphide and with diphenylsulphone. T. S. P.

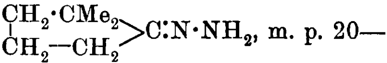
Transformations of *cyclo*Butyldimethylcarbinol. IV. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1211—1227. Compare Abstr., 1908, i, 530, 864).—*cyclo*Butyldimethylcarbinol reacts with oxalic acid, yielding *cyclo*pentane derivatives and a crystalline isomeric alcohol of higher b. p., 1 : 1-*dimethyl*cyclo*pentan*-2-*ol*,  $\left.\begin{array}{l}CH_2\cdot CMe_2\\ CH_2-CH_2\end{array}\right\rangle CH\cdot OH$, which, when oxidised with potassium permanganate or chromic acid, yields the corresponding pentanone (the semicarbazone of which has m. p. 191°) and *aa*-dimethylglutaric acid. 1 : 1-Dimethyl*cyclo*pentan-2-one,

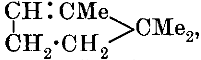


$$\left.\begin{array}{l}CH_2\cdot CH_2\\ CH_2-CO\end{array}\right\rangle CMe_2,$$

has b. p. 143—143·5°/752 mm., D_0^{20} 0·8988, n_D^{20} 1·4343, and always gives some aldehydic reactions. When oxidised with potassium permanganate it yields: (1) *as*-dimethylsuccinic acid; (2) *aa*-dimethylglutaric acid, hexagonal plates, m. p. 83·5—84°, of which the *silver* salt, $C_7H_{10}O_4Ag_2$, and *aniline* salt, m. p. 144·5°, were prepared. The latter when boiled yields *dimethylglutaranil*,  $CH_2\left\langle\begin{array}{l}CMe_2\cdot CO\\ CH_2-CO\end{array}\right\rangle NPh$, hexagonal plates, m. p. 122—122·5°.

When treated with hydrazine hydrate, 1 : 1-dimethyl*cyclo*-

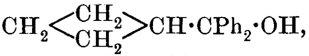
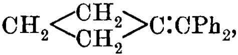
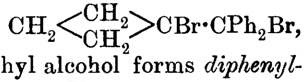
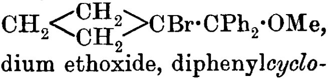
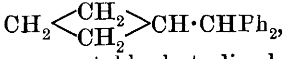
pentanone yields an *hydrazone*,  $\genfrac{}{}{0pt}{}{\mathrm{CH_2\cdot CMe_2}}{\mathrm{CH_2{-}CH_2}}\!>\!\mathrm{C{:}N\cdot NH_2}$, m. p. 20—24°, b. p. 101—104°/30 mm., D_0^{20} 0·9368, n_D^{20} 1·4859 ; it reduces ammoniacal silver solution, and is readily decomposed by water. With magnesium methyl iodide, the pentanone yields 1 : 1 : 2-trimethyl*cyclo*pentan-2-ol, b. p. 80—81°/49 mm., 156°/755 mm., D_0^{20} 0·9102, n_D^{20} 1·4513, which forms a crystalline *hydrate*, $(C_8H_{16}O),2H_2O$, m. p. 59—60°. Blanc's compound (*Compt. rend.*, 1906, **142**, 105), obtained similarly, was a hydrate and not the free pentanol. When distilled with oxalic acid, the trimethylpentanol yields 1 : 1 : 2-trimethyl*cyclo*pentene (*iso*laurolene),



$$\genfrac{}{}{0pt}{}{\mathrm{CH{:}CMe}}{\mathrm{CH_2\cdot CH_2}}\!>\!\mathrm{CMe_2},$$

b. p. 108·5—109°/754 mm., D_0^{15} 0·7868, D_{15}^{15} 0·7871, D_0^0 0·7824, n_D^{20} 1·4324, which with ammoniacal silver oxide solution yields a silver mirror, and when reduced with hydrogen iodide forms 1 : 1 : 2-trimethyl*cyclo*pentane, b. p. 113—114°/749 mm., D_{15}^{15} 0·7706, D_0^{20} 0·7661, n_D^{20} 1·4199.

In the formation of 1 : 1-dimethylpentanone by the oxidation of the pentanol, a volatile *acid*, $C_6H_{11}\cdot CO_2H$, is formed as a by-product ; the *silver* salt was prepared. Z. K.

Diphenyl*cyclo*butylcarbinol and its Transformations. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1227—1236).—Diphenyl*cyclo*butylcarbinol,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CH_2}}>\mathrm{CH\cdot CPh_2\cdot OH}$, is obtained by the action of *cyclo*butanecarboxylic acid on magnesium phenyl iodide, diphenyl being found as a by-product. It forms regular, rhombohedral crystals, m. p. 54—54·5°, b. p. 198°/13 mm., D_0^{20} 1·0906, n_D^{20} 1·5882, and with hydrogen bromide yields a *bromide*, $C_{17}H_{17}Br$, m. p. 94·5—95°. When boiled with oxalic acid, it forms *diphenyl*cyclo*butylidenemethane*,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CH_2}}>\mathrm{C{:}CPh_2}$, m. p. 58°, which with chromic acid mixture is oxidised to benzophenone, whilst with nitric acid the unsaturated hydrocarbon decomposes into benzophenone and succinic acid. It dissolves in a saturated solution of hydrogen bromide in glacial acetic acid, forming a *bromide*, seemingly identical with the one obtained from diphenyl*cyclo*butylcarbinol, but with bromine in carbon disulphide solution, it forms a *dibromide*,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CH_2}}>\mathrm{CBr\cdot CPh_2Br}$, m. p. 91—92°, which when boiled with methyl alcohol forms *diphenylbromo*cyclo*butylcarbinyl methyl ether*,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CH_2}}>\mathrm{CBr\cdot CPh_2\cdot OMe}$, m. p. 81—81·5°. When reduced with sodium ethoxide, diphenyl*cyclo*butylidenemethane forms either elongated plates or stout, hexagonal crystals of *diphenyl*cyclo*butylmethane*,  $\mathrm{CH_2}<\genfrac{}{}{0pt}{}{\mathrm{CH_2}}{\mathrm{CH_2}}>\mathrm{CH\cdot CHPh_2}$, m. p. 39·5°, $D_0^{43\cdot5}$ 1·0003, $n_D^{43\cdot5}$ 1·5636, which is very stable, but dissolves in fuming nitric acid, D 1·52, yielding *dinitrodiphenyl*cyclo*butylmethane*, $C_4H_7\cdot CH(C_6H_4\cdot NO_2)_2$, m. p. 179°, whilst when boiled with nitric acid, D 1·4, benzophenone and succinic acid are produced. When reduced with hydrogen iodide, diphenyl*cyclo*butylidenemethane forms a *hydrocarbon*, $C_{17}H_{18}$, m. p. 65°, isomeric with diphenyl*cyclo*butylmethane.

Z. K.

Production of β-Benzopinacolin. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1236—1237).—β-Benzopinacolin is most conveniently prepared by heating benzophenone with tin and fuming hydrochloric acid on the water-bath for about an hour, stirring the mixture from time to time. The mixture is then diluted with water, filtered, and the β-benzopinacolin is freed from tin by solution in boiling ethyl acetate, from which it crystallises in slender, colourless needles, m. p. 182·5°.

Z. K.

A Method of Isolating Cholesterol and Cerebrosides from Brain by means of Saponification with Barium Hydroxide in Methyl Alcohol. J. Lorrain Smith and W. Mair (*J. Path. Bact.*, 1910, **15**, 122).—Brain is hardened in formaldehyde, cut into slices, and dried. It is then pounded in a mortar, and extracted with chloroform in a Soxhlet apparatus. The chloroform is evaporated off, and the dry extract dissolved in methyl alcohol. A hot saturated solution of barium hydroxide in methyl alcohol is added, and the whole boiled with a reflux condenser for three hours. After cooling, the reaction should be alkaline. It is made nearly neutral by acetic acid, and evaporated to dryness. The residue is placed in a Soxhlet thimble, which is suspended in a wide-necked flask under a reflux condenser, and over acetone kept boiling on a water-bath. As cerebrosides are comparatively insoluble even in boiling acetone, a white precipitate soon appears. After six hours, the acetone contains practically all the cholesterol and most of the cerebrosides. The extraction is repeated with a fresh supply of acetone. The cerebrosides settle out on cooling the acetone; the cholesterol remains in solution. Lecithin and ordinary fats are by this method converted into insoluble barium soaps.

W. D. H.

The Effect of Glycerol on the Clearing Point of Cholesterol and Cerebrosides. J. Lorrain Smith and W. Mair (*J. Path. Bact.*, 1910, **15**, 122—123).—The clearing point of cholesterol (examined on the hot stage of a polarising microscope) is raised 5° by the presence of glycerol; that of cholesterol acetate is unaffected; the glycerol-cholesterol compound, if one exists, is easily decomposed by water, for, after the addition of water, cholesterol crystallises out unchanged.

On heating the white powder obtained by acetone from brain tissue, this substance (a cerebroside) assumes at 80° a fluid crystalline condition, and somewhat over 200° it clears sharply, showing only slight signs of decomposition; this corresponds with the melting point of other observers. When tested in glycerol, "myelin figures" appear at 100° and clear at 160°. When heated in water at comparatively low temperatures, the cerebroside gives myelin figures which are doubly refracting.

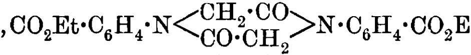
W. D. H.

Phytosterol and Cholesterol. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1910, **69**, 473—475).—A discussion of the views of the author and of others on the relationships of cholesterol and the phytosterols. W. D. H.

Compounds of Aluminium Chloride and Bromide with Acid Chlorides. BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1310—1318. Compare Perrier, Abstr., 1903, i, 578).—Aluminium chloride forms a crystalline compound with benzoyl chloride, $AlCl_3,BzCl$, m. p. 93°. The concentration-temperature curve consists of three branches, with a eutectic point at $-7\cdot5°$ at the composition $AlCl_3,6\cdot53BzCl$. When the mixture contains 61% aluminium chloride, viscid, resinous, vaselin-like substances are formed, which crystallise with great difficulty. Aluminium bromide yields a similar crystalline, molecular compound, $AlBr_3,BzCl$, m. p. 90°. The curve has two eutectic points, at $-5°$ and composition $AlBr_3,6\cdot66BzCl$, and at 7—8° at about the composition $AlBr_3,0\cdot54BzCl$.

Aluminium halides behave towards organic acids as they do to alcohols and water, yielding halogen acid with development of much heat. Z. K.

Esters of *p*-Aminobenzoic Acid. ALFRED EINHORN and RUDOLF SEUFFERT (*Ber.*, 1910, **43**, 2995—3001).—The physiological value of diethylaminoethyl *p*-aminobenzoate has made it desirable to study other basic esters of *p*-aminobenzoic acid.

On heating chloroacetamide with ethyl *p*-aminobenzoate in presence of potassium iodide and sodium acetate, *ethyl* 2 : 5-*diketopiperazine*-1 : 4-*dibenzoate*,  $CO_2Et\cdot C_6H_4\cdot N<\begin{matrix}CH_2\cdot CO\\ CO\cdot CH_2\end{matrix}>N\cdot C_6H_4\cdot CO_2Et$, crystallising in rhombic prisms, m. p. 217—218°, is formed. From the mother liquors, the *glycinamide* of *ethyl* p-*aminobenzoate*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, is obtained in long, thin needles, m. p. 142°.

When boiled with formaldehyde and diethylamine in alcoholic solution, *ethyl* p-*carboxyphenylglycinediethylaminomethylamide*,

$$CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot NEt_2,$$

is formed, crystallising in indefinite prisms, m. p. 97—98°.

With formaldehyde and piperidine, *ethyl* p-*carboxyphenylglycinepiperidinomethylamide*, $CO_2Et\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot C_5NH_{10}$, results; it crystallises in colourless needles, m. p. 102°. The *hydrochloride* crystallises in needles, m. p. 154°; the *hydrobromide* forms prisms, m. p. 162°.

On boiling an alcoholic solution of sodium *p*-nitrobenzoate, chloroacetamide and sodium iodide, p-*nitrobenzoyloxyacetamide*,

$$NO_2\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CO\cdot NH_2,$$

is formed in needles, m. p. 171—172°. When heated with formaldehyde and diethylamine, ethyl *p*-nitrobenzoate is obtained. On reduction, *p*-aminobenzoyloxyacetamide results in the form of needles, m. p. 159—160°.

Ethyl p-*nitrobenzoyloxyacetate*, $NO_2\cdot C_6H_4\cdot CO\cdot O\cdot CH_2\cdot CO_2Et$, prepared by the interaction of sodium nitrobenzoate and ethyl chloroacetate, forms colourless needles, m. p. 39—40°. *Ethyl* p-*aminobenzoyl*-

oxyacetate crystallises in prismatic needles, m. p. 84°. p-*Carboxy*-p-*phenylglycinamide*, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CO\cdot NH_2$, prepared from sodium *p*-aminobenzoate, chloroacetamide and sodium iodide, forms prisms, m. p. 251°. E. F. A.

Some Derivatives of *p*-Aminobenzonitrile. Marston T. Bogert and Louis Elsberg Wise (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1494—1499. Compare Bogert and Kohnstamm, Abstr., 1903, i, 559).

—Improved methods are given for the preparation of *p*-nitro- and *p*-amino-benzonitriles, and some of their derivatives are described.

p-*Formylaminobenzonitrile* forms small, colourless crystals, m. p. 188—189° (corr.). A new method for the preparation of *p*-acetylaminobenzonitrile is given, which yields colourless needles, m. p. 205·5° (corr.). p-*Acetylaminobenzamide* crystallises in colourless prisms, m. p. 274·5°, with preliminary softening and sublimation. By the nitration of *p*-acetylaminobenzonitrile, 3-*nitro*-4-*acetylaminobenzonitrile* is obtained in long, yellow needles, m. p. 131·5° (corr.). p-*Benzoylaminobenzonitrile* melts at 170—170·5° (corr.); p-*benzenesulphonylaminobenzonitrile* forms colourless, arborescent crystals, m. p. 175—176° (corr.).

Methyl-p-*cyano-oxanilate*, $CO_2Me\cdot CO\cdot NH\cdot C_6H_4\cdot CN$, crystallises in leaflets, m. p. 208·5—209·5° (corr.); the *ethyl* derivative forms flat prisms, m. p. 188·5—189° (corr.). *Di*-p-*cyano-oxanilide*,

$$CN\cdot C_6H_4\cdot NH\cdot CO\cdot CO\cdot NH\cdot C_6H_4\cdot CN,$$

melts above 288°.

3:4-*Diaminobenzonitrile* crystallises in colourless needles, m. p. 147·5° (corr.). N. C.

Hydrogen Persulphide. V. Aldehydes and Hydrogen Persulphide. Ignaz Bloch, Fritz Höhn, and Günther Bugge (*J. pr. Chem.*, 1910, [ii], **82**, 473—485. Compare Abstr., 1908, ii, 579).

—When benzaldehyde and crude hydrogen persulphide interact in the presence of zinc chloride or hydrogen chloride, the mixture becomes warm and a brown resin is gradually deposited, which becomes solid on pouring into water. On shaking this resin with alcoholic potassium hydroxide, phenylcarbithionic acid (dithiobenzoic acid), $C_6H_5\cdot CS_2H$ (compare Abstr., 1906, i, 847), is formed, and can be readily isolated (see succeeding abstract). A similar reaction takes place with other aldehydes, salicylaldehyde giving o-*hydroxyphenylcarbithionic acid* (*dithiosalicylic acid*), $HO\cdot C_6H_4\cdot CS_2H$, and anisaldehyde yielding p-*methoxyphenylcarbithionic acid* (*dithioanisic acid*), $OMe\cdot C_6H_4\cdot CS_2H$. The two latter acids are crystalline and intensely coloured, whereas phenylcarbithionic acid is a violet oil. They are all unstable in the air, undergoing rapid oxidation with the formation of resins. The salts of the heavy metals are coloured and comparatively easily soluble in organic solvents, some of them being soluble in ether.

On gentle oxidation, the dithio-acids give rise to thioacyldisulphides. Methyl and ethyl esters can also be obtained.

In the preparation of these carbithionic acids it is immaterial whether crude hydrogen persulphide or pure hydrogen disulphide or trisulphide is used.

In the absence of a condensing agent the reaction proceeds differently.

If benzaldehyde is gradually added to cooled hydrogen disulphide, the liquid becomes brown, and after a time a white precipitate of an additive compound of 2 molecules of benzaldehyde with 1 molecule of hydrogen disulphide is formed. A similar compound results when hydrogen disulphide is replaced by hydrogen trisulphide. Anisaldehyde, cinnamaldehyde, and salicylaldehyde react similarly (compare Abstr., 1908, i, 900).

These compounds are white, well crystallised, and possess a more or less irritating odour. They are comparatively unstable, but the benzaldehyde compound with hydrogen disulphide may be preserved for months. The disulphide are more stable than the trisulphide compounds. On treatment with ice-cold hydrochloric acid they are split up into their components; alcoholic potassium hydroxide gives potassium polysulphides and the reaction products of the aldehyde with alkali. On recrystallising the trisulphide compounds from carbon disulphide, there is a tendency for sulphur to be lost, with the formation of the disulphide compounds.

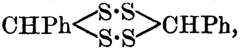
From the analogy of hydrogen persulphide to hydrogen peroxide, the above additive compounds are considered to be *dibenzylidene disulphide hydroxide* and *dibenzylidene trisulphide hydroxide*, with the formulæ: $\mathrm{OH{\cdot}CHPh{\cdot}S{\cdot}S{\cdot}CHPh{\cdot}OH}$ and

$$\mathrm{OH{\cdot}CHPh{\cdot}S{\cdot}S{\cdot}S{\cdot}CHPh{\cdot}OH}$$

respectively (compare dibenzylidene peroxide hydroxide,

$$\mathrm{OH{\cdot}CHPh{\cdot}O{\cdot}O{\cdot}CHPh{\cdot}OH}).$$

It is possible that the resinous intermediate product formed by the interaction of aldehydes and hydrogen persulphide in the presence of condensing agents is *dibenzylidene tetrasulphide*,

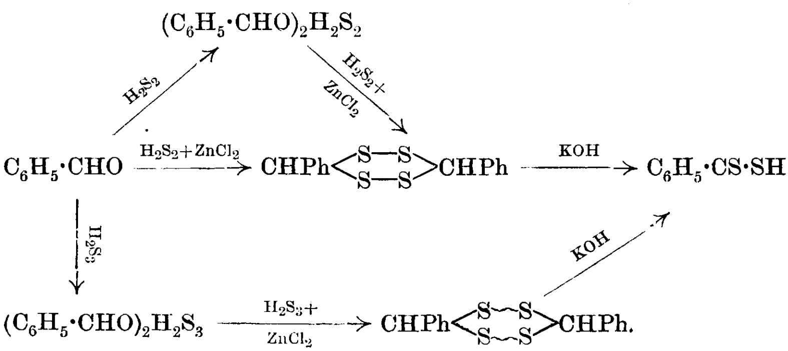


$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{S{\cdot}S}\\\mathrm{S{\cdot}S}\end{matrix}{>}\mathrm{CHPh},$$

corresponding with dibenzylidene peroxide, $\mathrm{CHPh}{<}\begin{matrix}\mathrm{O{\cdot}O}\\\mathrm{O{\cdot}O}\end{matrix}{>}\mathrm{CHPh}$.

This is supported by the fact that the analytical results agree approximately with the formula $C_{14}H_{12}S_4$; also, when dibenzylidene disulphide hydroxide is heated with zinc chloride or shaken with zinc chloride and hydrogen persulphide in the cold, the resinous intermediate product is formed, from which phenylcarbithionic acid is readily obtained.

The results obtained can be represented as follows:



Cinnamaldehyde behaves somewhat differently from the other aldehydes towards hydrogen persulphide. The methyl ester obtained from the resinous intermediate product contains two S-atoms in excess of that required by dithiocinnamic acid, and reacts with bromine without evolution of hydrogen bromide. The formula assigned to this ester is CSPh·CS·CS·SMe. Styrene also adds on sulphur, but the resulting compound will not further unite with bromine; thus hydrogen persulphide can be used to add on sulphur to unsaturated linkings. It behaves as a strong vulcanising agent towards rubber. T. S. P.

Dithio-acids (Carbithionic Acids). Fritz Höhn and Ignaz Bloch (*J. pr. Chem.*, 1910, [ii], **82**, 486—511).—To a solution of crude hydrogen persulphide in benzene are added zinc chloride and benzaldehyde, shaking and cooling meanwhile. After twelve hours, the reaction mixture is heated on the water-bath, and finally treated with steam for three hours, after which time an orange-brown resin is formed, which, on pouring in water, solidifies to a vitreous, amorphous mass. A purer product is obtained by using pure hydrogen disulphide and hydrogen chloride as the condensing agent. It could not be obtained crystalline, although it is readily soluble in carbon disulphide; it has m. p. 80—90°, and decomposes at 120°. The analytical figures agree approximately with the formula $C_{14}H_{12}S_4$. To prepare phenylcarbithionic acid from this substance, it is shaken for two hours with a saturated alcoholic solution of potassium hydroxide, and the resulting brownish-red solution, after filtering from insoluble matter, treated in one of the two following ways: (1) carbon dioxide is passed into the solution, and, after collecting the precipitated potassium hydrogen and potassium ethyl carbonates, the greater part of the alcohol is expelled from the filtrate, which is then diluted with water. Lead acetate is carefully added to the solution until the lead sulphide precipitate first formed is succeeded by a red precipitate of lead phenylcarbithionate. The lead sulphide is then collected, and excess of lead acetate added to the filtrate to precipitate all the phenylcarbithionic acid. (2). The greater part of the alcohol is expelled from the solution, and the hydrogen persulphide destroyed with sulphurous acid. The phenylcarbithionic acid is then precipitated as an oil with hydrochloric acid, dissolved in benzene, and the lead salt formed by shaking the benzene solution with a solution of lead acetate in excess of potassium hydroxide. The yield of lead salt is 70—75% of the theory.

Lead phenylcarbithionate, $Pb(CS_2Ph)_2$, forms red needles from xylene, m. p. 200°. It is not decomposed by water, hydrogen sulphide, or dilute acids, but reacts readily with alkali sulphides, giving lead sulphide and a solution of the alkali phenylcarbithionate. Solutions of *potassium* and *sodium phenylcarbithionate* are fairly stable, but on evaporation on the water-bath partial decomposition takes place with the formation of a resin. They give no precipitates with barium, strontium, calcium, and magnesium salts, but with salts of the heavy metals characteristic precipitates are produced. The *zinc* salt forms yellow needles from benzene, and the *mercury* salt brownish-yellow needles or plates from benzene. The *silver* salt forms an unstable, chocolate powder.

Phenylcarbithionic acid, $Ph{\cdot}CS_2H$, is obtained as a heavy, violet-coloured oil by the addition of hydrochloric acid to a solution of the potassium salt (compare Abstr., 1906, i, 847). The *methyl* ester, $Ph{\cdot}CS_2Me$, is readily obtained by the action of methyl sulphate on an alkaline solution of the potassium salt. It is a red oil with a peculiar disagreeable, although somewhat aromatic, odour, b. p. 154—157°/20 mm., 275—280°/760 mm. (decomp.); it oxidises in the air. The *ethyl* ester, $Ph{\cdot}CS_2Et$, is similar in properties to the methyl ester, and is obtained from silver phenylcarbithionate and ethyl iodide, b. p. 158—162°/13 mm., 165—168°/19 mm.

Salicylaldehyde was condensed with hydrogen persulphide in a similar manner to that described for benzaldehyde, hydrogen chloride being used as the condensing agent. From the condensation product, *lead* o-*hydroxyphenylcarbithionate*, $Pb(S_2C{\cdot}C_6H_4{\cdot}OH)_2$, was obtained as orange-yellow needles. It is much less stable than lead phenylcarbithionate, and undergoes decomposition on recrystallisation (from benzene or xylene); it is decomposed on warming with water. It was necessary to estimate the sulphur by decomposing the compound in a current of chlorine, using Schaefer's apparatus (Abstr., 1906, ii, 394). A solution of the *potassium* salt is obtained by treating the lead salt with a solution of potassium sulphide. It gives characteristic precipitates with salts of the heavy metals; the *mercury* salt forms bright yellow, microscopic needles.

o-*Hydroxyphenylcarbithionic acid*, $OH{\cdot}C_6H_4{\cdot}CS_2H$, obtained from the solution of the potassium salt by the addition of hydrochloric acid, forms orange-yellow needles from light petroleum, m. p. 48—50°, and slowly oxidises in the air. On treating the solution of the potassium salt with methyl sulphate, a mixture of *methyl* o-*hydroxyphenylcarbithionate*, $OH{\cdot}C_6H_4{\cdot}CS_2Me$, and *methyl* o-*methoxyphenylcarbithionate*,

$$OMe{\cdot}C_6H_4{\cdot}CS_2Me,$$

is obtained. The former forms yellow needles, m. p. 10—20°, and the latter orange-yellow lamellæ, m. p. 43—44°. *Ethyl* o-*hydroxyphenylcarbithionate*, $OH{\cdot}C_6H_4,CS_2Et$, obtained from the silver salt and ethyl iodide, is an orange-yellow oil.

Oxidation of *o*-hydroxyphenylcarbithionic acid by leading air through the solution gives o-*hydroxythiobenzoyl disulphide*,

$$(OH{\cdot}C_6H_4{\cdot}CS)_2S_2;$$

brown leaflets from chloroform, m. p. 125—126°, to a blood-red liquid. A better yield (60%) is obtained by adding finely powdered sulphur to a methyl-alcoholic solution of the acid, hydrogen sulphide being evolved. Oxidation of the sodium salt of the acid with iodine or potassium ferricyanide is not a satisfactory method for preparing the disulphide. The *acetyl* derivative of the disulphide is obtained by acetylation with acetyl chloride in pyridine-glacial acetic acid solution; rose-colored powder, sinters at 74°, but only melts completely above 100°.

Lead p-*methoxyphenylcarbithionate*, $(OMe{\cdot}C_6H_4{\cdot}CS_2)_2Pb$, is obtained from the condensation product of anisaldehyde with hydrogen persulphide as a dark reddish-brown powder. It can be recrystallised without decomposition, and forms orange-yellow needles from benzene. The reaction with potassium sulphide is a reversible one. To prepare the *potassium* salt, the free acid, obtained directly from the resinous condensation product by treatment with alcoholic potassium hydroxide and precipitation with hydrochloric acid, is dissolved in potassium hydroxide; it forms pale brownish-red needles. p-*Methoxyphenylcarbithionic acid*, $OMe\cdot C_6H_4\cdot CS_2H$, can be obtained as pale brownish-red crystals from light petroleum, but it is so unstable that it could not be prepared pure. A solution of the sodium or potassium salt gives characteristic precipitates with salts of the heavy metals; the *bismuth*, *zinc*, and *mercury* salts are crystalline. By oxidation of the potassium salt with iodine, a precipitate of p-*methoxythiobenzoyl disulphide*,

$$(OMe\cdot C_6H_4\cdot CS)_2S_2,$$

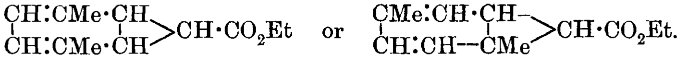
is obtained; m. p. 161—163°. *Methyl* p-*methoxyphenylcarbithionate* forms salmon-pink leaflets from methyl alcohol; m. p. 31° to a blood-red liquid. The *ethyl* ester forms yellow-orange needles, m. p. 25—26° to a red liquid.

A pure lead salt could not be obtained from the condensation product of cinnamaldehyde with hydrogen persulphide. By treating the condensation product directly with methyl sulphate, a substance was obtained possessing the formula $C_{10}H_8S_4$; orange-brown needles from methyl alcohol, m. p. 98—99° to a red liquid. The substance may probably be $CPhS\cdot CS\cdot CS_2Me$.

Pure hydrogen di- or tri-sulphide reacts with styrene, forming an almost colourless oil, with a very unpleasant odour. Phenanthrene and stilbene do not react with the pure hydrogen persulphides, whereas the latter are decomposed by linalool and geraniol. T. S. P.

Aminomethylbenzoic Acids [Aminotoluic Acids]. HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1910, **44**, 507—508).—The acid obtained as the chief product of the nitration of *m*-toluic acid is not 4-nitro-*m*-toluic acid, as stated in an earlier paper (Abstr., 1910, i, 666), but is the 2-nitro-derivative, as was originally recorded by Jacobsen (Abstr., 1882, 185), and confirmed later by Findeklee (Abstr., 1906, i, 21) and Müller (Abstr., 1909, i, 160). The supposed derivatives of 4-amino-*m*-toluic acid described by the authors (*loc. cit.*) are therefore derivatives of 2-amino-*m*-toluic acid. E. G.

Ethyl Diazoacetate and *p*-Xylene. EDUARD BUCHNER and PAUL SCHULZE (*Annalen*, 1910, **377**, 259—284).—Ethyl diazoacetate reacts with *p*-xylene in much the same manner as with toluene (Buchner and Feldmann, Abstr., 1904, i, 57) and *m*-xylene (Buchner and Delbrück, *ibid.*, 1908, i, 87). Among the products is an ethyl dimethylnorcaradienenecarboxylate, which must be represented by one of the two formulæ:



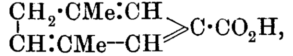
$$\left.\begin{matrix}\text{CH:CMe}\cdot\text{CH}\\ \text{CH:CMe}\cdot\text{CH}\end{matrix}\right>\text{CH}\cdot\text{CO}_2\text{Et} \quad\text{or}\quad \left.\begin{matrix}\text{CMe:CH}\cdot\text{CH}-\\ \text{CH:CH}-\text{CMe}\end{matrix}\right>\text{CH}\cdot\text{CO}_2\text{Et.}$$

The former of these is the more probable, as the ester is transformed readily into ethyl *β*-*p*-tolylpropionate, and, as in other cases, the $>CH\cdot CO_2Et$ group condenses with the carbon atoms of the hexa-ring, which are as far removed from the methyl substituents as possible. The condensation product is therefore *ethyl* 2 : 5-*dimethyl*-$\Delta^{2:4}$-*norcara-*

dienenecarboxylate. On distillation, a 53—55% yield of an oil, b. p. 128—136°/12 mm., is obtained, but this contains, in addition to the above ester, two isomeridic condensation products, namely, appreciable amounts of an ethyl *cyclo*heptatrienecarboxylate and small amounts of ethyl β-*p*-tolylpropionate. The separation of these compounds is best accomplished by means of ammonia, as in the three esters the carbethoxy-group is attached repectively to secondary, tertiary, and primary carbon atoms (compare E. Fischer and Dilthey, Abstr., 1902, i, 269). It is an advantage to use a mixture of the methyl esters, as they react more readily with the ammonia. The addition of copper powder as a catalyst in the condensation does not give any better yields, but leads to the formation of appreciable amounts of methyl fumarate, a compound which is not formed in the absence of the metal.

2 : 5-*Dimethyl*-$\Delta^{2:4}$-*norcaradiene-7-carboxylamide*, $C_{10}H_{13}ON$, obtained by shaking the mixture of methyl esters for two days with a solution of ammonia saturated at 0°, crystallises from ethyl alcohol in colourless needles, m. p. 163—164°. The yield is small, only about 0·4 gram from 10 grams of condensation product. β-*p*-Tolylpropionamide is also formed, but is much more readily soluble in concentrated ammonia solution. The unsaturated amide turns yellow on exposure to the air, reduces permanganate, and dissolves in concentrated sulphuric acid to a red solution. When boiled with dilute sulphuric acid, it yields *p*-xylylacetic acid (compare Guerbet, Abstr., 1898, i, 424), and when heated for five minutes with 5% sodium hydroxide solution, yields an acid, m. p. 98—99°, which is probably 2 : 5-*dimethyl*-$\Delta^{2:4:7}$-cyclo*heptatriene-7-carboxylic acid.*

The isomeric 2:5-*dimethyl*-$\Delta^{7:2:5}$-cyclo*heptatriene-7-carboxylic acid*,



$$\left.\begin{array}{l} \mathrm{CH_2 \cdot CMe{:}CH} \\ \mathrm{CH{:}CMe{-}CH} \end{array}\right> \mathrm{C \cdot CO_2H},$$

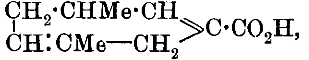
is most readily obtained by heating the crude condensation product for ten hours at 160—170° in an evacuated sealed tube, then distilling under reduced pressure, and hydrolysing with 25% methyl-alcoholic potassium hydroxide, first at the ordinary temperature and then for thirty minutes on the water-bath. On the addition of sufficient sulphuric acid to precipitate 40% of the total acid present, the pure crystalline acid is obtained, and the addition of more sulphuric acid precipitates 10—12 grams of crystalline β-*p*-tolylpropionic acid (Kröber, Abstr., 1890, 969). The $\Delta^{2:5:7}$-acid is formed together with the tolylpropionic acid when the crude condensation product is heated with 15% sulphuric acid for fifteen to thirty hours, and may also be obtained by heating the amide of the dicyclic acid for five hours with water in an evacuated tube at 160—170°, and subsequent hydrolysis. When a temperature of 180—190° is used, the ammonium salt of the heptatriene acid is formed directly. The $\Delta^{2:5:7}$-acid, $C_{10}H_{12}O_2$, crystallises from 30% ethyl alcohol or 30% acetic acid in long, pale yellow, glistening needles, m. p. 136—137°. Its solution in concentrated sulphuric acid is yellow, but gradually turns reddish-brown. The calcium, copper, lead, iron, zinc, and silver salts are all very sparingly soluble. The *methyl* ester has b. p. 120—121°/12 mm.; the *amide,*

$C_{10}H_{13}ON$, crystallises from water in colourless needles, m. p. 136—137°; the *dibromide*, $C_{10}H_{12}O_2Br_2$, crystallises from light petroleum in colourless needles, m. p. 126° (decomp.), after changing colour at 110°, and the *tetrabromide*, $C_{10}H_{12}O_2Br_4$, has m. p. 185° (decomp.), after turning yellow at 160°.

2 : 5-*Dimethyl*-$\Delta^{2:5}$-cyclo*heptadiene*-7-*carboxylic acid*,

$$C_7H_7Me_2{\cdot}CO_2H,$$

prepared by reducing the heptatriene acid with 3% sodium amalgam in alkaline solution whilst carbon dioxide is passed through, has m. p. 38—40° in the crude state, and is too unstable to purify. The *amide*, $C_{10}H_{15}ON$, prepared from the chloride, crystallises from water in needles, m. p. 142°, and turns yellow on exposure to the air. The *dihydrobromide*, $C_{10}H_{16}O_2Br_2$, obtained by leaving the acid in contact with glacial acetic acid saturated with hydrogen bromide at 0°, crystallises from light petroleum in small needles, m. p. 120° (decomp.), and when boiled for three hours with sodium hydroxide solution yields 2 : 5-*dimethyl*-$\Delta^{2:6}$-cyclo*heptadiene*-7-*carboxylic acid*,



$$\begin{array}{l}\mathrm{CH_2{\cdot}CHMe{\cdot}CH}\\ \mathrm{CH{:}CMe{-}CH_2}\end{array}\!\!>\mathrm{C{\cdot}CO_2H},$$

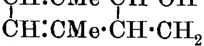
which crystallises from dilute alcohol in colourless needles, m. p. 82°. The corresponding *amide* has m. p. 147—148°, and turns yellow on exposure to the air. 2 : 5-*Dimethyl*cyclo*heptane*-7-*carboxylic acid*,

$$C_7H_{11}Me_2{\cdot}CO_2H,$$

is formed when an ethereal solution of the $\Delta^{2:5:7}$-triene acid is reduced with hydrogen in the presence of finely divided platinum; it is an oil which does not solidify when kept in a freezing mixture, and yields an *amide*, $C_{10}H_{19}ON$, which crystallises from 30% alcohol in glistening needles, m. p. 185—186°. 7-*Bromo*-2 : 5-*dimethyl*cyclo*heptane*-7-*carboxylic acid*, $C_7H_{10}Me_2Br{\cdot}CO_2H$, prepared by the Volhard-Zelinsky method, crystallises from concentrated formic acid in stout, colourless needles, m. p. 152—153°, after softening at 120°.

β-p-*Tolylpropionamide*, $C_6H_4Me{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$, crystallises from hot water or ether in flat needles, m. p. 135°. The corresponding acid does not readily decolorise permanganate, and is oxidised by alkaline permanganate to terephthalic acid.

The conversion of the bicyclic condensation product into *p*-xylylacetic acid is represented as taking place by the addition and subsequent elimination of water, the intermediate hypothetical product being



$\begin{array}{l}\mathrm{CH{:}CMe{\cdot}CH{\cdot}OH}\\ \mathrm{CH{:}CMe{\cdot}CH{\cdot}CH_2{\cdot}CO_2H}\end{array}$. Similarly, with the conversion of the condensation product into β-*p*-tolylpropionic acid, a hypothetical intermediate product, formed by the addition of water, is assumed, namely, $CH(OH)_2{\cdot}CMe{:}CH{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$.

The constitution of the 2 : 5-dimethyl-$\Delta^{2:5:7}$-*cyclo*heptatriene-7-carboxylic acid is discussed in detail. J. J. S.

Preparation of Substituted Cinnamic Acids. THEODOR POSNER (*J. pr. Chem.*, 1910, [ii], 82, 425—440).—The paper contains a description of the preparation of a large number of substituted cinnamic acids and their esters. The esters of nuclear-substituted cinnamic acids are obtained best by boiling the acids for six hours with methyl or ethyl alcohol containing 10% of concentrated sulphuric acid. The following new compounds are described: m-*aminocinnamic acid acetate*, $C_9H_9O_2N,C_2H_4O_2$, is precipitated when acetic acid is added to the ammoniacal filtrate obtained after the reduction of *m*-nitrocinnamic acid by ferrous sulphate and ammonium hydroxide; it forms yellow crystals, m. p. 267° (decomp.). o-*Acetylaminocinnamic acid*, $NHAc\cdot C_6H_4\cdot CH\colon CH\cdot CO_2H$, m. p. 250—251°, is prepared from the acid and acetic anhydride. *Ethyl* o-*hydroxycinnamate*, m. p. 85—86°, is prepared by boiling *o*-coumaric acid with 2% alcoholic hydrogen chloride for six hours. *Methyl* p-*hydroxycinnamate* has m. p. 139—140°. *α*-*o*-Methoxycinnamic acid and its methyl ester are more conveniently obtained by methyl sulphate in the cold than by Perkin's method with methyl iodide at 150° (Trans., 1877, **39**, 418). *β*-*o*-Methoxycinnamic acid is most conveniently obtained by boiling salicylaldehyde methyl ether (prepared from salicylaldehyde, aqueous sodium hydroxide, and methyl sulphate), sodium acetate, and acetic anhydride for nine hours. *m*-Methoxycinnamic acid is best prepared, although in only moderate yield, from *m*-methoxybenzaldehyde and malonic acid by Knoevenagel's method; its *methyl* ester has b. p. 305—307°/748 mm. The esterification of 3 : 4-dihydroxycinnamic acid by methyl alcohol and sulphuric acid yields anomalous results, the products being a *substance*, $C_{11}H_{12}O_4$, m. p. 131—132°, which is insoluble in sodium carbonate, and another *substance*, $C_{10}H_{10}O_4$, m. p. 159—160°, which is soluble in sodium carbonate and is reprecipitated by sulphuric acid. *Methyl* 3 : 4-*methylenedioxycinnamate* has m. p. 133—134°. *Ethyl β-phenyl-α-methylacrylate*, $CHPh\colon CMe\cdot CO_2Et$, conveniently prepared from ethyl propionate, sodium, and benzaldehyde in the cold, has b. p. 220—230°. *Methyl β-phenyl-α-ethylacrylate*, $CHPh\colon CEt\cdot CO_2Et$ b. p. 250—260°, is obtained in a similar manner from ethyl butyrate. *Methyl ββ-diphenylacrylate* has b. p. 194·6—194·8°/13 mm. C. S.

Crystallisation of Sodium Salicylate Solution. Charles A. Hill (*Pharm. J.*, 1910, [iv], **31**, 730—731).—Solutions of sodium salicylate, made by dissolving the commercial salt in its own weight of water, sometimes deposit spontaneously at the ordinary temperature in winter large masses of transparent crystals. This crystallisation is rarely obtained even below 0° unless the cold solution is inoculated with a crystal. The author obtained these crystals as large, well-defined prisms, exhibiting fluorescence and passing under the influence of heat or pressure into the anhydrous salt; analysis shows them to have the composition $C_7H_5O_3Na,6H_2O$.

The author also shows that commercial sodium salicylate is anhydrous. N. C.

Acylated Salicylic Acid Anhydrides. Alfred Einhorn and Rudolf Seuffert (*Ber.*, 1910, **43**, 2988—2995).—Acylated salicylic acids [*o*-acyloxybenzoic acids] are converted by the action of chlorocarboxylic acid alkyl esters in presence of pyridine into alkyl *o*-acyloxybenzoyl carbonates, and these, when warmed on the water-bath, form anhydrides. Other acid chlorides act similarly towards *o*-acyloxybenzoic acids, yielding mixed anhydrides; these are decomposed on heating with the formation of the two simple anhydrides. The mixed anhydrides also slowly decompose at the ordinary temperature in contact with pyridine.

Ethyl o-*acetoxybenzoyl carbonate*, $OAc\cdot C_6H_4\cdot CO\cdot O\cdot CO\cdot OEt$, was obtained as a colourless, viscid oil. *Amyl* o-*acetoxybenzoyl carbonate* is a faintly yellow, viscid oil. The *valeryloxy-* and *benzoyloxy-ethyl* esters are likewise viscid oils. *Ethyl* o-*cinnamoyloxybenzoyl carbonate* crystallises in needles, m. p. 57°.

o-*Acetyloxybenzoic anhydride*, $(OAc\cdot C_6H_4\cdot CO)_2O$, crystallises in lustrous plates, m. p. 85°.

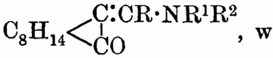
o-*Benzoyloxybenzoic anhydride*, $(OBz\cdot C_6H_4\cdot CO)_2O$, forms prismatic needles, m. p. 110—111°. o-*Cinnamoyloxybenzoic anhydride*,

$$(CHPh{:}CH\cdot CO\cdot O\cdot C_6H_4\cdot CO)_2O,$$

separates in refractive prisms, m. p. 129—130°.

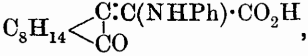
Benzoic o-*acetyloxybenzoic anhydride*, $C_6H_4(OAc)\cdot CO\cdot O\cdot CO\cdot C_6H_5$, crystallises in needles, m. p. 75—76°. *Benzoic* o-*benzoyloxybenzoic anhydride* crystallises in rhombic plates, m. p. 74—75°. *Cinnamic* o-*cinnamoyloxybenzoic anhydride* forms needles, m. p. 78—79°.

E. F. A.

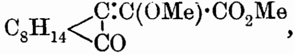
Derivatives of Camphoroxalic Acid. XIII. J. BISHOP TINGLE and S. J. BATES (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1499—1517. Compare Abstr., 1899, i, 444; 1900, i, 302; 1901, i, 632; 1905, i, 799; 1906, i, 902; 1908, i, 125, 126).—The authors have made a further study of the condensation products of camphoroxalic acid and amines, and the action of various reagents on them. The results confirm the view that the constitution of these compounds is given by the formula  $C_8H_{14}<\begin{array}{l}C{:}CR\cdot NR^1R^2\\ \vert\\ CO\end{array}$, where $R = H$ or CO_2H; R^1 and $R^2 = H$, alkyl or aryl.

A comparison between the compounds resulting from the condensation of camphoroxalic acid with thiosemicarbazide and with semicarbazide shows that in the former there is much less tendency to form cyclic derivatives.

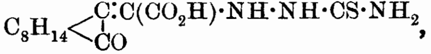
Phenylcamphoformeneaminecarboxylic acid,



$$C_8H_{14}<\begin{array}{l}C{:}C(NHPh)\cdot CO_2H\\ \vert\\ CO\end{array},$$

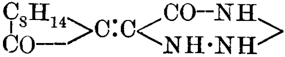
was prepared by the method of Bishop Tingle and A. Tingle, and the effect of bromine, chlorides of phosphorus, and oxidising agents observed. By the action of methyl sulphate, *methyl phenylcamphoformeneaminecarboxylate* is obtained as yellow crystals, m. p. 127°. *Methyl methoxycamphoroxalate*,  $C_8H_{14}<\begin{array}{l}C{:}C(OMe)\cdot CO_2Me\\ \vert\\ CO\end{array}$, is obtained as an oil by the action of methyl sulphate and sodium carbonate on methyl camphoroxalate.

Thiosemicarbazylcamphoformeneaminecarboxylic acid,

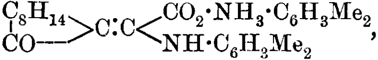


$$C_8H_{14}<\begin{array}{l}C{:}C(CO_2H)\cdot NH\cdot NH\cdot CS\cdot NH_2\\ \vert\\ CO\end{array},$$

exists in two modifications, one melting at 148—149°, the other at

120—125°. By fusion it forms a *compound*, m. p. 170°. The *ethyl* ester of the acid forms white crystals, m. p. 150—151°. By the action of acetic anhydride on the acid, *thiosemicarbazylcamphoformeneaminecarboxylactimide*,  $\begin{array}{l}C_8H_{14}\\ |\\ CO\text{---}\end{array}\!>C{:}C<\begin{array}{l}CO\text{--}NH\\ NH\cdot NH\end{array}\!>CS$, is obtained as bright red crystals, m. p. 181—182°.

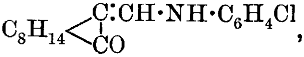
m-4-Xylidine m-4-xylidylcamphoformeneaminecarboxylate,



$$\begin{array}{l}C_8H_{14}\\ |\\ CO\text{---}\end{array}\!>C{:}C<\begin{array}{l}CO_2\cdot NH_3\cdot C_6H_3Me_2\\ NH\cdot C_6H_3Me_2\end{array},$$

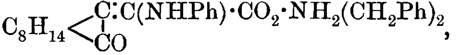
forms brown crystals, m. p. 93—94°; the *acid* crystallises in yellow crystals, m. p. 117—118°.

p-*Chlorophenylcamphoformeneaminecarboxylic acid* crystallises in yellow needles, m. p. 182—183°.

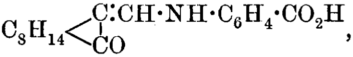
p - *Chlorophenylcamphoformeneamine*,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_6H_4Cl\\ |\\ CO\end{array}$, forms white crystals, m. p. 194—195°.

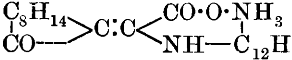
Dibenzylamine camphoroxalate has m. p. 135—136°.

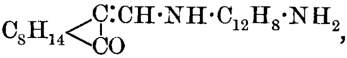
Dibenzylamine phenylcamphoformeneaminecarboxylate,



$$C_8H_{14}<\begin{array}{l}C{:}C(NHPh)\cdot CO_2\cdot NH_2(CH_2Ph)_2\\ |\\ CO\end{array},$$

forms white crystals, m. p. 185°. m-*Carboxyphenylcamphoformeneaminecarboxylic acid* crystallises in white crystals, m. p. 136—137°. By the action of heat on the acid, m-*carboxyphenylcamphoformeneamine*,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_6H_4\cdot CO_2H\\ |\\ CO\end{array}$, is obtained in long, yellow needles, m. p. 116—117°.

By the condensation of benzidine and camphoroxalic acid, a yellow substance, m. p. 208°, is produced, which is probably an inner ammonium salt, and has the constitution  $\begin{array}{l}C_8H_{14}\\ |\\ CO\text{---}\end{array}\!>C{:}C<\begin{array}{l}CO\cdot O\cdot NH_3\\ \qquad\quad |\\ NH\text{—}C_{12}H_8\end{array}$.

Benzidylcamphoformeneamine,  $C_8H_{14}<\begin{array}{l}C{:}CH\cdot NH\cdot C_{12}H_8\cdot NH_2\\ |\\ CO\end{array}$, melts at 317—318°. By the condensation of camphylamine and camphoroxalic acid, a small quantity of a white *sublimate*, m. p. 105°, is obtained.

N. C.

Chemistry of Alcapton-urine (Homogentisic Acid and Certain of its Derivatives). CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1910, **69**, 329—365).—Homogentisic acid in the presence of ammonia and air gives, not only the brown coloration described by earlier authorities, but, under suitable conditions, an intensely brilliant reddish-violet coloration. The conditions necessary for the production of the coloration are: (*a*) concentration of homogentisic acid 0·25 to 2%. With more dilute solutions, yellowish-brown, and with more concentrated solutions blackish-brown, colorations are obtained. (*b*) Concentration of the ammonia 1 to 4%. (*c*) Oxygen concentration. It is essential that the amount of oxygen absorbed per unit of time shall not be too large. This is accomplished by using comparatively narrow tubes; thus with 20 c.c. of liquid, the reaction was given when tubes of 0·75 to 2·0 cm.

diameter were used, but only brown or brownish-red colorations were obtained with tubes 3·0 to 5·0 cm. diameter. If the volume of liquid is large and the tube very narrow, the time required for the coloration to appear may be considerable. Moderately concentrated solutions of many substances, for example, ammonium sulphate or chloride (1/50 saturated), potassium chloride (1/4—1/3 saturated), potassium hydroxide (1%), aniline (1/2%), carbamide (8%), alcohol (20%), prevent the formation of the coloration. Glycerol, dextrose, and sucrose at concentrations of 20% have no effect, and sodium chloride or sulphate solutions up to 1/3 saturated do not interfere. It has been found possible to isolate small amounts of two distinct compounds from the reddish-purple solution. These are termed α- and *β-alcaptochromes*. The α-compound crystallises from hot water in thin, hexagonal plates, with a metallic lustre and green reflex, and when heated above 105° decomposes without melting or subliming. It is only sparingly soluble in most solvents; the solutions have a yellow colour and do not fluoresce. The orange-yellow pyridine solution, when diluted with water, turns blood- or cherry-red. The compound is acidic, and dissolves in dilute alkali solutions, yielding colorations which resemble methyl-violet solutions. Such solutions are readily decolorised by the addition of a solution of ferrous sulphate plus a tartrate, but the colour is restored on shaking with air. The solutions in sodium or potassium hydrogen carbonate have a somewhat more reddish colour, and this changes to yellow when carbon dioxide is passed in.

The solution in ammonium hydroxide has a violet colour, and the colour can be detected with a dilution of 1 in 20 millions; it becomes more red when heated, but returns to the original colour as it cools. The *ammonium* salt has been isolated as a solid with a green, metallic lustre. The acid also dissolves in concentrated sulphuric or hydrochloric acids, but does not appear to yield salts with them. The constitution suggested for the α-alcaptochrome is that of a 4-*imino*-p-*benzoquinone*-2-*acetic acid*, $NH:C_6H_3O\cdot CH_2\cdot CO_2H$.

The following hydroxylic derivatives do not yield colorations when treated in the same manner as homogentisic acid. Catechol, resorcinol, β-resorcylic acid, phloroglucinol, pyrogallol, gallic acid, tannin, protocatechuic acid. Neither do quinol, quinhydrone, dianilinoquinol, quinol dimethyl ether, arbutin, or gentisic acid. Toluquinol, on the other hand, gives an intense reddish-violet solution with an orange fluorescence. The coloured substance has been isolated as a magma of reddish-brown, crystalline needles, which dissolve in alkalis, yielding solutions with a reddish-violet colour and orange fluorescence. The addition of acetic acid or carbon dioxide to such solutions precipitates the colouring matter.

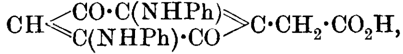
Hydroxyquinol gives a bluish-violet-coloured non-fluorescent solution. The coloured compound has been isolated as an amorphous, violet-brown, flocculent mass, insoluble in most solvents.

The coloration described by Langstein and Meyer (*Arch. Klin. Med.*, 1903, **78**, 161) as characteristic of homogentisic acid lactone is quite different from the alcaptochrome reaction, and by means of the latter it is shown that ammonium hydroxide solutions do not readily hydrolyse the lactone, whereas solutions of sodium hydroxide do.

It is shown that many aromatic derivatives containing free hydroxyl groups in positions 1 and 4 react with aniline in the presence of air, yielding coloured, crystalline compounds, which are insoluble in water, but dissolve in organic solvents, and also give characteristic colorations with concentrated sulphuric acid. The method of procedure consists in mixing an aqueous solution of the hydroxy-compound with sufficient saturated aqueous solution of aniline or one of its homologues, and exposing to the air for several weeks in shallow dishes. The amorphous precipitates are removed, washed with 1% potassium carbonate solution, then with water, and crystallised from glacial acetic acid.

Quinol yields 2 : 5-dianilo-*p*-benzoquinone with aniline, 2 : 5-*p*-toluidino-*p*-benzoquinone with p-toluidine,and 2:5-*m*-xylidino-*p*-benzoquinone with *m*-xylidine.

Homogentisic acid (or alcapton-urine) and aniline under the given conditions yield 3 : 6-*dianilino*-p-*benzoquinone*-3-*acetic acid*,



$$CH{<}\begin{matrix}CO\cdot C(NHPh)\\ C(NHPh)\cdot CO\end{matrix}{>}C\cdot CH_2\cdot CO_2H,$$

which crystallises from glacial acetic acid in brownish-violet prisms with a coppery lustre, m. p. 228°. With sulphuric acid it gives a majenta-red coloration, which changes rapidly to cherry-red. The corresponding p-*toluidino*-derivative, $C_{22}H_{20}O_4N_2$, forms dark reddish-brown crystals, m. p. 231°, and gives a pure blue coloration with concentrated sulphuric acid; the m-*xylidino*-derivative, $C_{24}H_{24}O_4N_2$, forms brownish-yellow crystals, m. p. 241°, and also gives a blue coloration with sulphuric acid.

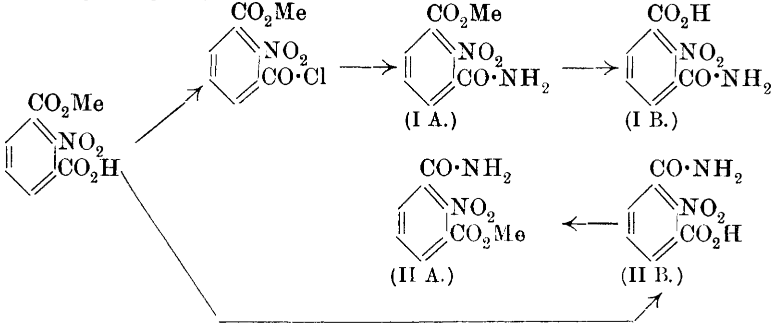
Quinhydrone, homoquinol, hydroxyquinol, gentisic acid, and 3-methoxy-1-propyl-2 : 5-quinol also react with aniline and air in a similar manner.

Homogentisic acid lactone acts very slowly with aniline and air, and then probably only as the result of hydrolysis; quinol dimethyl ether does not react.

The product described previously (Abstr., 1909, ii, 331) as obtained from normal urine, aniline, and air is also formed in the absence of urine if a small amount of a catalyst, for example, a ferrous salt, is present, and is regarded as dianilino-*p*-benzoquinonemonoanil. Its formation in the case of urine is due to the presence of small amounts of some catalyst, and not to the presence of quinol.

J. J. S.

Ester-acids and Amido-acids of the *iso*Phthalic Acid Series. The Question of Equivalence of Positions 2 and 6 in the Benzene Nucleus. Alfred Wohl (*Ber.*, 1910, **43**, 3474—3489).—The non-existence of two isomeric ortho-disubstituted derivatives of benzene is usually explained at the present time by the assumption that the free affinities of the six nuclear carbon atoms are not arranged in three separate pairs of unsaturated systems, but are so distributed that they mutually neutralise one another. The isomerism of 1 : 2- and 1 : 6-derivatives, if such are capable of existence, is due, not to the movements of a migratory atom or group as in typical cases of tautomerism, but to a difference in the distribution of the free affinities of the carbon atoms. Hitherto, all attempts to discover isomeric ortho-disubstituted benzene derivatives have depended on reactions which seek to introduce substituents directly into positions 2 or 6, that is, on reactions which interfere with the benzene nucleus itself, the natural result being that the free affinities of the nuclear carbon atoms become arranged in the position of greatest stability, and only one ortho-disubstituted derivative has been discovered. The author's method of attacking the problem is indicated by the annexed scheme; only the hydroxylic hydrogen atoms are attacked, the benzene nucleus itself being uninterfered with. The substances I A and II A are found to be identical, not isomeric, and so also I B and II B. Similar results have been obtained with 2-hydroxy*iso*phthalic acid and with *iso*phthalic acid itself.



[With E. NAGELSCHMIDT.]—*Methyl hydrogen* iso*phthalate*,

$CO_2H{\cdot}C_6H_4{\cdot}CO_2Me$,

m. p. 193°, is obtained by boiling a methyl-alcoholic solution of methyl *iso*phthalate and one equivalent of sodium hydroxide for two to three hours, filtering any precipitated sodium salt, pouring the filtrate into water, extracting the unchanged ester with ether, and carefully acidifying the aqueous solution with hydrochloric acid; the first portion of the precipitate is almost pure methyl hydrogen *iso*phthalate. This is converted by thionyl chloride into the *chloride*,

$CO_2Me{\cdot}C_6H_4{\cdot}COCl$,

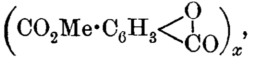
which reacts with cold concentrated aqueous ammonia to form the *amide*-ester, $CO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, m. p. 148·5° (corresponding with I A above); by hydrolysis with methyl-alcoholic sodium hydroxide, the amide-ester yields the *amic-acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$, m. p. 280° (I B). The amic-acid (II B), obtained by treating methyl hydrogen *iso*phthalate with methyl-alcoholic ammonia, has m. p. 280°, is identical with the preceding amic acid, and is converted into the amide-ester, m. p. 148·5° (II A, identical with I A), by shaking the potassium salt obtained from it by methyl-alcoholic potassium methoxide with methyl sulphate. *Ethyl hydrogen* iso*phthalate*, prepared like the corresponding methyl ester, has m. p. 115—117°.

*Methyl 2-nitro*iso*phthalate*, $NO_2{\cdot}C_6H_3(CO_2Me)_2$, m. p. 135°, obtained by boiling the acid with methyl alcohol and concentrated sulphuric acid, is converted into the following compounds by reactions similar to the preceding. *Methyl hydrogen 2-nitro*iso*phthalate*, $CO_2H\cdot C_6H_3(NO_2)\cdot CO_2Me$, m. p. 197°; *ester-chloride*, m. p. 121°; *ester-amide*, m. p. 190—191°; *amic-acid*, m. p. 252°.

Methyl hydrogen 2-hydroxy*iso*phthalate, by treatment with aqueous methyl-alcoholic ammonia, yields the *amic acid*,

$$CO_2H\cdot C_6H_3(OH)\cdot CO\cdot NH_2,$$

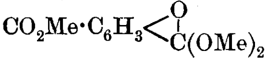
m. p. 245° (decomp.), which is converted into the *amide-ester*, $CO_2Me\cdot C_6H_3(OH)\cdot CO\cdot NH_2$, m. p. 185°, by treatment with potassium methoxide, and subsequently with methyl sulphate, as above. Attempts to prepare the ester-chloride, $CO_2Me\cdot C_6H_3(OH)\cdot COCl$, have not been very successful. Methyl hydrogen 2-hydroxy*iso*phthalate is dehydrated by thionyl chloride, yielding a *substance*, $C_9H_6O_4$, which is probably a multimolecular β-lactone,



$$\left(CO_2Me\cdot C_6H_3<\begin{matrix}O\\|\\CO\end{matrix}\right)_x,$$

is converted by acetyl chloride and phosphorus pentachloride into the acetylated anhydride described below, and reacts with phosphorus pentachloride alone to form an impure ester-chloride, from which, however, an ester-amide, m. p. 185°, identical with the above, can be prepared.

Methyl hydrogen 2-hydroxy*iso*phthalate is converted by acetic anhydride and one drop of concentrated sulphuric acid at 40—50° into the *acetoxy*-derivative, $CO_2Me\cdot C_6H_3(OAc)\cdot CO_2H$, m. p. 118—119°, but when heated with acetyl chloride on the water-bath, yields an acetylated *anhydride*, $C_{22}H_{18}O_{11}$, m. p. 144—146°, which does not give a colour reaction with ferric chloride, and is only slowly converted into the original ester-acid by hot water.

When boiled with methyl alcohol and sulphuric acid, 2-hydroxy*iso*phthalic acid yields the *methyl* ester, $OH\cdot C_6H_3(CO_2Me)_2$, m. p. 72°, the potassium salt of which, obtained by interaction with methyl-alcoholic potassium methoxide, reacts with the calculated quantity of methyl sulphate, diluted with twice its weight of benzene, to form a *substance*, $C_{11}H_{12}O_5$, b. p. 170—171°/11 mm., to which the constitution  $CO_2Me\cdot C_6H_3<\begin{matrix}O\\|\\C(OMe)_2\end{matrix}$ is given. When the potassium salt is heated with methyl sulphate alone, it is converted into a *substance*, $C_{11}H_{12}O_8S$, m. p. 110°, which has acidic properties, develops a wine-red coloration with ferric chloride in aqueous acetone, and retains its sulphur after being boiled with hydrochloric acid; probably it is the trimethyl ester of 2-hydroxy-5-sulpho-*iso*phthalic acid. C. S.

Δ^1-Tetrahydrobenzaldehyde from *cyclo*Hexanone. WALTHER BORSCHE and R. SCHMIDT (*Ber.*, 1910, 3400—3401).—*o-Hydroxyhexahydrobenzylaniline*, $OH\cdot C_6H_{10}\cdot CH_2\cdot NHPh$, obtained by reducing the anil of hydroxymethylene*cyclo*hexanone (Abstr., 1910, i, 881) with sodium and boiling alcohol, crystallises from dilute alcohol in colourless plates, m. p. 98—100°, and on oxidation with chromic anhydride in glacial acetic acid solution yields aniline-black and Δ^1-tetrahydrobenzaldehyde (Wallach, Abstr., 1906, i, 565). The method is not a suitable one for the preparation of the aldehyde, as the yield is only about 10% of the theoretical (compare Farbwerke vorm. Meister, Lucius & Brüning, Abstr., 1902, i, 102). J. J. S.

Anthranil. XVIII. Methods of Preparation of *o*-Nitrosobenzaldehyde. EUGEN BAMBERGER and ANDOR FODOR (*Ber.*, 1910, **43**, 3321—3335).—For one reason or another *o*-nitrosobenzaldehyde cannot be prepared by the oxidation of *o*-hydroxylaminobenzaldehyde, the electrolytic reduction of *o*-nitrobenzaldehyde, the reduction of *o*-nitrobenzyl chloride by zinc and acetic acid, or by the oxidation of *o*-hydroxylaminobenzaldoxime or of anthranilphenylhydrazine by ferric chloride. It can be prepared by the following methods, none of which, however, are really satisfactory: (1) Hydrochloric acid and sodium nitrite are allowed to react with anthranil under the conditions mentioned by Bamberger and Lublin (Abstr., 1909, i, 509), and the resulting white, crystalline crust on the sides and bottom of the vessel is separated mechanically from the yellow precipitate of *o*-aldehydophenylnitrosohydroxylamine, washed with water at 0°, and purified by distillation with steam. (2) It has been isolated from the products of the hydrolysis of *o*-aldehydophenylnitrosohydroxylamine by dilute sulphuric acid (*loc. cit.*). (3) An alkaline solution of *o*-aldehydophenylnitrosohydroxylamine is treated with not too large a quantity of 3% potassium permanganate at 0°; the ethereal extract of the resulting solution contains *o*-nitrosobenzaldehyde. It is also formed when the oxidation is performed in 2*N*-sulphuric acid at 0°. (4) The oxidation of anthranil in 2*N*-sulphuric acid at 0° by 3% potassium permanganate also yields *o*-nitrosobenzaldehyde; when too much of the oxidising agent is added, *o*-nitrobenzaldehyde is produced; p-*nitrophenylhydrazone*, m. p. 257·5—258·5° (decomp.). The production of *o*-nitrosobenzaldehyde by the oxidation of anthranil furnishes a final argument against Heller's contention, that anthranil and methylanthranil are not similarly constituted homologues, because the former yields *oo'*-azoxybenzoic acid, the latter *o*-nitrosoacetophenone, by oxidation (Abstr., 1908, i, 267; compare also Bamberger and Lublin, *loc. cit.*).

o-Nitrosobenzaldehyde has m. p. 113—113·5° with previous blackening, not 109—110° as stated previously. It can be purified by very rapid distillation with steam, although the loss by decomposition is great. Its solutions have a grass-green colour, which is generally intensified by warming. C. S.

Persulphides of Aldehydes. GÜNTHER BUGGE and IGNAZ BLOCH (*J. pr. Chem.*, 1910, [ii], **82**, 512—519. Compare this vol., i, 46). —To 18 grams of freshly distilled benzaldehyde are gradually added 4·5 c.c. of pure hydrogen disulphide. The liquid becomes warm, turns yellow in colour, and after a time gives a white precipitate of *dibenzylidene disulphide hydroxide*, $OH\cdot CHPh\cdot S\cdot S\cdot CHPh\cdot OH$; silvery plates or prisms from carbon disulphide; very stable when pure, but decomposes on heating; the molecular weight, determined cryoscopically in bromoform solution, was 257. It is decomposed by alcoholic potassium hydroxide, potassium polysulphide, potassium benzoate, and benzyl alcohol being produced, but no phenylcarbithionic acid. On heating with zinc chloride, it gives a condensation product, from which phenylcarbithionic acid is readily obtained. The same condensation product may also be obtained in the cold by treatment with hydrogen persulphide.

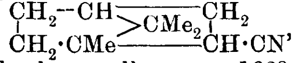
Dibenzylidene trisulphide dihydroxide, $OH\cdot CHPh\cdot S_3\cdot CHPh\cdot OH$, is similarly obtained from benzaldehyde and hydrogen trisulphide; white prisms from carbon disulphide; it is much less stable than the disulphide hydroxide, showing a great tendency to lose sulphur, but is similar to it in its reactions.

Dianisylidene disulphide dihydroxide, $[OMe\cdot C_6H_4\cdot CH(OH)]_2S_2$, and *dianisylidene trisulphide dihydroxide*, $[OMe\cdot C_6H_4\cdot CH(OH)]_2S_3$, are similar in properties to the dibenzylidene compounds. The trisulphide hydroxide is very unstable, sinters at 25°, m. p. 47—55° with decomposition.

The preparation of *dicinnamylidene disulphide dihydroxide*,
$$[CHPh{:}CH\cdot CH(OH)]_2S_2,$$
is not always successful; it forms white crystals, which sinter at 26° and decompose between 37° and 40°, and unites with bromine, as also does *dicinnamylidene trisulphide hydroxide*, $[CHPh{:}CH\cdot CH(OH)]_2S_3$; this forms white crystals, decomposing at 35°, which at times are very unstable.

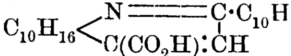
The additive compounds of salicylaldehyde with the hydrogen persulphides could not be obtained pure, as they are only stable below $-10°$. T. S. P.

Hydropinenealdehyde and Hydropinenecarboxylic Acid. JOSEF HOUBEN and HANS DOESCHER (*Ber.*, 1910, **43**, 3435—3442. Compare Abstr., 1908, i, 27).—A somewhat modified method for the preparation of hydropinenealdehyde is described; when carefully sublimed it is obtained as colourless needles, m. p. 131°. The oxime, when boiled with acetic anhydride for three hours, yields the *nitrile* of hydropinenecarboxylic acid,



$$\begin{array}{ccc} CH_2\text{--}CH & \text{——} & CH_2 \\ | & >CMe_2 & | \\ CH_2\cdot CMe & \text{———} & CH\cdot CN \end{array}$$

which crystallises from 60% alcohol in slender needles, m. p. 163°. The aldehyde gives Doebner's reaction with β-naphthylamine and pyruvic acid (Abstr., 1894, i, 261, 532), yielding the *β-naphthacinchonic acid*,



$$C_{10}H_{16}<\begin{array}{l} N\text{=====}C\cdot C_{10}H_7 \\ \quad\quad\quad\quad\;\; | \\ C(CO_2H){:}CH \end{array}$$

m. p. 294°.

The hydropinenecarboxylic acid, obtained by oxidising the aldehyde by exposure to the air, crystallises from 60% alcohol, and has m. p. 88—90°, after sintering at 80°. The acid prepared from magnesium pinene hydrochloride has m. p. 72—74° (Houben, Abstr., 1906, i, 21), and from bornyl iodide, 69—71° (Zelinsky, *ibid.*, 1903, i, 185). The *ethyl* ester, $C_{13}H_{22}O_2$, is a pleasant-smelling oil, with b. p. 116—117°/12·5 mm.; it can be obtained pure by the esterification of the acid or in an impure form by the action of ethyl chloroformate on magnesium pinene hydrochloride, and on hydrolysis yields an acid, m. p. 82°, the analytical data of which do not agree with those of a hydropinenecarboxylic acid. The *anhydride*, $(C_{10}H_{17}\cdot CO)_2O$, can be prepared by heating the acid with excess of acetyl chloride, removing the excess, and heating the residue at 200° under atmospheric pressure; it crystallises from alcohol in small needles, m. p. 210°, and when boiled with 5% potassium hydroxide solution yields an acid, m. p. 78°. The *amide*, $C_{10}H_{17}\cdot CO\cdot NH_2$, is formed together with the ammonium salt of the acid by the action of dry ammonia on a chloroform solution of the anhydride. It crystallises from light petroleum in small prisms, m. p. 138—139°. The *anilide*, $C_{10}H_{17}\cdot CO\cdot NHPh$, crystallises in glistening, felted needles, m. p. 151°.

The acid obtained from the aldehyde appears to be a mixture.

J. J. S.

Action of Sodium Disulphide on 4-Nitro-2-methoxytoluene. Jan J. Blanksma (*Rec. trav. chim.*, 1910, **29**, 407—409).—4-Nitro-2-methoxytoluene was prepared by the method of Nölting and Collin (Abstr., 1884, ii, 1006). When it is treated with sodium sulphide and sulphur and distilled, the distillate yields colourless crystals of 2-*methoxy*-p-*toluidine*, m. p. 58°; the *acetyl* derivative crystallises in colourless leaflets, m. p. 130°. The residue after distillation yields 4-*amino*-2-*methoxybenzaldehyde* as colourless crystals, m. p. 136°; the *acetyl* derivative melts at 145°.

4-Hydroxy-2-methoxybenzaldehyde and 2 : 4-dimethoxybenzaldehyde were also prepared from 4-amino-2-methoxybenzaldehyde. N. C.

Some Derivatives of 3-Nitrocumaldehyde. G. Pizzuti (*Gazzetta*, 1910, **40**, ii, 236—241).—3-*Nitrocumaldehydeoxime*, $C_{10}H_{12}O_3N_2$, crystallises in colourless needles, m. p. 74—76°, which become reddish-yellow in the light. 3-*Nitrocumaldehydephenylhydrazone*, $C_{16}H_{17}O_2N_3$, forms red scales, m. p. 123° (giving a yellow liquid), and also long, red needles, m. p. 120°. 3-*Nitrocumaldehydesemicarbazone*, $C_{11}H_{14}O_3N_4$, crystallises in rosettes of colourless needles, m. p. 222° (previously softening); when exposed to light, the substance becomes yellow. 3-Nitrocumaldehyde condenses with rhodanic acid, yielding 3-*nitro*-4-iso*propylbenzylidenerhodanic acid*, $C_{13}H_{12}O_3N_2S_2$ (compare Bargellini, Abstr., 1906, i, 536), which forms bright yellow scales, m. p. 180°. The compound dissolves in concentrated sulphuric acid, producing a pale yellow coloration. When 3-nitrocumaldehyde is warmed with 1 molecule of phenylmethylpyrazolone in alcoholic solution, a *compound*, $C_{19}H_{19}O_3N_3$, resulting from the combination of equimolecular quantities of the two substances, is obtained. It forms yellow scales, which begin to decompose at 180°, and at 205—208° are completely fused and decomposed, with production of a red liquid. When two molecules of the pyrazolone are taken in the reaction, a *compound* containing 10·66—10·69% of nitrogen is obtained. It crystallises in pale yellow needles, m. p. 151—153° (becoming red at 140°). When kept at 100°, it loses 4% in weight. The substance remaining contains the same percentage of nitrogen as the compound $C_{19}H_{19}O_3N_3$ mentioned above, but it still has m. p. 153°. R. V. S.

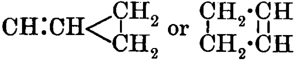
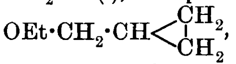
Trimethylene [*cyclo*Propane] Derivatives. Louis Michiels (*Bull. Soc. chim. Belg.*, 1910, **24**, 396—416).—A number of *cyclo*propane derivatives have been prepared, and their interaction with various reagents investigated, with a view to comparing the behaviour of the trimethylene residue with isomeric open-chain groups. The results show that the trimethylene residue exhibits a specific character, and that in particular the hydrogen atom of the ⁚CH group is less easily replaced than in the corresponding *iso*propyl derivatives. The *cyclo*propyl series of alcohols, whether primary or secondary, are readily esterified by haloid acids (compare Bruylants, Abstr., 1909, i, 226).

cyclo*Propyl propyl ketone*, $COPr^{\alpha}\cdot CH{<}\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}$, D^{20} 0·9077, n_{D}^{20} 1·43733, b. p. 150°/747 mm., is a colourless, mobile liquid with a mint-like odour. cyclo*Propyl butyl ketone*, D^{20} 0·8782, n_{D}^{20} 1·43513, b. p. 171—172°/747 mm., resembles its lower homologue in odour and appearance, as does also cyclo*propyl* iso*butyl ketone*, D^{20} 0·8735, n_{D}^{20} 1·43282, b. p. 161°/757 mm. These three ketones were prepared by Bruylants' method (*loc. cit.*), using the magnesium alkyl bromide appropriate to each case.

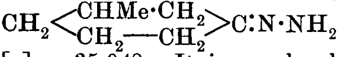
Attempts to prepare *di*cyclo*propyl ketone* by the catalytic action of heated alumina or thoria on *cyclo*propanecarboxylic acid or its ethyl ester were unsuccessful, although in one experiment a *product*, boiling at 160—170°, and yielding a *semicarbazone*, m. p. 85—86°, was obtained.

cyclo*Propyl chloromethyl ketone*, $C_3H_5\cdot CO\cdot CH_2Cl$, D^{20} 1·2036, n_{D}^{20} 1·46235, b. p. 180°/762 mm., or 103°/40—45 mm., obtained by the action of sulphuryl chloride on *cyclo*propyl methyl ketone, is a colourless, mobile liquid, the vapour of which is irritant to the mucous membrane. It reacts with potassium cyanide, and with sodium ethoxide yields a substance which reduces Fehling's solution.

The ketones described above on reduction by sodium in alcohol furnish the corresponding carbinols, and the following were thus prepared: cyclo*Propylpropylcarbinol*, $OH\cdot CHPr^{\alpha}\cdot CH{<}\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}$, D^{20} 0·8693, n_{D}^{20} 1·43663, b. p. 154—155°/750 mm., is a viscous, colourless liquid having a camphoraceous odour. The *acetate*, D^{20} 0·9013, b. p. 174—175°/764 mm., is colourless, mobile, and of agreeable piperaceous odour. cyclo*Propylbutylcarbinol*, D^{20} 0·8721, n_{D}^{20} 1·43984, b. p. 175°/751 mm., resembles its lower homologue; on saturation with hydrogen bromide it furnishes two monobromo-compounds, the one probably cyclo*propylbutylcarbinyl bromide*, b. p. 150°/40 mm., and the *other*, b. p. 120°/40 mm., probably an ethylenic compound derived from the dibromooctane, D^{20} 1·3145, n_{D}^{20} 1·48302, obtained when a mixture of the two monobromo-compounds is further treated with hydrogen bromide, the trimethylene ring being thereby opened (compare Dalle, Abstr., 1902, i, 525; Perkin, Abstr., 1902, i, 597; and Demjanoff and Fortunatoff, Abstr., 1907, i, 1033). cyclo*Propyl*iso*butylcarbinol*, D^{20} 0·8648, n_{D}^{20} 1·43553, b. p. 167°/751 mm., is viscous and possesses a camphoraceous odour. cyclo*Propylethylpropylcarbinol*, $OH\cdot CEtPr^{\alpha}\cdot CH{<}\begin{array}{l}CH_2\\ \mid\\ CH_2\end{array}$, D^{20} 0·8843, n_{D}^{20} 1·45147, b. p. 178—179°/735 mm., obtained by the action of magnesium ethyl bromide on *cyclo*propyl propyl ketone, is a strong smelling liquid. It yields a *bromide*, b. p. 208°/739 mm. (decomp.), which on treatment with potassium hydroxide in alcohol at 150° furnishes a mixture of *hydrocarbons*, D^{20} 0·7894, n_D^{20} 1·43737, b. p. 147—149°/757 mm. (compare Bruylants, *loc. cit.*).

*cyclo*Propylcarbinol is readily esterified by hydrogen bromide in the cold, and from the resulting bromide may be obtained, by treatment with sodium iodide in methyl alcohol, the iodide, which with potassium hydroxide in alcohol gives (1) a small yield of a *hydrocarbon*, possibly  $CH{:}CH<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$ or $\begin{matrix}CH_2\cdot CH\\ |\qquad \|\\ CH_2\cdot CH\end{matrix}$ (compare Demjanoff, Abstr., 1908, i, 85), b. p. − 3° to 1°, which combines with bromine to form a tetrabromide, $CH_2Br\cdot CHBr\cdot CHBr\cdot CH_2Br$ (?), m. p. 112—114°, and (2) cyclo*propylcarbinyl ethyl ether*,  $OEt\cdot CH_2\cdot CH<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, b. p. 98—101°, a liquid of ethereal odour. With dry potassium hydroxide, but little action occurs, and the ether appears to be the chief product. *cyclo*Propylcarbinyl iodide differs markedly from the isomeric *iso*butyl iodide in its behaviour with potassium hydroxide in alcohol, and similarly, whilst *iso*butyric chloride is readily chlorinated, the chloride of *cyclo*propylcarboxylic acid is recovered practically unchanged after treatment with chlorine. T. A. H.

Action of Hydrazine Hydrate on 1-Methyl*cyclo*hexan-3-one.

A. Merkin (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1204—1211).—When 1-methyl*cyclo*hexan-3-one is treated with hydrazine hydrate, it yields (1) the ketazine, $C_7H_{12}{:}N\cdot N{:}C_7H_{12}$, b. p. 229°/140 mm., 210°/71 mm., a − 51·59° to − 45·84°; (2) 1-*methyl*cyclo*hexan*-3-*onehydrazone*,  $CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2—CH_2\end{matrix}>C{:}N\cdot NH_2$, b. p. 154°/71 mm., D_0^{17} 0·9603, n_D^{17} 1·5043, $[a]_D$ − 35·94°. It is a colourless liquid, which decomposes and turns yellow in air, forms the above ketazine on distillation, and combines with water, forming a crystalline *hydrate*. With benzaldehyde it forms benzaldazine, m. p. 93°, and methyl*cyclo*hexanone, and when reduced with sodium and alcohol, it yields aminomethyl*cyclo*hexane and *methyl*cyclo*hexylmethyl*cyclo*hexylidenehydrazine*,

$$C_7H_{12}{:}N\cdot NH\cdot C_7H_{13},$$

which with hydrochloric acid yields methyl*cyclo*hexylhydrazine hydrochloride, $C_7H_{13}\cdot NH\cdot NH_2,HCl$; the free hydrazine has b. p. 208—209°.

The thiosemicarbazide, $NHPh\cdot CS\cdot NH\cdot NH\cdot C_7H_{13}$, m. p. 135°, crystallises from methyl alcohol in needles and in rhombic plates, $[a]_D$ − 15·94°. By treating methyl*cyclo*hexylhydrazine with pyruvic acid in hydrochloric acid solution, prismatic crystals of the *hydrazone*,

$$C_7H_{13}\cdot NH\cdot N{:}CMe\cdot CO_2H,$$

m. p. 96—98°, $[a]_D$ − 16·62° are produced, together with a *substance*, m. p. 236—237°, $[a]_D$ − 11·05°, which is also obtained by treating the hydrazine with hydrochloric acid, and when heated with fuming hydrochloric acid in a sealed tube at 180° is partly converted into a gelatinous mass soluble in alkalis. The methyl*cyclo*hexylhydrazine re-obtained from the methyl*cyclo*hexylhydrazone of pyruvic acid yields a *thiosemicarbazide*, m. p. 135—136°, $[a]_D$ − 23·68°, showing that the original hydrazine consists of a mixture of stereoisomeric hydrazines.

The ketazine, $C_7H_{12}{:}N_2{:}C_7H_{12}$, when treated with hydrazine hydrate and solid potassium hydroxide on a water-bath, is partly converted into 1-*methyl*cyclo*hexan-3-onehydrazone.* Z. K.

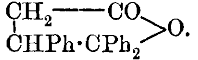
Compounds of Aluminium Chloride and Bromide with Acetophenone and Benzophenone. Boris N. Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1298—1307).—Aluminium bromide reacts more readily with benzophenone than does the chloride. It forms a crystalline, molecular compound, $AlBr_3,COPh_2$, m. p. 142°, which is instantly decomposed by water, with formation of benzophenone. The solubility curve of the two substances is very similar to those obtained for aluminium bromide with the nitro-derivatives of aromatic hydrocarbons and their derivatives (Abstr., 1909, i, 900; 1910, i, 234). It has two eutectic points, at 38° and composition $AlBr_3,4{\cdot}51COPh_2$, and at the same temperature but composition $AlBr_3,0{\cdot}49COPh_2$. Aluminium chloride also forms a molecular compound, $AlCl_3,COPh_2$, m. p. 130° (Perrier gives 119°). The solubility curve has two eutectic points, at 39·5° and composition $AlCl_3,4{\cdot}92COPh_2$, and at 60° at the composition $AlCl_3,0{\cdot}57COPh_2$. When working with these substances it is best to use no third substance, such as sulphuric acid, as solvent. Aluminium halides with acetophenone also yield molecular compounds, but the system is difficult to investigate, since the salts crystallise very slowly, and readily yield resinous products.

Curves and tables are given. Z. K.

Organic Syntheses by means of Sunlight. V. Behaviour of Acids and Ethers [including Esters] with Benzophenone. Emanuele Paternò and G. Chieffi (*Gazzetta*, 1910, **40**, ii, 321—331. Compare Abstr., 1909, i, 240; 1910, i, 41).—Acetic acid and benzophenone do not react when exposed to sunlight. Propionic acid and benzophenone yield a small quantity of a yellow, resinous acid *substance.* Benzophenone and butyric acid give benzopinacone and a yellow *resin*, m. p. 74—75°, which has the properties of an acid, and contains both benzophenone and butyric acid groups. Between benzophenone and benzoic acid no reaction occurs. Phenylacetic acid and benzophenone yield benzopinacone and *β-hydroxy-αββ-triphenylpropionic acid*, $OH{\cdot}CPh_2{\cdot}CHPh{\cdot}CO_2H$, which forms small, flat needles, m. p. 205—208°. The *silver* salt was prepared. Phenylpropionic acid and benzophenone give benzopinacone, an *acid*, m. p. 271—273°, and a substance, m. p. 161—163°. These two products, however, contain traces of benzopinacone. The acid has the formula $C_{18}H_{18}O_4$, and is either diphenyladipic acid,

$$CO_2H{\cdot}CH_2{\cdot}CHPh{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H,$$

or dibenzylsuccinic acid. It resists boiling with nitric acid, and does not decolorise permanganate. The substance of m. p. 161—163° has the formula $C_{22}H_{18}O_2$, and is probably the *lactone*,



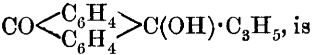
$$\begin{array}{l} CH_2\text{———}CO \\ | \\ CHPh{\cdot}CPh_2 \end{array}\!\!>\!O.$$

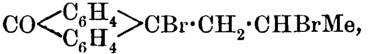
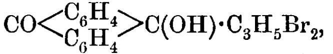
Benzophenone reacts with ethyl ether, producing benzopinacone and a *resin*, $C_{17}H_{18}O_2$, which in the authors' opinion probably has the structure $CPh_2{<}\begin{smallmatrix}-O-\\CH_2\end{smallmatrix}{>}CH{\cdot}OEt$, although owing to the difficulty of purifying the substance some of the analytical results do not agree very well with that formula. Benzophenone and *iso*amyl ether yield benzopinacone, a heavy, viscous *oil*, the analysis of which agrees with the formula $C_{23}H_{32}O_2$ required by a product analogous to that from ethyl ether. Acetal and benzophenone give benzopinacone and a heavy *oil*. Glycerol dimethyl and diethyl ethers behave similarly. Amyl formate and benzophenone yield benzopinacone and a heavy, viscous oil, which appears to be a *lactone* analogous to that obtained from phenylpropionic acid. The formation of benzopinacone was also observed when benzophenone was kept in sunlight with ethyl acetate, ethyl ethylmalonate, ethyl tartrate, the methyl ethers of *m*-cresol, *p*-cresol and resorcinol, and with ethyl phenylpropionate. In most cases the formation of resinous substances was also noted. Benzophenone and benzyl acetate yield in addition to benzopinacone, a *substance*, m. p. 218—219° (compare following abstract). R. V. S.

Organic Syntheses by means of Sunlight. VI. The Product of the Reaction between Benzophenone and Benzyl Acetate. Emanuele Paternò and G. Forlì-forti (*Gazzetta*, 1910, **40**, ii, 332—341. Compare preceding abstract).—The substance forms small, hard, colourless crystals, and has the formula, $C_{22}H_{20}O_3$, of an additive product of equimolecular quantities of benzophenone and benzyl acetate. The authors ascribe to it the structure of the *acetyl* derivative of *triphenylethylene glycol*, $OH\cdot CPh_2\cdot CHPh\cdot OAc$, and advance the following reasons in support of this formula: (1) when the substance is heated with alcoholic potassium hydroxide, benzhydrol, benzoic acid, and acetic acid are formed; (2) when heated with alcohol in a sealed tube at 200° for eight hours, the compound yields ethyl acetate and a substance, $C_{20}H_{16}O$, m. p. 134—135°, apparently identical with triphenylvinyl alcohol (Biltz, Abstr., 1899, i, 439), which is a product of dehydration of triphenylethylene glycol; (3) by the action of acetyl chloride on the substance, triphenylvinyl alcohol is obtained, whilst acetyl chloride in presence of acetic acid leads to the formation of a *substance* crystallising in needles, m. p. 103—105°, which has the composition of an acetyl derivative of that alcohol.
R. V. S.

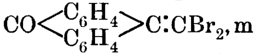
Some Properties of Piperonyloin. Henry A. Torrey and J. B. Sumner (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1492—1494).—The piperonyloin was prepared by Perkin's method (Trans., 1891, **59**, 150), some modifications being introduced. A comparison was made of the behaviour of piperonyloin and of benzoin under similar conditions, and it was found that piperonyloin is much less reactive than benzoin; thus it is not affected by reducing agents or acetyl chloride, and it does not form an oxime. The only substances found with which it reacts easily are carbamide and ammonium thiocyanate. *Piperonyloincarbamide*, $C_{17}H_{12}O_5N_2$, forms pale pink crystals, decomposing at 265°. The *thiocarbamide* crystallises in long, felted, nearly white needles, decomposing at 260°, and probably has the formula $C_{17}H_{12}O_4N_2S$. N. C.

Allyloxanthranol and Some of its Derivatives. H. KONDO (*Ber.*, 1910, **43**, 3182—3187).—The investigation was undertaken with the object of preparing benzanthrone (Bally, Abstr., 1905, i, 237).

9-*Allyloxanthranol*,  $CO<\substack{C_6H_4\\C_6H_4}>C(OH)\cdot C_3H_5$, is prepared in a similar manner to amyloxanthranol (compare Liebermann, Abstr., 1882, 855; Liebermann and Roka, Abstr., 1908, i, 427) by the action of allyl bromide on anthraquinone. It crystallises in large, colourless, measurable crystals, m. p. 108°. On reduction with sodium amalgam, 9-propyloxanthranol, m. p. 164° (Hallgarten, Abstr., 1889, 894), is formed.

With hydrogen bromide, 9-*β-bromopropyloxanthranyl bromide*,  $CO<\substack{C_6H_4\\C_6H_4}>CBr\cdot CH_2\cdot CHBrMe$, is obtained in colourless, prismatic crystals, m. p. 129°. With bromine in carbon disulphide solution, 9-*αβ-dibromopropyloxanthranol*,  $CO<\substack{C_6H_4\\C_6H_4}>C(OH)\cdot C_3H_5Br_2$, is obtained; it crystallises in colourless, slender prisms, m. p. 147°.

The elimination of hydrogen bromide from the dibromide is incomplete in presence of pyridine and quinoline. With alcoholic potassium hydroxide, heat is required to render it complete, and decomposition products are readily formed. On the addition of acid, a compound, $C_{17}H_{12}O_2$, possibly allylenyloxanthranol, is obtained of a faint yellow hue, m. p. 111°. It gives a green coloration with concentrated sulphuric acid. With bromine in carbon disulphide, a small quantity of a blood-red, crystalline precipitate is formed, which is very easily decomposed, becoming yellow. With dilute alkali hydroxides, a yellow potassium salt is obtained, which fluoresces like eosin in alcoholic solution.

From the carbon disulphide mother liquors a yellow compound, 9-*dibromomethyleneanthrone*,  $CO<\substack{C_6H_4\\C_6H_4}>C:CBr_2$, m. p. 167°, is obtained, which is quantitatively converted into anthraquinone by moisture.

E. F. A.

Some Derivatives of 2-Acetyl-α-naphthol. HENRY A. TORREY and E. J. CARDARELLI (*J. Amer. Chem. Soc.*, 1910, **32**, ii, 1477—1488).—2-Acetyl-α-naphthol was prepared by Friedländer's method (Abstr., 1895, i, 668), and various derivatives obtained and examined. During experiments on the action of benzaldehyde on 2-acetyl-α-naphthol, a second form of 2-acetyl-α-naphthol was obtained in brown plates, m. p. 98°, instead of the original yellowish-green needles, m. p. 103°. It is thought that the brown form has a quinonoid structure, and that the yellow form is the phenol. Several methods were tried, unsuccessfully, to obtain a quinoline from 2-acetyl-α-naphthol.

4-Amino-2:(?)-diacetyl-α-naphthol forms yellowish-white needles, arranged like chestnut burs, and melting at 212°. Friedländer gives m. p. 107° for this compound, but the authors could not obtain this melting point.

4-Amino-2-acetyl-α-naphthol reacts quantitatively with aldehydes;

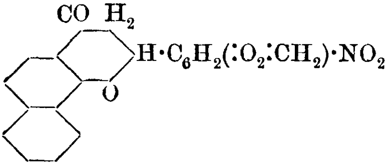
4-*benzylideneamino-2-acetyl-α-naphthol* forms plates between the colours of brass and bronze, m. p. 159°; the corresponding *piperonylidene* derivative crystallises in brown plates, m. p. 178°, and the *cinnamylidene* derivative in brownish-yellow needles, m. p. 144°.

4-*Nitro-2-cinnamoyl-α-naphthol*, $OH\cdot C_{10}H_5(NO_2)\cdot CO\cdot CH{:}CHPh$, crystallises in two forms, a yellow one and a red one; the melting point varies from 202° to 208°. 2-m-*Nitrocinnamoyl-α-naphthol* forms red, microscopic needles, m. p. 210°; it absorbs bromine easily, forming a vermilion-coloured substance. By the action of sodium hydroxide on a mixture of 2-acetyl-α-naphthol and 6-nitropiperonal, the ketol, 2-(*β-hydroxy-β-6′-nitropiperonylpropionyl*)*-α-naphthol*,

$$CH_2O_2{:}C_6H_2(NO_2)\cdot CH(OH)\cdot CH_2\cdot CO\cdot C_{10}H_6\cdot OH,$$

is obtained. It forms lemon-yellow needles, m. p. 201—202°.

The *monoacetate* of the ketol crystallises in cream needles, m. p. 188—190°; it forms a *tribromo*-derivative. The *diacetate* of the ketol forms golden, rectangular crystals, m. p. 197—198°. By the action of bromine on the ketol, two *substances* are obtained, one red, m. p. 252°, and one yellow, m. p. 220°.



2-(6-*Nitropiperonyl*)*-naphthaflavanone*(annexed formula) crystallises in red needles with an orange tinge, m. p. 226°; bromine acts on it to give the *substance*, $C_{20}H_{12}O_6NBr$, which forms an orange powder decomposing at 250—255°. N. C.

Some Derivatives of Hydroxyquinol. I. and II. GUIDO BARGELLINI and GHERSCH AVRUTIN (*Gazzetta*, 1910, **40**, ii, 342—347, 347—353. Compare Reigrodski and Tambor, Abstr., 1910, i, 578).—I. In some of their results the authors have been anticipated by the publication cited above. 2 : 4 : 5-Trimethoxyacetophenone has b. p. 285—290°/33 mm. When oxidised with permanganate, it yields asaronic acid. Its *oxime* forms colourless crystals, m. p. 126—127°. The *semicarbazone* crystallises in small laminæ, m. p. 186—188°. 2 : 4 : 5-Trimethoxychalkone has m. p. 117—118° (Reigrodski and Tambor gave 113—114°). 4 : 2′ : 4′ : 5′-*Tetramethoxychalkone* (from trimethoxyacetophenone and anisaldehyde) crystallises in small, yellow needles, m. p. 123—124°, and dissolves in concentrated sulphuric acid, producing an intense red coloration. 3 : 4 : 2′ : 4′ : 5′-*Pentamethoxychalkone* (from veratraldehyde) forms yellow scales, m. p. 155°, and gives a red coloration when dissolved in concentrated sulphuric acid. 3 : 4-*Methylenedioxy*-2′ : 4′ : 5′-*trimethoxychalkone* (from piperonaldehyde) crystallises in yellow laminæ, m. p. 182—183°. It gives a reddish-violet coloration with concentrated sulphuric acid.

II. When triacetylhydroxyquinol is heated with acetic acid and zinc chloride, or with chloroacetic acid and zinc chloride, or with zinc chloride alone, a mixture of two substances is obtained, namely, a red *compound*, crystallising in needles, m. p. 200—202° (decomp.), and a colourless *substance*, crystallising in silvery scales, m. p. 165—166°. Both have the composition $(C_2H_2O)_n$, which agrees with that of trihydroxyacetophenone and its three acetyl derivatives. Both substances yield trimethoxyacetophenone when treated with methyl sulphate. R. V. S.

Turmeric Oil. II. Oxidation Products of Curcumone. Hans Rupe and A. Steinbach (*Ber.*, 1910, **43**, 3465—3471. Compare Rupe, Lucksch, and Steinbach, Abstr., 1909, i, 598).—Potassium permanganate is the only oxidising agent which, by its attack on curcumone, gives some insight into the constitution of the ketone. When curcumone is treated with 4% potassium permanganate at the ordinary temperature, *p*-tolyl methyl ketone, terephthalic acid, and *p*-acetylbenzoic acid are produced. When curcumone is shaken for eight hours with aqueous sodium hypobromite at 0° in a bottle protected from light, a considerable quantity of the ketone is recovered unchanged, together with bromoform and an *acid*, $C_{12}H_{16}O_2$, m. p. 33—34°, b. p. 168—170°/12 mm., $[\alpha]_D^{20}$ 31·15° in alcohol, which is purified best through the *calcium* salt, $Ca(C_{12}H_{15}O_2)_2,3H_2O$; it receives the name *curcumic acid*, and is apparently identical with Jackson and Menke's turmeric acid. A small quantity of another *acid*,

$$C_{12}H_{16}O_3(?),$$

m. p. 150—151°, has also been isolated, which is oxidised to terephthalic acid by potassium permanganate. The oxidation of curcumic acid by 4% potassium permanganate in the presence of sodium carbonate at 0° yields *p*-tolyl methyl ketone, terephthalic acid, and a dibasic *acid*, $C_{12}H_{14}O_4$, m. p. 226—228°, which may be identical with Jackson and Menke's *apo*turmeric acid, m. p. 221°.

The preceding results indicate that curcumone, $C_{13}H_{18}O$, is a derivative of benzene containing two para-substituents, one of which is methyl, and the second, one or other of the groups

$$\cdot CHMe\cdot CH_2\cdot CH_2\cdot COMe,$$

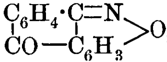
·CHMe·CHMe·COMe, or ·CMeEt·COMe. Curcumic acid contains a carboxyl group in the place of the group ·COMe. C. S.

Dianilino-*p*-benzoquinoneanil. William Küster (*Ber.*, 1910, **43**, 2962—2964).—The compound obtained by Küster and Fuchs (Abstr., 1907, i, 572) by the action of aniline on hæmin is now shown to be dianilino-*p*-benzoquinoneanil and to be free from iron. Apparently hæmin acts as a ferric salt, and brings about to some extent the oxidation of aniline at the ordinary temperature. E. F. A.

Nitranilic Acid [3 : 6-Dinitro-2 : 5-dihydroxy-*p*-benzoquinone]. Rudolf Nietzki (*Ber.*, 1910, **43**, 3457—3459).—Potassium nitroanilate is obtained in 75—80% yield by adding the paste, obtained by stirring quinol with acetic anhydride and a few drops of concentrated sulphuric acid, to cold nitric acid, D 1·48, adding subsequently concentrated sulphuric acid, and pouring the mixture, after being kept for twelve hours at 0°, on to ice; the solid product is treated with ice and potassium hydroxide (compare Henle, *Annalen*, 1906, **350**, 334). C. S.

Action of Hydroxylamine on Some Ortho-substituted Derivatives of Anthraquinone. Martin Freund and Fritz Achenbach (*Ber.*, 1910, **43**, 3251—3260).—*o*-Chlorinated anthraquinones react with hydroxylamine more readily than anthraquinone itself, and the oximes formed lose hydrogen chloride when boiled with alkali, yielding cyclic compounds resembling those prepared by Meyer and Cathcart from *o*-halogenated benzophenones (Abstr., 1892, 992; 1893, i, 94).

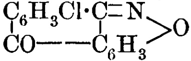
1-Chloroanthraquinone reacts with hydroxylamine hydrochloride and alcohol at 180°, yielding a mixture of two oximes, but when these are boiled with dilute sodium hydroxide solution, the one, presumably the *syn*-compound, is transformed into anthrone*iso*oxazole,



$$\begin{matrix} C_6H_4\cdot C{=}N \\ | \qquad\quad | \\ CO—C_6H_3 \end{matrix}\!>\!O,$$

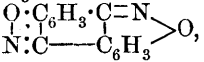
whereas the other, the *anti*oxime, is not decomposed.

1 : 5-Dichloroanthraquinone and hydroxylamine hydrochloride at 185° yields a mixture of oximes, and when these are boiled with alkalis an insoluble product consisting of a mixture of 5-chloro-10-anthrone-1 : 9-*iso*oxazole,



$$\begin{matrix} C_6H_3Cl\cdot C{=}N \\ | \qquad\qquad | \\ CO——C_6H_3 \end{matrix}\!>\!O,$$

and anthradi*iso*oxazole,



$$\begin{matrix} O{:}C_6H_3\cdot C{=}N \\ | \quad | \qquad\quad | \\ N{:}C——C_6H_3 \end{matrix}\!>\!O,$$

is formed together with two oximes which remain dissolved in the alkali; these are the *anti*-forms of the mono- and di-oximes of 1 : 5-dichloroanthaquinone.

*Anthrone*isoo*xazole*, $C_{14}H_7O_2N$, crystallises from hot chlorobenzene in slender, nearly colourless needles, m. p. 298·5°. 1-*Chloroanthraquinone*-anti-*monoxime*, $C_{14}H_8O_2NCl$, crystallises from a mixture of methyl alcohol and water in golden-yellow plates, m. p. 219—222° (decomp.). 1 : 5-*Dichloroanthraquinone*-anti-*monoxine*, $C_{14}H_7O_2NCl_2$, crystallises from hot glacial acetic acid in yellow needles, m. p. 252° after sintering at 235°.

1:5-*Dichloroanthraquinone*-anti-anti-*dioxime*, $C_{14}H_8O_2N_2Cl_2$, is, unlike the monoxime, insoluble in hot chlorobenzene, and forms a grey powder, m. p. 245° (decomp.).

1-*Chloroanthrone*isoo*xazole*, $C_{14}H_6O_2NCl$, crystallises from glacial acetic acid, and has m. p. 229° after sintering at 225°. *Anthradi*iso-*oxazole*, $C_{14}H_6O_2N_2$, is sparingly soluble in hot chlorobenzene, and has m. p. 304°.

1-*Methoxyanthraquinonemonoxime*, $C_{15}H_{11}O_3N$, crystallises from alcohol in dark brown needles, m. p. 198°. The corresponding 1-*phenoxy*-derivative, $C_{20}H_{13}O_3N$, crystallises from 75% acetic acid in brown needles, m. p. 175° after sintering at 155°.

The *monoxime* of anthrarufin dimethyl ether, $C_{16}H_{13}O_4N$, has m. p. 196° after sintering at 185°. J. J. S.

Action of Bornyl Chloride on Aromatic Amines. FRITZ ULLMANN and ALFRED SCHMID (*Ber.*, 1910, **43**, 3202—3209).—Bornyl chloride reacts with primary aromatic amines, yielding a mixture of camphene and bornylarylamine.

Bornylaniline, $C_{10}H_{17}\cdot NHPh$, obtained by boiling a mixture of bornyl chloride and aniline for three hours, is a colourless, strongly refractive, viscid liquid, b. p. 140°/2 mm., and forms a *hydrochloride*,

m. p. 198°, and an *acetyl* derivative, m. p. 123°. On nitration, the latter yields *acetobornyl*-p-*nitroanilide*, $C_{10}H_{17}\cdot NAc\cdot C_6H_4\cdot NO_2$, white, glistening leaflets, m. p. 185°.

Acetylbornyl-p-*phenylenediamine*, $C_{10}H_{17}\cdot NAc\cdot C_6H_4\cdot NH_2$, obtained by reducing the nitro-compound with stannous chloride and hydrochloric acid, crystallises in colourless needles, m. p. 148°.

When bornyl chloride is boiled with aniline and the product distilled under ordinary pressure, a 96% yield of camphene is obtained.

Bornyl-o-*toluidine*, $C_{10}H_{17}\cdot NH\cdot C_6H_4\cdot Me$, prepared from bornyl chloride and *o*-toluidine, crystallises in needles, m. p. 55°, b. p. 160°/4 mm.; the *hydrochloride* has m. p. 180°.

Bornyl-p-*toluidine* has b. p. 162°/3 mm., crystallises in needles, m. p. 33°, and yields a crystalline *hydrochloride*, m. p. 214° (decomp.).

Bornyl-m-4-*xylidine*, b. p. 176°/7 mm., crystallises from methyl alcohol in large needles, m. p. 79°.

The action of bornyl chloride on *m*-tolylenediamine leads to the formation of camphene and *diamino-ditolylamine*, $C_{14}H_{17}N_3$, glistening, colourless leaflets, m. p. 154—155°.

The same product is obtained by heating *m*-tolylenediamine with its hydrochloride at 200°. The *diacetyl* derivative, has m. p. 247°.

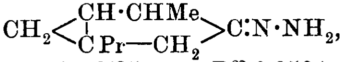
F. B.

Catalytic Reduction. III. ALADAR SKITA and H. RITTER (*Ber.*, 1910, **43**, 3393—3399. Compare Abstr., 1908, i, 855; 1909, i, 479).—*d*-Pulegone is reduced by hydrogen under two atmospheres pressure, in presence of colloidal platinum, to *d*-menthone, whilst the product obtained with other reducing agents is *l*-menthone (Beckmann, Abstr., 1889, 721). Phorone yields di*iso*butylcarbinol, whilst mesityl oxide is only reduced to methyl *iso*butyl ketone. This difference may be explained by the different positions of the carbonyl group.

Using a lower pressure of hydrogen (one and a-half atmospheres), phorone may be reduced only to valerone, whilst under as high a pressure as five atmospheres it may be reduced to methyl*iso*butylcarbinol. *iso*Phoroneoxime yields, under four atmospheres, 5-amino-1 : 1 : 3-trimethyl*cyclo*hexane.

Phenylacetaldehyde is converted into phenylethyl alcohol, and quinone into quinol. C. H. D.

Action of Hydrazine Hydrate on Thujone. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1198—1204).—By the action of an excess of hydrazine hydrate on thujone in alcoholic solution, the latter is converted quantitatively into *thujonehydrazone*,



$$CH_2<\begin{matrix}CH\cdot CHMe\\ |\\ CPr—CH_2\end{matrix}>C:N\cdot NH_2$$

a colourless liquid with a faint odour, b. p. 149°/35 mm., D_0^{22} 0·9504, n_D^{22} 1·4952, $[a]_D$ +123·75°, which readily reduces ammoniacal silver oxide, and dissolves in hydrochloric acid with formation of thujone, b. p. 202—203·5°/739 mm., a +33·36°; the original thujone had a +65·0°. When reduced with sodium in alcoholic solution, the hydrazone yields *thujylhydrazine*, $C_{10}H_{17}\cdot NH\cdot NH_2$, b. p.

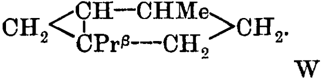
142—144°/38 mm., 242—244°/741 mm., D^{20}_{0} 0·9302, $[\alpha]_D + 76·67°$, n^{20}_D 1·4800, which is oxidised on exposure to air and reduces ammoniacal silver oxide. Thujone, b. p. 202—204°/739 mm., α +26·28°, and impure thujylamine, b. p. 196—199°, α +50·30°, are formed as by-products. When mixed with phenylthiocarbimide, the hydrazone forms the *phenylthiosemicarbazide*, NHPh·CS·NH·NH·$C_{10}H_{17}$, which forms prismatic needles, m. p. 134·5—135°, $[\alpha]_D$ +51·89° in chloroform solution, whilst with potassium ferricyanide in potassium hydroxide solution the hydrazine yields thujene, b. p. 157·5—158°/741 mm., D^{20}_{0} 0·8164, n^{20}_D 1·4398, $[\alpha]_D + 53·41°$. Thujene has a faint odour, and reacts very slowly with alkaline potassium permanganate. In chloroform solution it absorbs bromine, forming an unstable *bromide*; it also combines with hydrogen bromide, forming a heavy *bromide*, which when boiled with potassium hydroxide yields an unsaturated *hydrocarbon*, $C_{10}H_{18}$, b. p. 162—165°, D^{20}_{20} 0·8139, n^{20}_D 1·4512, α +3·32°.

Z. K.

Semicarbazide and Cyclic Nitrosochlorides. HANS RUPE and H. ALTENBURG (*Ber.*, 1910, **43**, 3471—3474).—The ease with which the semicarbazide group replaces the oximino-group in aliphatic oximino-ketones (Rupe and Kessler, Abstr., 1910, 93) has induced the authors to examine the behaviour of some cyclic nitrosochlorides. An alcoholic solution of *d*-β-bislimonene nitrosochloride is boiled for one hour with a concentrated aqueous solution of semicarbazide hydrochloride. When the product is distilled directly with steam, carvone is obtained, but when the product is first neutralised by sodium hydrogen carbonate and is then distilled with steam, the oxime and the semicarbazone of carvone are obtained. Bisterpineol nitrosochloride, under similar conditions, yields terpineol by direct distillation with steam, the residue containing 8-hydroxydihydrocarvonesemicarbazone. The latter, together with hydrazodicarbonamide, is obtained when potassium acetate is added to the aqueous-alcoholic solution before boiling.

l-Carvoxime is produced when the product of the reaction between magnesium and *d*-limonene nitrosochloride in dry ether is decomposed by cold water and dilute sulphuric acid.

C. S.

Hydrogenation of Isomeric Thujenes and of Sabinene. Thujane. LEO A. TSCHUGAEFF and W. FOMIN (*Compt. rend.*, 1910, **151**, 1058—1062. Compare Abstr., 1905, i, 71).—Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 768) has shown that reduction of *l*-α-thujene by Sabatier and Senderens' method leads to rupture of the trimethylene ring and production of a hydrocarbon, $C_{10}H_{20}$. When the reduction, however, is effected at the ordinary temperature by hydrogen and platinum-black, *thujane*, $C_{10}H_{18}$, is obtained; this has b. p. 157°/758 mm., D^{16}_{4} 0·8161, n^{20}_D 1·43759, $[\alpha]_D$ +62·03°. When prepared from *d*-β-thujene, the product has b. p. 157°/759 mm., D^{16}_{4} 0·8191, n^{16}_D 1·44102, $[\alpha]_D$ +34·72°, whilst under the same conditions sabinene gives a hydrocarbon, b. p. 157—158°/760 mm., D^{17}_{4} 0·8190, n^{17}_D 1·44393, $[\alpha]_D$ +18·56°. The hydrocarbons are probably identical, except in their optical rotations, and their stability towards oxidising agents suggests that they have the constitution  $CH_2<\begin{matrix}CH—CHMe\\ CPr^{\beta}—CH_2\end{matrix}>CH_2$.

W. O. W.

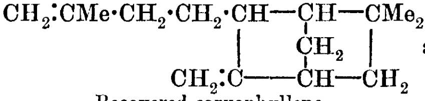
Constituents of Ethereal Oils. Regeneration of Caryophyllene.

Friedrich W. Semmler and Erwin W. Mayer (*Ber.*, 1910, **43**, 3451—3455. Compare Schreiner and Kremers, Abstr., 1902, i, 108; Schimmel & Co., *Bericht*, October, 1910, 173).—By the elimination of hydrogen chloride from caryophyllene dihydrochloride by means of a saturated methyl-alcoholic solution of potassium hydroxide or a concentrated solution of sodium methoxide, a hydrocarbon is obtained with the following properties: b. p. 121—122·5°/12 mm., D_4^{20} 0·8996, a_D +19°, n_D^{20} 1·4990. This hydrocarbon yields the same dihydrochloride, m. p. 69—70°, as is obtained from the original caryophyllene. Both dihydrochlorides are dextrorotatory, although the natural hydrocarbon is lævo- and the regenerated hydrocarbon dextro-rotatory. The conclusion is drawn that the natural hydrocarbon contains the same caryophyllene as the regenerated, but contains, in addition, a lævorotatory compound (compare Deussen and Lewinsohn, Abstr., 1908, i, 353; 1909, i, 171).

The products obtained by eliminating the hydrogen chloride by means of dilute alkalis or of sodium acetate and acetic acid are not homogeneous. When, however, the dihydrochloride is boiled for three-quarters of an hour with quinoline, an isomeric caryophyllene with the following properties is obtained: b. p. 122—123°/13 mm., D_4^{20} 0·927, n_D^{20} 1·50246, and a_D^{20} −57° in a 1-dcm. tube.

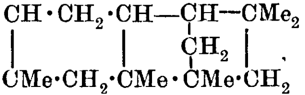
This hydrocarbon is regarded as the pure tricyclic caryophyllene.

The following formulæ are suggested:



Recovered caryophyllene.

and



Tricyclic caryophyllene.

J. J. S.

Philippine Terpenes and Essential Oils. IV.

Raymond F. Bacon (*Philippine J. Sci.*, 1910, **5**, 257—265. Compare Abstr., 1909, i, 658).—The volatile oils from a number of plants indigenous to, or cultivated in, the Philippines are described.

Cinnamomum mindanaense bark furnishes a yellow oil, D_{30}^{30} 0 960, n_D^{30} 1·5300, a_D^{30} + 7·9°, containing 60% of an aldehyde, and having a strong odour of cinnamon. *Canarium villosum* yields an oleo-resin, which on distillation furnishes about 11% of oil, distilling mainly between 154° and 180°, and containing pinene and dipentene. Native grown ginger-root furnished 0·072% of a pale yellow oil, D_{30}^{30} 0·8850, n_D^{30} 1·4830, a_D^{30} + 5·9°, and saponification number 14; this had an odour similar to that of orange-peel oil, and was completely soluble in two or more volumes of 90% alcohol. *Ocimum sanctum* leaves gave 0·6% of greenish-coloured oil, having a_D^{30} 0, n_D^{30} 1·5070, D_{30}^{30} 0·952, and saponification value 2·8. It had an anise-like odour, and the fraction boiling at

85—95°/9 mm. gave homoanisic acid on oxidation. *Curcuma Zedoaria* roots furnished 0·065 to 0·25% of brown oil, D_4^{30} 0·933, n_D^{30} 1·4920 to 1·5070, α_D^{30} + 1°10′, saponification value 2, and soluble in two or more volumes of 80% alcohol. The oil boiled from 60° to 166°/7 mm., and the higher fractions contained a sesquiterpene alcohol, D_{30}^{30} 1·01, m. p. 67°, b. p. 160°/7 mm., which appears to be the chief odoriferous constituent of the oil, and to belong to the tricyclic group. It gave a deep red colour with sulphuric acid. Turmeric roots furnished a brownish-coloured oil, having D_{30}^{30} 0·390, n_D^{30} 1·5030, α_D^{30} + 8·6°, ester number 81, and miscible with 75% or stronger alcohol in all proportions (compare Rupe, Luksch, and Steinbach, Abstr., 1909, i, 598). The yellow flowers of *Michelia champaca* furnished 0·2% of oil, which when kept, deposited (1) a crystalline solid, (2) an amorphous solid. The residual brown oil so obtained had D_{30}^{30} 0·9543—1·020, n_D^{30} 1·4550—1·4830, saponification number 160—180; that having the higher constants had the finer odour. It is considered likely that the reputed Manila champaca oils examined by previous investigators were not derived wholly from champaca flowers. T. A. H.

Essential Oil of Spanish Wild Marjoram. Bernabé Dorronsoro (*Anal. Fis. Quim.*, 1910, **8**, 315—328).—Spanish wild marjoram (*Mejorana silvestre, Thymus Mastichina*, L.) is distilled largely in the south and centre of Spain. Authentic samples of the oil taken in the years 1898–1909 gave values D_{15}^{20} 0·907—0·945, n_D^{23} 1·4630—1·4654, and α_D^{25} varying from − 1°40′ to + 9°20′ (200 mm. tube).

The saponification value of the oil had a range 12·7—18·5 with samples taken during the years 1898–1909; the esters calculated as linalyl acetate ranged from 4·44—6·47%; the acetylation number ranged from 29·2—45·6, and the alcohol, calculated as $C_{10}H_{18}O$, varied from 8·20—13·0. The analysis of a 5 kilogram sample gave the following result: *d*-pinene, 7—8%; cineol or eucalyptol, 64—72%; phenols, less than 0·1%; ketones, less than 0·1%; esters (as linalyl acetate), 4·44—6·47%, and free alcohols (linalool), 8·2—14·1%.

The remarkable point with regard to this oil is the production from a species of *Thymus* of a high proportion of cineol and the entire absence of thymol, cineolic acid, and methylheptenone; the oxidation products of cineol are also absent. W. A. D.

So-called Crystalline Chlorophyll—a Mixture. M. Tsvett (*Ber.*, 1910, **43**, 3139—3141).—The green crystals of chlorophyll discovered by Borodin, and recently investigated by Willstätter, have been regarded (Tsvett, Abstr., 1908, i, 669) either as a compound of the genuine chlorophyllins with possibly a third substance, or as an isomorphous mixture of two chlorophyllin derivatives. By means of the adsorption analysis of crystalline chlorophyll, dissolved in ether and diluted with ten volumes of light petroleum, the chromatogram is proved to show two zones—a superior greenish-yellow and an inferior greenish-blue. Accordingly, crystalline metachlorophyllin is an isomorphous mixture of α- and β-metachlorophyllins. E. F. A.

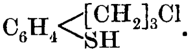
Di-ω-hydroxy-2 : 5-dimethylfuran. JAN J. BLANKSMA (*Rec. trav. chim.*, 1910, **29**, 403—406).—Although hexoses yield δω-hydroxymethylfurfuraldehyde when heated with oxalic acid, the author found that hexonic acids and the hexitols do not give di-ω-hydroxy-2 : 5-dimethylfuran under similar conditions. This substance may, however, be prepared by the action of sodium hydroxide on hydroxymethylfurfuraldehyde, hydroxymethylpyromucic acid being formed at the same time.

The crystals of *di-ω-hydroxy-*2 : 5-*dimethylfuran* are colourless, m. p. 80°; the *diacetyl* derivative forms colourless crystals, m. p. 64°.

The *semicarbazone* of hydroxymethylfurfuraldehyde crystallises in large, colourless crystals, m. p. 192°; its p-*bromophenylhydrazone* forms pale yellow crystals, m. p. 142°, which darken when exposed to sunlight. N. C.

Cyclic Sulphides. JULIUS VON BRAUN (*Ber.*, 1910, **43**, 3220—3226. Compare Abstr., 1910, i, 274).—The action of potassium sulphide on αζ-di-iodohexane yields only a very small quantity of hexamethylene sulphide, $(CH_2)_6S$, so that the tendency to the formation of the cyclic sulphides, $(CH_2)_nS$, diminishes progressively as *n* increases from 4 to 6.

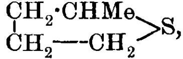
If, however, two adjacent carbon atoms of a benzene ring are included in the chain, the formation of a cyclic sulphide containing a 6-membered ring takes place very readily; thus tetrahydrobenzthiopyran is produced in almost quantitative yield from *o*-ω-chloropropylthiophenol,



$C_6H_4<^{[CH_2]_3Cl}_{SH}$.

It has been shown previously by the author (Abstr., 1910, i, 821) that the action of αζ-di-iodohexane on amines is accompanied by an isomerisation of the hexamethylene chain, the compounds produced containing the α-pipecoline ring and not a 7-membered ring. In order to determine if a similar transformation occurs in the formation of cyclic sulphides, the interaction of potassium sulphide and αδ-di-iodopentane has been investigated. The cyclic sulphide so obtained is different from that produced by the action of potassium sulphide on αε-di-iodopentane, so that no isomerisation of the pentamethylene chain has taken place in the latter reaction.

αδ-Di-iodopentane reacts vigorously with concentrated aqueous potassium sulphide in the presence of a little alcohol, yielding a *compound*, $C_{11}H_{18}O$, b. p. 229—230°, 122°/24 mm., and 2-*methyltetrahydrothiophen*,

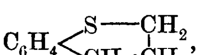


$\begin{matrix} CH_2\cdot CHMe \\ | \\ CH_2\text{---}CH_2 \end{matrix}>S$, b. p. 134°, a colourless liquid with a disagreeable odour, which yields a *methiodide*, crystallising in long, stout prisms, subliming at 172—173°, and transformed when kept in a desiccator into an amorphous, horny mass; the *platinichloride*, $(C_5H_{10}SMe)_2PtCl_6$, crystallises in reddish-yellow leaflets, m. p. 197° (decomp.).

The cyclic *sulphide*, $C_6H_{12}S$, is produced in a yield of 6% by the interaction of potassium sulphide and αζ-di-iodohexane in aqueous-alcoholic solution. It is a colourless oil, and gives a *methiodide*, crystallising in colourless needles, m. p 147°.

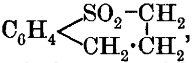
The *platinichloride* crystallises from water in reddish-yellow leaflets, m. p. 193°.

The main product of the action of potassium sulphide on $\alpha\zeta$-di-iodohexane forms an *oil*, which solidifies on cooling, and probably consists of $I\cdot[CH_2]_6\cdot(S\cdot[CH_2]_6)_n\cdot S\cdot[CH_2]_6\cdot I$.

Thiochroman (*tetrahydrobenzthiopyran*),  $C_6H_4<\begin{matrix}S-CH_2\\ CH_2\cdot CH_2\end{matrix}$, b. p. 128—130°/15 mm., is obtained as an almost odourless, pale yellow oil by the addition of potassium xanthate to a diazotised solution of o-ω-chloropropylaniline, slowly heating the *diazoxanthate*,

$$Cl\cdot[CH_2]_3\cdot C_6H_4\cdot N_2\cdot S\cdot CS\cdot OEt,$$

thus produced to 70°, and boiling the resulting dark-coloured *oil*, probably $Cl\cdot[CH_2]_3\cdot C_6H_4\cdot S\cdot CS\cdot OEt$, with alkali in aqueous-alcoholic solution. It does not react readily with methyl iodide, and on treatment with methyl sulphate yields a dark viscid, liquid *additive product*, which solidifies after several weeks' keeping.

Thiochromansulphone,  $C_6H_4<\begin{matrix}SO_2-CH_2\\ CH_2\cdot CH_2\end{matrix}$, white crystals, m. p. 88·5°, is produced by oxidising thiochroman with potassium permanganate in aqueous solution. F. B.

Ephedrine and ψ-Ephedrine. Franz Wilhelm Calliess (*Apoth. Zeit.*, 1910, **25**, 677—678).—Schmidt has shown previously (Abstr., 1908, i, 452) that when either of these bases is treated with hydrochloric acid at 100°, an equilibrium mixture of both is formed. It is now shown that ephedrine on acetylation is completely converted into ψ-ephedrine. The hydrochloride of either base on treatment with acetic anhydride yields an *acetyl* derivative, $C_{10}H_{14}ONAc,HCl$, m. p. 175°, $[\alpha]_D$ +96·7°, crystallising in colourless columns or tablets, which on hydrolysis by hydrochloric acid furnishes ψ-ephedrine. The *platinichloride* of the acetyl derivative, m. p. 184°, and the *aurichloride*, m. p. 165°, were prepared. T. A. H.

Components of Opium. Leopold van Itallie and Max Kerbosch (*Arch. Pharm.*, 1910, **248**, 609—613).—Samples of opium from the Levant, India, China, America, France, Persia, and Egypt have been examined for the presence of morphine, narcotine, papaverine, thebaine, codeine, and narceine, the six commonest of the twenty-odd alkaloids in opium. The six alkaloids have been found in all of the samples except in the Indian opiums from Bengal, Patna, and Benares; these three do not contain papaverine. A reason for this peculiarity is being sought; it is not to be explained by difference in origin, because, as far as information is available, Bengal, Patna, and Benares opiums are obtained from the same plant, *Papaver somniferum* var. *album*, as Persian, Egyptian, Levantine, and other Indian opiums.

C. S.

Action of Hydrogen Peroxide on Thebaine, Morphine, and their Ethers. Martin Freund and Edmund Speyer (*Ber.*, 1910, **43**, 3310—3314).—When heated on the water-bath with 30%

hydrogen peroxide, thebaine, morphine, codeine, and dionine are converted into substances which are regarded as amine-oxides, since they are re-converted into the original alkaloids by sulphurous acid. They are characterised, however, by their stability towards acidified potassium iodide, and by their very slight physiological activity. *Thebaine oxide*, $C_{19}H_{21}O_4N$, m. p. about 80°, forms a *hydrochloride*, m. p. 238—239° (decomp.), colourless needles. *Morphine oxide*, $C_{17}H_{19}O_4N$, m. p. 274—275°, prismatic crystals, forms a *nitrate*, $C_{17}H_{19}O_4N,HNO_3,1\frac{1}{2}H_2O$, m. p. 206—208°, which loses water when heated, yielding a *substance*, $C_{34}H_{38}O_{13}N_4$, from which the hydrated nitrate is regenerated by crystallisation from water. *Codeine oxide*, $C_{18}H_{21}O_4N$, m. p. 230—231°, rectangular plates, forms a *nitrate*, m. p. 187°, and a *hydrobromide*, m. p. 196°. *Dionine oxide*, $C_{19}H_{23}O_4N$, m. p. 220—221°, felted needles, forms a *hydriodide*, which crystallises in elongated plates. C. S.

Narcotine and Hydrastine. PAUL RABE and ANDREW MCMILLAN (*Annalen*, 1910, **377**, 223—258).—A résumé of the development of the constitutional formulæ of hydrastine, narcotine, and narceine is given.

A proof is given that in Rabe's nornarceine (Abstr., 1907, i, 790) the carbonyl group is attached directly to the benzene nucleus; hence the same arrangement obtains in narceine itself (compare Freund and Oppenheim, Abstr., 1909, i, 410). The crude oximino-compound, m. p. 167—169°, obtained by treating nornarceine with alcoholic sodium ethoxide and ethyl nitrite, is suspended in chloroform at 0°, and converted by phosphorus pentachloride into hemipinic acid and 2-*cyano*-3-*methoxy*-4 : 5-*methylenedioxy*-1-β-*methylaminoethylbenzene*,

$$CH_2O_2{:}C_6H(OMe)(CN){\cdot}CH_2{\cdot}CH_2{\cdot}NHMe,$$

m. p. 61°, which forms a *hydrochloride*, m. p. 206—207° (decomp.), *picrate*, m. p. 168°, *picrolonate*, decomp. 232°, and a methiodide, m. p. 226°, identical with Freund and Oppenheim's compound (*loc. cit.*). In a similar manner, methylhydrasteine forms an *oximino*-compound,

$$C_{22}H_{24}O_8N_2,$$

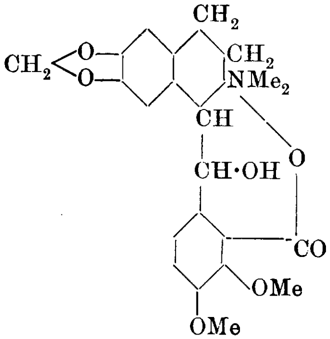
m. p. 189—190°, which is converted by phosphorus pentachloride into hemipinic acid and 2-*cyano*-4 : 5-*methylenedioxy*-1-β-*dimethylaminoethylbenzene*, $CH_2O_2{:}C_6H_2(CN){\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$, which forms a *picrate*, m. p. 188—189°, and *methiodide*, m. p. 260° (decomp.). The authors have little doubt that Beckett and Wright's oxynarcotine is identical with nornarceine; the substances have the same composition, $C_{22}H_{25}O_8N$, the same crystalline form, and behave alike as regards their solubility in organic solvents and in alkali hydroxides, and their insolubility in alkali carbonates.

In the authors' opinion, gnoscopine is not a natural product of the plant, but is produced by racemisation of narcotine during its isolation from opium. Although the different behaviour of narcotine and gnoscopine towards acids and alkalis might well lead to the belief that they are differently constituted, there can be no doubt that the latter is *r*-narcotine (Abstr., 1910, i, 335). Since hot dilute acetic acid converts gnoscopine into cotarnine, meconine, and nornarceine (Abstr., 1907, i, 790), the changes produced by heating *l*-narcotine with dilute acetic acid are represented by the diagram :

$$\begin{tikzcd}
& l\text{-Narcotine} \arrow[dl] \arrow[dr] \arrow[dd] & \\
\text{Nornarceine} & & \text{Cotarnine + Meconine.} \\
& \text{Gnoscopine} \arrow[ul] \arrow[ur] &
\end{tikzcd}$$

Similar changes are effected by heating *l*-narcotine with aqueous barium hydroxide or with dilute alcohol; hot 10% sulphuric acid, however, only slowly decomposes *l*-narcotine into cotarnine and meconine, the formation of gnoscopine and nornarceine not being observed.

The behaviour of the quaternary ammonium derivatives of hydrastine and narcotine has been examined. The aqueous solution obtained by treating hydrastine methiodide (or, better, methochloride) with moist silver oxide deposits a substance, m. p. 242°, which receives, in preference to Freund's formula, the annexed constitution of an oxybetaine on account of its neutral character and inability to form a methiodide. When hydrastine methiodide or methochloride is treated with aqueous alkalis instead of with silver oxide, it is converted into methylhydrastine. Both this substance and the oxybetaine are unstable, and change into the basic keto-acid, methylhydrasteine. In the decomposition of hydrastine methiodide or of the hydroxide, no trace of meconine or of methylhydrastinine has been observed; even when the methochloride is boiled with dilute acetic acid, meconine is not formed, only the oxybetaine, m. p. 242°.

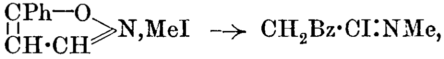


The quaternary ammonium compounds of narcotine behave in a similar manner. When the methochloride is treated with water and silver oxide, an alkaline solution is obtained, which, by keeping, deposits narceine and becomes neutral; it then contains an oxybetaine, which, however, cannot be isolated, all experiments with this object resulting in its transformation into narceine. When narcotine methochloride is treated with aqueous sodium hydroxide, it is converted into methylnarcotine (*methiodide*, $C_{23}H_{25}O_7N,MeI$, m. p. about 260°), which is changed by methyl iodide and methyl alcohol into the methiodide of narceine methyl ester by addition of methyl iodide, opening of the lactone ring, and addition of methyl alcohol. Methylnarcotine is converted with great ease, even by boiling water, into the basic keto-acid, narceine.

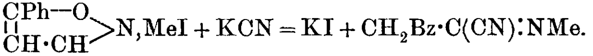
An important result of the preceding experiments is the following. Hydrastine and narcotine and their derivatives, containing tervalent nitrogen, experience a rupture of the carbon chain by hydrolytic decomposition, and yield meconine, cotarnine, etc. Derivatives containing quinquevalent nitrogen, however, retain the carbon chain unbroken, but yield basic keto-acids by opening of the *iso*quinoline ring. C. S.

Vegetable Betaines and Stachydrine. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, **69**, 326—328. Compare Abstr., 1909, i, 323).—A reply to Engeland. Purely polemical. J. J. S.

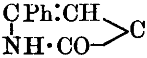
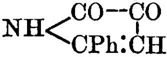
Conversion of Hydroxymethyleneacetophenone into Benzoylpyruvic Acid and Some New Derivatives. OTTO MUMM and GEORG MÜNCHMEYER (*Ber.*, 1910, **43**, 3335—3345).—The iminochlorides of aromatic acid-anilides undergo displacement of the halogen by the cyano-group by treatment with aqueous potassium cyanide, and react with the sodium salts of organic acids to form diacylanilides (Abstr., 1910, i, 311). The formation of diacylamines from the methiodides of 5-alkyl*iso*oxazoles and the sodium salts of organic acids is probably due to the intermediate change of the *iso*oxazole to an imino-iodide, thus:



$$\begin{matrix}CPh{-}O\\ \|\\ CH{\cdot}CH\end{matrix}\!\!>\!N{,}MeI \longrightarrow CH_2Bz{\cdot}CI{:}NMe,$$

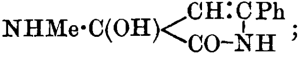
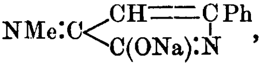
which is then converted into the diacylamine, $CH_2Bz{\cdot}CO{\cdot}NMeX$ (X = acyl). If this is so, the methiodides of 5-alkyl*iso*oxazoles should react with potassium cyanide in accordance with the equation  $\begin{matrix}CPh{-}O\\ \|\\ CH{\cdot}CH\end{matrix}\!\!>\!N{,}MeI + KCN = KI + CH_2Bz{\cdot}C(CN){:}NMe$. This is the case (in practice, the more easily obtainable methosulphate is employed), the reaction thus furnishing a method of converting hydroxymethyleneacetophenone through the *iso*oxazole into benzoylpyruvic acid.

In Claisen's method of preparing hydroxymethyleneacetophenone, the yield is increased by 50% by using $1\frac{1}{2}$ mols. of ethyl formate instead of 1 mol. 5-Phenyl*iso*oxazole, obtained from hydroxymethyleneacetophenone by Zöpfchen's process, is treated with an equal molecular quantity of methyl sulphate, and the resulting additive compound treated with aqueous potassium cyanide in the cold, whereby *α-methylimino-β-benzoylpropiontrile*, $CH_2Bz{\cdot}C({:}NMe){\cdot}CN$, m. p. 128°, yellow needles, is obtained. The nitrile is converted into ethyl benzoylpyruvate by equal parts of concentrated hydrochloric acid and alcohol, into benzoylpyruvic acid by boiling dilute hydrochloric acid, into *α-methylimino-β-benzoylpropionic acid*, $CH_2Bz{\cdot}C({:}NMe){\cdot}CO_2H$, m. p. 163°, yellow needles, by cold concentrated hydrochloric acid, and into *benzoylpyruvamide*, $CH_2Bz{\cdot}CO{\cdot}CO{\cdot}NH_2$, m. p. 138° (decomp.), by cold dilute hydrochloric acid; the amide develops a dark red coloration with ferric chloride, and by treatment with sodium hydroxide or sodium carbonate forms a *sodium* derivative which decomposes after a long time, yielding acetophenone. With a methyl-alcoholic solution of sodium methoxide or potassium hydroxide, the nitrile yields methyl methyliminobenzoylacetate. C. S.

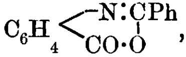
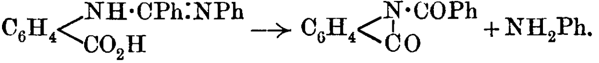
2:3-Diketo-5-phenylpyrroline, a Uninuclear Analogue of Isatin. OTTO MUMM and GEORG MÜNCHMEYER (*Ber.*, 1910, **43**, 3345—3359).—By passing hydrogen chloride into a well-cooled paste of α-methylimino-β-benzoylpropionitrile (preceding abstract) in methyl alcohol, a dark red substance, *2-keto-3-methylimino-5-phenylpyrroline hydrochloride*,  $\begin{matrix}\text{CPh:CH}\\ |\\ \text{NH}\cdot\text{CO}\end{matrix}\!>\text{C:NMe,HCl}$ (see below for constitution), is obtained, which crystallises with $2H_2O$ (m. p. about 114°) or with H_2O (m. p. 147—150°), according to the method of isolation; the *picrate*, $C_{17}H_{13}O_8N_5$, m. p. 178°, is anhydrous. By treatment with cold water it is converted quantitatively into methylamine hydrochloride and 2 : 3-*diketo-5-phenylpyrroline*,  $\text{NH}\!<\!\begin{matrix}\text{CO}-\text{CO}\\ \quad\ |\\ \text{CPh:CH}\end{matrix}$, m. p. 210°, which crystallises in brick-red leaflets. The proof that these two substances are cyclic compounds, not derivatives of benzoylpyruvic acid, rests on their colour, the absence of the ferric chloride reaction, and the analogy of the latter compound to isatin. The formation of the former is explained by the intermediate production of an imino-ether, $CH_2Bz\cdot C(:NMe)\cdot C(:NH)\cdot OMe$, since the substance is only produced in alcoholic solution. 2 : 3-Diketo-5-phenylpyrroline forms an *oxime*, yellow plates, decomp. 213° (from which a *dioxime*, m. p. 181—182°, can be obtained, the absence of colour of which renders it doubtful whether the compound has a cyclic structure), a *phenylhydrazone*, yellowish-red needles, m. p. 240° (decomp.), and a p-*nitrophenylhydrazone*, dark red needles, m. p. about 285° (decomp.); the production of the same three substances from 2-keto-3-methylimino-5-phenylpyrroline hydrochloride determines the presence of the oximino-group in position 3. Diketophenylpyrroline forms colourless solutions in aqueous sulphurous acid or sodium hydrogen sulphite; an impure additive compound can be isolated in the latter case. Diketophenylpyrroline shows its analogy to isatin, not only by responding to the indophenin reaction, but also by its behaviour with cold sodium hydroxide, whereby a bluish-violet solution is obtained, the colour of which disappears after a few minutes, and, after acidification, γ-*iminobenzoylpyruvic acid*, $NH:CPh\cdot CH_2\cdot CO\cdot CO_2H$, m. p. 161°, is formed, which differs from the isomeric benzoylpyruvamide (*loc. cit.*) in forming a stable *sodium* salt, and in developing an orange-red coloration with ferric chloride. γ-*Iminobenzoylpyruvamide*,

$$NH:CPh\cdot CH_2\cdot CO\cdot CO\cdot NH_2,$$

m. p. 158—159°, is obtained by treating diketophenylpyrroline with concentrated ammonia at the ordinary temperature; it has neither acidic nor basic properties, develops an orange-red coloration with ferric chloride, and, like the γ-imino-acid itself, is converted into benzoylpyruvic acid by evaporating its solution in 50% alcohol containing a little hydrochloric acid.

By treatment with cold aqueous sodium hydrogen carbonate, 2-keto-3-methylimino-5-phenylpyrroline hydrochloride is converted into a *hydroxide*, m. p. 110—120°, which, on account of its faint greenish-yellow colour and feebly basic character, receives the constitution of a ψ-base,  $\text{NHMe}\cdot\text{C(OH)}\!<\!\begin{matrix}\text{CH:CPh}\\ \quad\ |\\ \text{CO}-\text{NH}\end{matrix}$; it is characterised by forming equally intensely coloured salts with either sodium hydroxide or with hydrochloric acid. These salts are therefore constituted alike; the sodium salt receives the constitution  $NMe{:}C<\begin{array}{l}CH{=\!=}CPh\\ C(ONa){:}N\end{array}$, the hydrochloride that given above. C. S.

Action of Pyridine on Iridiodisulphates. Marcel Delépine (*Compt. rend.*, 1910, **151**, 878—880. Compare Abstr., 1909, ii, 408).—A solution of ammonium iridiodisulphate does not lose its green colour when mixed with pyridine, but a change takes place, especially on boiling the liquid. The solution then contains *pyridino-iridiodisulphuric acid*, $OHIr(C_5H_5N)(SO_4H)_2$, and gives crystalline precipitates with salts of sodium, potassium, rubidium, cæsium, thallium, silver, strontium, barium, lead, and chromium. Salts have been analysed having the following formulæ, in which R represents the group $[OH\cdot(C_5H_5N)Ir(SO_4)_2]''$:—$R(NH_4)_{1\cdot5},5H_2O$, $RNa_{4/3}H_{2/3},1\cdot5H_2O$, $RK_{4/3}H_{2/3},2H_2O$, $RBa_{2/3}H_{2/3},3H_2O$, $RAg_{4/3}H_{2/3},H_2O$. The salts are deep green and form olive-green solutions. The barium salt is very sparingly soluble, and owing to its crystalline form can be used to characterise the acid or its salts. W. O. W.

[Constitution of Benzoylanthranil.] Gustav Heller (*Ber.*, 1910, **43**, 3365).—Mumm and Hesse regard the constitution,  $C_6H_4<\begin{array}{l}-N{:}CPh\\ CO\cdot O\end{array}$, of benzoylanthranil as being definitely proved by the formation of benzoylanthranil and aniline by the interaction of anthranilic acid and benzanilideiminochloride (Abstr., 1910, i, 770). The author fails to see why the reaction cannot be explained by the following scheme, which leads to the constitution of benzoylanthranil proved by his own experiments: $CO_2H\cdot C_6H_4\cdot NH_2 + CClPh{:}NPh \longrightarrow$  $C_6H_4<\begin{array}{l}NH\cdot CPh{:}NPh\\ CO_2H\end{array} \longrightarrow C_6H_4<\begin{array}{l}N\cdot COPh\\ CO\end{array} + NH_2Ph.$ C. S.

Quinoline-5-carboxylic Acid. I. Zyg. von Jakubowski (*Ber.*, 1910, **43**, 3026—3032. Compare Abstr., 1909, i, 264).—To prepare quinoline-5-carboxylic acid, *o*-amino-*p*-toluonitrile is condensed with glycerol in presence of arsenic acid to 5-methylquinolyl-8-carboxylic acid. On distillation with calcium hydroxide, 5-methylquinoline is obtained, and this is oxidised to the 5-carboxylic acid, which is similar to the ψ-quinoline-*ana*-carboxylic acid described by Lellmann and Alt (compare Abstr., 1887, 502, 737, 973; 1888, 296, 499).

5-*Methylquinoline*-8-*carboxylic acid*, $C_9NH_6Me\cdot CO_2H$, crystallises in small needles of silvery lustre, m. p. 173—174°. The *ammonium*, *calcium*, and *copper* salts are described: the *hydrochloride* forms concentrically grouped needles; the *nitrate*, long needles of silky lustre; the *picrate*, slender, yellow needles, m. p. 205—207°; the *platinichloride*, pale yellow, concentrically intergrown needles, and the *dichromate*, orange rods.

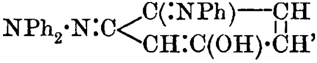
By the distillation of 5-methylquinoline-8-carboxylic acid with calcium oxide, a by-product is formed, which crystallises in colourless needles, m. p. 200—202°. This is probably a new dimethyldiquinonyl; it is not identical with 5 : 5′-dimethyl-8 : 8′-diquinonyl. The main product is 5-*methylquinoline*, a colourless liquid, b. p. 253—255°/735 mm. The *picrate* forms light yellow plates, which soften at 200°, m. p. 210—213°. The *mercurichloride* forms small, colourless needles; the *platinichloride*, bright orange needles; the *methiodide*, yellow, silky needles, m. p. 105°.

On oxidation with a mixture of chromic and sulphuric acids, quinoline-5-carboxylic acid is obtained. E. F. A.

Aromatic Hydrazines. VIII. Oxidation of Diphenylhydrazine.

HEINRICH WIELAND and ERNST WECKER (*Ber.*, 1910, **43**, 3260—3271).—The reddish-violet dye prepared by the action of acid oxidising agents, more particularly of hypochlorous acid, on diphenylhydrazine (compare E. Fischer, Abstr., 1878, 313) is the hydrochloride of quinoneanildiphenylhydrazone,

$$NPh{:}C_6H_4{:}N{\cdot}NPh_2,HCl.$$

This constitution follows from: (*a*) analysis; (*b*) the products of reduction, namely, diphenylamine and *p*-aminodiphenylamine; (*c*) its oxidation value as determined by Willstätter and Piccard's method (*Ber.*, 1908, **41**, 1474). Attempts to synthesise the dye by the condensation of quinoneanil with diphenylhydrazine hydrochloride showed that the chief products were tetraphenyltetrazen and *p*-hydroxydiphenyl, together with a brilliant bluish-violet dye, which on reduction gave diphenylamine and an unknown *p*-hydroxyaminodiphenylamine. In the formation of this bluish-violet dye, an additive product is probably formed, which is oxidised by the excess of quinoneanil to an orthoquinonoid compound,  $NPh_2{\cdot}N{:}C{<}\begin{matrix}C({:}NPh)\text{—}CH \\ \quad\quad\quad\quad\quad\;\, \| \\ CH{:}C(OH){\cdot}CH\end{matrix}$, the hydrochloride of which is the dye.

It is shown that in the formation of the red dye, diphenylhydroxylamine is probably an intermediate product, which condenses with the diphenylhydrazine, yielding the triazo-derivative, $NH(NPh_2)_2$. This then undergoes a type of molecular rearrangement resembling that of diazoamino-compounds, thus yielding $NHPh{\cdot}C_6H_4{\cdot}NH{\cdot}NPh_2$, which is oxidised to the dye base, $NPh{:}C_6H_4{:}N{\cdot}NPh_2$. Further confirmation of this view is afforded by the fact that tetraphenylhydrazine, which is known to be readily hydrolysed to diphenylamine and diphenylhydroxylamine (Wieland, Abstr., 1907, i, 1076; 1908, i, 1014), reacts with a glacial acetic acid solution of diphenylhydrazine at 55—60°, yielding the red dye. Di-*p*-tolylhydrazine does not yield a dye when oxidised, but when warmed with glacial acetic acid and tetraphenylhydrazine gives a red dye. The formation of a dye cannot therefore be merely due to the oxidising action of the tetraphenylhydrazine on the diphenyl or di-*p*-tolylhydrazine, but must be due to the hydrolysis to diphenylhydroxylamine, which then condenses with the secondary hydrazine.

p-Substituted tetraphenylhydrazines do not yield dyes with di-*p*-tolylhydrazine.

Quinoneanildiphenylhydrazone hydrochloride, $C_{24}H_{19}N_3,HCl$, is deposited in glistening, bronzy-green crystals, m. p. 147°, when light petroleum is added to its alcoholic ethereal solution. The yield is poor, and the method of purification is tedious. Both the solid and its solutions are stable. It dyes cotton mordanted with tannin a brilliant violet-red. Its solution in concentrated sulphuric acid has a greenish-blue colour, but turns reddish-violet when diluted. When boiled for some time with mineral acids, it yields small amounts of diphenylamine, and when shaken with 20% sulphuric acid and lead peroxide yields quinone. The *base* has only been obtained in the form of an amorphous, reddish-brown powder. The majority of its salts and double salts are sparingly soluble in water, and do not crystallise well. Solutions do not give any characteristic absorption bands.

p-Methyl- and *p*-methoxy-diphenylhydrazine give similar dyes, but the di-*p*-tolyl and dianisyl compounds do not.

p-*Hydroxy*-o-*quinoneanildiphenylhydrazone hydrochloride*,

$$C_{24}H_{19}ON_3,HCl,$$

obtained by condensing quinoneanil with diphenylhydrazine hydrochloride, is more soluble in water than the red dye, and the solutions have more of a bluish tint. The *base* has a fiery brownish-red colour, and is amphoteric; it dissolves in both acids and alkalis, giving brilliant violet solutions. When reduced with stannous chloride, it yields p-*hydroxy*-o-*aminodiphenylamine*, $NHPh\cdot C_6H_3(OH)\cdot NH_2$, which crystallises from alcohol, has m. p. 170—171°, and dissolves in both acids and alkalis.

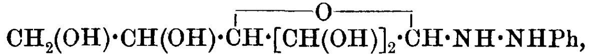
These solutions are readily oxidised to blue amphoteric dyes.

J. J. S.

Phenylhydrazones of Dextrose. Robert Behrend and Willy Reinsberg (*Annalen*, 1910, **377**, 189—220).—The phenylhydrazone of dextrose, like dextrose itself, exists in two forms, which exhibit birotation, and, when dissolved, give ultimately identical solutions by the formation of the same equilibrium mixture. The theory advanced by Behrend and Lohr (Abstr., 1908, i, 765) that one of these dextrose-phenylhydrazones is a true hydrazone,

$$CH_2(OH)\cdot[CH(OH)]_4\cdot CH{:}N\cdot NHPh,$$

and the other a hydrazide,



$$CH_2(OH)\cdot CH(OH)\cdot\overbrace{CH\cdot[CH(OH)]_2\cdot CH}^{O}\cdot NH\cdot NHPh,$$

has been proved in the following ways.

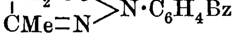
By treatment with acetic anhydride in pyridine, dextrose-β-phenylhydrazone yields an amorphous acetate, whilst dextrose-α-phenylhydrazone gives a crystalline acetate, m. p. 152—153°, together with an amorphous acetate (Hofmann, Abstr., 1909, i, 519). (The author shows that these are penta-acetates, and that the last-mentioned, amorphous acetate is a mixture of the other two.) True hydrazones yield *N*-acetyl derivatives only with difficulty, and are not attacked by acetic anhydride in cold pyridine. Since the crystalline dextrose-α-phenylhydrazone penta-acetate, by treatment with aqueous-alcoholic potassium hydroxide and benzaldehyde, yields acetylphenylbenzylidenehydrazine, whilst the amorphous dextrose-β-phenylhydrazone penta-acetate under similar conditions gives phenylbenzylidenehydrazine, it follows that dextrose-α-phenylhydrazone penta-acetate contains an acetyl group attached to a nitrogen atom and is therefore produced from a hydrazide, and that dextrose-β-phenylhydrazone penta-acetate does not contain an acetylated nitrogen atom and is therefore produced from a true hydrazone. Dextrose-α-phenylhydrazone and dextrose β-phenylhydrazone have the hydrazide and the hydrazone constitution respectively. This conclusion is supported by the fact that dextrose-α-phenylhydrazone penta-acetate yields α-acetylphenylhydrazine by hydrolysis with 5% hydrochloric acid, whilst the β-isomeride resinifies.

Another proof of the theory is furnished by condensing dextrose with α-acetylphenylhydrazine in warm alcohol containing a little acetic acid. The condensation product is a syrup from which a crystalline substance cannot be isolated, but from which, after treatment with acetic anhydride in cold pyridine, dextrose-α-phenylhydrazone penta-acetate has been obtained; this acetate, therefore, certainly has an acetyl group attached to a nitrogen atom. If the original syrupy condensation product contains a true hydrazone, there must still be five hydroxyl groups in its dextrose nucleus capable of acetylation. The fact that the product obtained by acetylating the syrup in pyridine contains, in addition to dextrose-α-phenylhydrazone penta-acetate, a *hexa-acetate*, shows that a true hydrazone must be present in the syrupy mixture of the dextroseacetylphenylhydrazines. This hexa-acetate, $C_{24}H_{30}O_{11}N_2$, which is separated from the accompanying penta-acetate by solution in ether, is an amorphous powder having $[\alpha]_D + 143{\cdot}1°$ in pyridine and 137·9° in benzene without mutarotation.

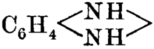
Dextrose-α-phenylhydrazone penta-acetate, obtained by Hofmann's method (*loc. cit.*), has m. p. 152—153°, and $[\alpha]_D + 11{\cdot}97°$ in pyridine. The acetate separated by ether from the crude acetylated product partly melts at 130°, resolidifies, and then has m. p. 150—152°; if after being heated to 150° the acetate is recrystallised from alcohol, it has m. p. 152° without previous fusion at 130°. When the crude acetylated product is treated with an amount of ether insufficient for complete solution, the residual sparingly soluble substance has m. p. 110°, then resolidifies, and changes into the acetate, m. p. 152—153°. The latter can be converted into the substance having m. p. 110° by gently boiling its solution in ether. In pyridine the two substances have the same specific rotation, $[\alpha]_D + 17{\cdot}5°$, without mutarotation. The relation between the two substances is not yet settled; it appears to be due to polymorphism.

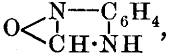
α-Acetylphenylhydrazine can be obtained in 76·84% yield by hydrolysing β-formyl-α-acetylphenylhydrazine with concentrated hydrochloric acid; when the hydrolysis is effected by aqueous potassium hydroxide, β-formylphenylhydrazine is produced. C. S.

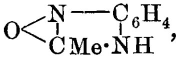
1-Benzoylphenyl-3-methyl-5-pyrazolone. HENRY A. TORREY and H. R. RAFSKY (*J. Amer. Chem. Soc.*, 1910, **32**, 11, 1489—1492).—The pyrazolone was prepared by Michael's method from the hydrochloride of *p*-hydrazinobenzophenone and acetoacetic acid. Modifications were introduced in the preparation of *p*-aminobenzophenone (Döbner, *Annalen*, 1881, **210**, 267) and of *p*-hydrazinobenzophenone (Ruhemann and Blackman, Trans., 1889, i, 613).

1-*Benzoylphenyl*-3-*methyl*-5-*pyrazolone*,  $\begin{matrix}CH_2{\cdot}CO \\ | \\ CMe{=}N\end{matrix}\!\!>\!N{\cdot}C_6H_4Bz$, forms brownish-yellow crystals, m. p. 170—171°. It gives a white, flocculent precipitate with silver nitrate, and does not reduce Fehling's solution. Its *hydrochloride* was obtained as a pale brown powder, m. p. 196° (decomp.), turning dark at 180°. A small amount of 1-*benzoylphenyl*-2 : 3-*dimethyl*-5-*pyrazolone* was obtained, m. p. 125°. N. C.

Oxidoanhydro-compounds. I. STEFAN VON NIEMENTOWSKI (*Ber.*, 1910, **43**, 3012—3026).—The two first members of the series of oxyanhydro-compounds, namely, benziminazole oxide and 2-methylbenziminazole oxide, were hitherto unknown; they have now been obtained by reduction of *o*-nitroformanilide and *o*-nitroacetanilide with ammonium sulphide in alcoholic solution.

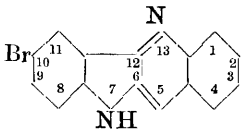
Benziminazole oxide, when treated with benzoyl chloride and sodium hydroxide, undergoes intramolecular rearrangement to *o*-phenylenecarbamide,  $C_6H_4<\substack{NH\\NH}>CO$, m. p. 310°. The same rearrangement is observed on heating with hydrochloric acid in sealed tubes at 200°, on fusion with potassium hydroxide, and on heating with zinc dust at 230°. Apparently, the carbamide is the stable isomeride; it has not been found possible to convert it into oxidobenziminazole.

o-Nitroformanilide is prepared by heating *o*-nitroaniline with anhydrous formic acid. The reduction product, *benziminazole oxide*,  $O<\begin{matrix}N—C_6H_4\\ | \qquad | \\ CH\cdot NH\end{matrix}$, forms colourless needles, m. p. 210°, to a colourless liquid, decomp. 212°. It gives a reddish-yellow coloration with ferric chloride. The *hydrochloride* forms slender needles, m. p. 200—214°; the *aurichloride* forms golden-yellow, prismatic needles in tree-like aggregates, m. p. 172°; the *platinichloride* separates in stout, bright orange rods, decomp. 220°.

2-*Methylbenziminazole oxide*,  $O<\begin{matrix}N—C_6H_4\\ | \qquad | \\ CMe\cdot NH\end{matrix}$, forms snow-white needles, m. p. 251°. The *hydrochloride* forms colourless needles; the *aurichloride* separates in golden-yellow, broad rods, m. p. 175° (decomp.); the *platinichloride*, in lustrous, yellow columns, m. p. 245°; the *sulphate* forms colourless needles or transparent plates, m. p. 174°. Those reagents which convert the lower homologue into phenylenecarbamide are without action. E. F. A.

Some Derivatives of Quindoline. FRITZ FICHTER and FRANZ ROHNER (*Ber.*, 1910, **43**, 3489—3499. Compare Fichter and Boehringer, Abstr., 1907, i, 92).—Quindoline is obtained in 75—80% yield by boiling the sodium salt of flavindine (quindolinecarboxylic acid) with 10% potassium hydroxide and zinc dust until the solution is colourless, filtering rapidly, and passing air through the filtrate, whereby quindoline is precipitated.

The reaction between quindoline and bromine in cold glacial acetic acid yields an unstable, dark yellow *bromo-perbromide*, $C_{15}H_{10}N_2Br_3$, which is converted by crystallisation from alcohol into 10-*bromoquindolinium bromide*, $C_{15}H_{10}N_2Br_2$, yellow needles; this substance, which contains one ionisable bromine atom, is converted by alcoholic potassium hydroxide into 10-*bromoquindoline*, (annexed constitution), m. p. 304°, pale yellow needles. The position of the halogen atom is determined only by the fact that bromine first attacks the indole imino-group and then wanders to the para-position. The attack of bromine at position 7 is rendered probable by the fact that substitution does not occur when 7-acetylquindoline and bromine react in glacial acetic acid; a dark red, unstable perbromide is obtained, which is converted by crystallisation into 7-*acetylquindolinium bromide*, $C_{17}H_{12}ON_2,HBr$, m. p. 272°, yellow needles, from which quindoline is produced by the action of alkalis.



A concentrated solution of quindoline in glacial acetic acid reacts with solid sodium nitrite, in the cold forming pale yellow needles of *quindolinium nitrite*, $C_{15}H_{10}N_2,HNO_2$, when heated yielding 7-*nitrosoquindoline*, m. p. 275°, dark red needles, which forms a blue solution in strong, alcoholic potassium hydroxide, and yields quindoline by hydrolysis with alcoholic hydrogen chloride. By reduction with tin and hydrochloric acid, quindoline is converted into 5 : 13-*dihydroquindoline*, m. p. 172° (rapidly heated), which is oxidised very easily, even by atmospheric oxygen, to quindoline. On treatment with acetic anhydride in the cold, dihydroquindoline yields 13-*acetyl*-5 : 13-*dihydroquindoline*, m. p. 162°, a monoacidic base, which oxidises less readily than dihydroquindoline. When boiled with acetic anhydride, dihydroquindoline is converted into 7 : 13-*diacetyl*-5 : 13-*dihydroquindoline*, m. p. 235°. Acetyldihydroquindoline and an excess of bromine in glacial acetic acid yield a yellow *perbromide*, from which 5 : 10-*dibromo*-13-*acetyl*-5 : 13-*dihydroquindoline*, m. p. 242°, is readily obtained. This substance suffers hydrolysis and oxidation when boiled with 40% sulphuric acid, yielding 5 : 10-*dibromoquindoline*, m. p. 221°, yellow needles.

13-*Methyl*-5 : 13-*dihydroquindolinium iodide*, $C_{16}H_{14}N_2HI$, is obtained by the methylation of dihydroquindoline or by the reduction of 13-methylquindolinium iodide by tin and hydrochloric acid, during which the *stannochloride*, $C_{16}H_{14}N_2,2HCl,SnCl_2$, is obtained. 13-*Methyl*-5 : 13-*dihydroquindolinium perchlorate*, $C_{16}H_{14}N_2,HClO_4$, obtained from an alcoholic solution of the iodide and perchloric acid, crystallises in golden leaflets. The base corresponding with these salts is so unstable that it changes in air into 13-methylquindolinium carbonate (*loc. cit.*).

C. S.

Pechmann's Isomeric Hydrazidines. Max Busch and Richard Ruppenthal (*Ber.*, 1910, **43**, 3001—3011).—Pechmann (Abstr., 1896, i, 32) has described two forms, m. p. 119° and 174° respectively, of diphenylbenzenylhydrazidine, to which he assigned the formulæ NHPh·CPh:N·NHPh and NPh:CPh·NH·NHPh, the isomerism being regarded as due to desmotropism.

It is now shown that the more fusible isomeride contains an asymmetric disubstituted hydrazine, and has the formula

NPh:CPh·NPh·NH₂.

It unites with aldehydes, forming hydrazones, and loses a nitrogen atom under the influence of nitrous acid, forming diphenylbenzenylamidine, $\mathrm{NPh{:}CPh{\cdot}NHPh}$.

The less fusible isomeride has the formula, $\mathrm{NPh{:}CPh{\cdot}NH{\cdot}NHPh}$, assigned to it by Pechmann, and is converted on oxidation into the azo-compound, $\mathrm{NPh{:}CPh{\cdot}N{:}NPh}$.

By the interaction of benzanilide imide chloride and phenylhydrazine both isomerides are formed, the chloride attacking both the α- and β-nitrogen atoms of the hydrazine. The β-hydrazidine,

$$\mathrm{NPh{:}CPh{\cdot}NH{\cdot}NHPh},$$

predominates, and it was not found possible by altering the conditions to increase the proportion of the α-hydrazidine. The two isomerides are not convertible into one another. α-Diphenylbenzenylhydrazidine forms a stable *acetate*, soluble in very dilute acetic acid.

α-*Diphenylbenzylidenebenzenylhydrazidine*,

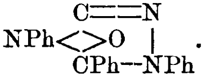
$$\mathrm{NPh{:}CPh{\cdot}NPh{\cdot}N{:}CHPh},$$

crystallises in colourless bunches of interlaced needles, which become yellow at 155°, m. p. 159—160°.

On leaving the α-diphenylbenzenylhydrazidine overnight with benzaldehyde in benzene solution, it decomposes, forming benzanilide.

Diphenyl-m-*nitrobenzylidenebenzenylhydrazidine* forms yellow needles, m. p. 173°.

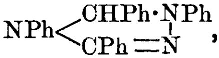
The α-hydrazidine interacts with carbonyl chloride, forming a compound, $C_{20}H_{15}ON_3$, crystallising in microscopic, transparent prisms, m. p. 301—302°, which is considered to be end*oxytriphenyldihydrotriazole*,



$\mathrm{NPh}{<}{>}\mathrm{O}\begin{matrix}\mathrm{C{\equiv}N}\\ |\\ \mathrm{CPh{-}NPh}\end{matrix}$.

Benzeneazophenyliminophenylmethane, $\mathrm{NPh{:}CPh{\cdot}N{:}NPh}$, crystallises in reddish-brown needles, m. p. 101—102°.

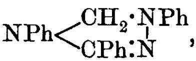
β-Diphenylbenzenylhydrazine, when boiled in alcoholic solution with benzaldehyde, forms *tetraphenyldihydrotriazole*,



$\mathrm{NPh}{<}\begin{matrix}\mathrm{CHPh{\cdot}NPh}\\ \mathrm{CPh{=}N}\end{matrix}$,

which separates in greenish-yellow needles, m. p. 119—120°.

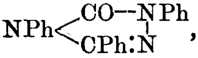
Similarly, the β-hydrazidine unites with formaldehyde, yielding *triphenyldihydrotriazole*,



$\mathrm{NPh}{<}\begin{matrix}\mathrm{CH_2{\cdot}NPh}\\ \mathrm{CPh{:}N}\end{matrix}$,

which crystallises in stunted, transparent, greenish-yellow needles, softening at 120°, m. p. 124°, to a clear oil; it is faintly basic.

With carbonyl chloride, *triphenyltriazolone*,

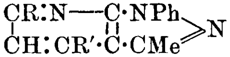
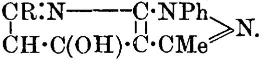


$\mathrm{NPh}{<}\begin{matrix}\mathrm{CO{-}NPh}\\ \mathrm{CPh{:}N}\end{matrix}$,

is formed; it crystallises in colourless needles of silky lustre, m. p. 223—224°, and has neither basic nor acid properties. E. F. A.

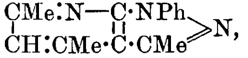
Action of Phenylhydrazine on Ethyl Benzoylacetate. OTTO KÜHLING (*Ber.*, 1910, **43**, 3399).—The product previously described (Abstr., 1910, i, 780) as ketoanilinodiphenyltetrahydrotriazine can be prepared by mixing acetic acid solutions of ethyl benzoylacetate and phenylhydrazine (excess). Whether the compound has the constitution originally given or whether it is the phenylhydrazide of ethyl benzoylacetate phenylhydrazone has not been determined.

J. J. S.

Synthesis of Derivatives of 1 : 2 : 7-Pyrazopyridine [1 : 2 : 7-Benztriazole] : a New Series of Homo (C·C) Condensed, Heterodicyclic Compounds. CARL BÜLOW and KARL HAAS (*Ber.*, 1910, **43**, 3401—3412).—The fact that Walther's "5-imino-1-phenyl-3-methylpyrazolone" (Abstr., 1897, i, 297) contains a labile hydrogen atom attached to the carbon atom in the α-position to the carbon to which the amino-group is attached, and condenses with solutions of benzenediazonium salts (Michaelis, Abstr., 1905, i, 478), led the authors to the conclusion that the compound would condense with β-diketones or with esters of β-ketonic acids, yielding compounds of the types :  $\begin{array}{l} \mathrm{CR{:}N{-}C{\cdot}NPh} \\ \mathrm{CH{:}CR'{\cdot}C{\cdot}CMe} \end{array}\!\!>\!\mathrm{N}$ and  $\begin{array}{l} \mathrm{CR{:}N{-}{-}C{\cdot}NPh} \\ \mathrm{CH{\cdot}C(OH){\cdot}C{\cdot}CMe} \end{array}\!\!>\!\mathrm{N}$.

These are somewhat analogous to the hetero-condensed, heterocyclic condensation products already described (Abstr., 1909, i, 615 ; 1910, i, 80, 81, 203, 595), but contain a C·C-group common to the two nuclei in place of a C·N-group, and in addition the smaller ring contains a CH-group in place of a nitrogen atom. Monomethylene substituted β-ketones and β-ketonic esters react in a similar manner. The hydroxy-derivatives obtained when β-ketonic esters are used are not so strongly acetic as the heterohydroxylic acids previously described (Abstr., 1910, i, 595). As a rule, they cannot be titrated accurately by standard alkalis, using phenolphthalein as indicator, and solutions of their salts are decomposed by carbon dioxide. They form a link between the heterohydroxylic acids and the phenols proper.

1-*Phenyl*-3 : 4 : 6-*trimethyl*-1 : 2 : 7-*benztriazole*,



$$\begin{array}{l} \mathrm{CMe{:}N{-}C{\cdot}NPh} \\ \mathrm{CH{:}CMe{\cdot}C{\cdot}CMe} \end{array}\!\!>\!\mathrm{N},$$

obtained by boiling a glacial acetic acid solution of acetylacetone and 5-amino-1-phenyl-3-methylpyrazole for five hours, crystallises in large, colourless, compact, prismatic needles, m. p. 128°, and is feebly basic. The *aurichloride*, $C_{15}H_{15}N_3,HAuCl_4,H_2O$, forms long, glistening, yellow needles ; the *platinichloride*, $2C_{15}H_{15}N_3,H_2PtCl_6,2H_2O$, crystallises in brown, compact, rhombic cubes, which change colour at 200° ; the additive *compound* with silver nitrate forms long, colourless needles.

1-*Phenyl*-3 : 4 : 5 : 6-*tetramethyl*-1 : 2 : 7-*benztriazole*, $C_{16}H_{17}N_3$, prepared in a similar manner from methylacetylacetone, crystallises from alcohol in colourless needles, m. p. 138—139°, and 1 : 4-*diphenyl*-3 : 6-*dimethyl*-1 : 2 : 7-*benztriazole*, $C_{20}H_{17}N_3$, obtained from benzoylacetone, crystallises from 96% alcohol in slender needles, m. p. 136—137°, after sintering at 133°. It is sometimes accompanied by a by-product melting at 156—160°.

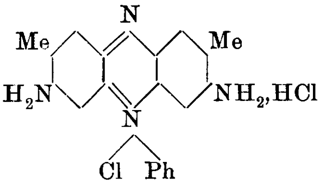
4-*Hydroxy*-1-*phenyl*-3 : 6-*dimethyl*-1 : 2 : 7-*benztriazole*, $C_{14}H_{13}ON_3$, obtained by boiling a glacial acetic acid solution of ethyl acetoacetate with the aminophenylmethylpyrazole, crystallises from hot water in glistening needles. It can be titrated by means of standard potassium hydroxide solution, and the solution of the potassium salt gives precipitates with salts of most of the heavy metals. The *aurichloride*, $C_{14}H_{13}ON_3,HAuCl_4$, forms compact, yellow crystals, and the *platinichloride*, compact, yellowish-brown needles. The base has the properties of a feeble febrifuge. 4-*Hydroxy*-1-*phenyl*-3 : 5 : 6-*trimethyl*-1 : 2 : 7-*benztriazole*, $C_{15}H_{15}ON_3$, obtained from ethyl methylacetoacetate, crystallises from 90% alcohol in compact, rhombic plates, m. p. 224—226°; the *aurichloride* forms stout, yellow rods. 4-*Hydroxy*-1-*phenyl*-3 : 6-*dimethyl*-4-*ethyl*-1 : 2 : 7-*benztriazole*, $C_{16}H_{17}ON_3$, sinters at 181°, and has m. p. 183—184°.

The dissociation constant of 7-hydroxy-5-methyl-1:2:4:9-benztetrazole (Abstr., 1910, i, 595) is practically the same as that of valeric acid. J. J. S.

Synthesis of Safranines. III. N. N. Orloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 939—949. Compare Abstr., 1910, i, 782—783).—The safranines can be readily obtained by the condensation of *p*-benzoquinonedichlorodi-imide or its homologues and analogues with 4-phenyltolylene-2 : 4-diamine or its homologues and analogues, the best yields being obtained with one molecule of the former to two of the latter. The safranines of various constitutions (containing benzene, toluene, or naphthalene nuclei) all have similar physical properties, their red colour becoming bluish as the molecular weight increases.

Aminoazotoluene, on reduction and subsequent treatment with bleaching powder, yields p-*toluquinonedichlorodi-imide*, $C_7H_6N_2Cl_2$, m. p. 74°, decomposes at 155°, and forms long, yellow, needle-shaped crystals.

3 : 7-*Diamino*-5-*phenyl*-2 : 8-*dimethylphenazonium chloride*, to which the annexed formula, namely, that of ordinary tolusafranine, is assigned, obtained by the condensation of *p*-toluquinonedichlorodi-imide with 4-phenyltolylene-2 : 4-diamine, forms bright yellowish-green crystals. Alkali hydroxides precipitate the free *base* from ethereal solutions of the hydrochloride. The *dichromate*, $(C_{20}H_{19}N_4)_2Cr_2O_7$, was analysed. By removing one amino-group from the hydrochloride, 3-*amino*-5-*phenyl*-2 : 8-*dimethylphenazonium chloride* is formed. The aqueous solution is precipitated by picric acid, tannin, and sodium acetate. Ammonia and the alkali carbonates precipitate the *base*, of which the *dichromate*, $(C_{20}H_{18}N_3)_2Cr_2O_7$, was analysed.



The *acetyl* derivative of aminotolusafranine when treated with ammonia yields tolusafranine. When the second amino-group is removed from the monoamine, the chromogen, 5-*phenyl*-2 : 8-*dimethylphenazonium*, is obtained in the form of its ferric chloride compound,

$$C_{20}H_{17}N_2FeCl_4.$$

It forms brown crystals, m. p. 190°, which, when treated with ammonia and then with hydrochloric acid, yields dimethyl*apo*safranine hydrochloride, which is identical in all respects with the monoaminophenazonium from which the chromogen was obtained. Z. K.

Quinonoid Compounds. XXIV. Aniline-black. IV. Richard Willstätter and Carl Cramer (*Ber.*, 1910, **43**, 2976—2988. Compare Abstr., 1909, i, 535, 975).—Aniline-black is regarded as containing eight para-substituted benzene nuclei. The two stages of oxidation product contains three and four quinonoid nuclei respectively. A quantitative determination of these has been made by reduction with phenylhydrazine carbamate in an atmosphere of carbon dioxide and measurement of the nitrogen liberated. Reduction takes place in sharply differentiated stages, according to the temperature. In the case of dichromate black, one molecule of hydrogen is introduced at 30—35°, the colour changing to light blue; at 75—80° the colour becomes grey, and a further reduction takes place; lastly, between 120° and 150°, the colourless leuco-base is formed. The hydrolysed blacks are more stable; thus hydrolysed dichromate black is stable until 80°, loses a second quinonoid nucleus at 130—150°, and can only be completely reduced on the addition of a trace of Green's black, which acts as a catalyst. Chlorate-black contains four quinonoid nuclei; the first is attacked at 35—40°, the second at 80—110°, and the remaining two at 120—150°, the colour changing from dark violet through dull blue and brown to a light brownish-grey. Hydrolysed chlorate-black retains two nuclei at 150°, but parts with these in presence of Green's black.

Green's black, obtained on oxidising aniline salts with atmospheric oxygen in presence of copper sulphate and phenylenediamine, is very readily reduced, all four nuclei being attacked below 110°. When hydrolysed Green's black loses the quinonoid nuclei in turn at 80—100°, 115—130°, 130—140°, 140—150°. The behaviour of Green's black is attributed to the catalytic action of traces of impurity. The apparatus used is described and experimental data given of its testing with seven quinonoid compounds. E. F. A.

History of Diazohydrazides. Emil Fischer (*Ber.*, 1910, **43**, 3500—3501).—Dimroth and de Montmollin (Abstr., 1910, i, 898), in their account of the diazohydrazides, omit to mention that the first member of this class to be discovered was diazobenzene-ethylhydrazide, obtained by the author from diazobenzene chloride and ethylhydrazine in aqueous solution (*Annalen*, 1879, **199**, 306). C. S.

Biochemical Classification of the Proteins. Jose Rodriguez Carracido (*Anal. Fis. Quim.*, 1910, **8**, 261—263; *Revista Chim.*, 1910, **6**, 314—315).—A scheme for the classification of the proteins founded more on biochemical than on chemical considerations. W. A. D.

General Protein Chemistry. III. The Denaturation of Serum Albumin. Léonor Michaelis and Peter Rona (*Biochem. Zeitsch.*, 1910, **29**, 494—500).—If serum albumin is changed by heating, and then caused to coagulate by bringing the mixture to the isoelectric point, two stages in the denaturation can be detected. If the heating is not too long continued, the protein is obtained in the first stage of change, in which by the action of hydrochloric acid, it is rendered soluble and converted apparently in the original protein.

If the heating be continued for a longer time, the second stage is reached in which the coagulum is soluble in acid only with difficulty, and in which the reaction is irreversible. S. B. S.

The Fractional Precipitation of the Milk Proteins. ALBERT J. J. VANDERVELDE (*Biochem. Zeitsch.*, 1910, **29**, 461—464).—As protein-α is described, that protein which is precipitated on the addition of acid, and as protein-β, that which separates from the filtrate from protein-α on coagulation. The author has estimated the amounts of these proteins in the whole milk, and in the fractions obtained by the additions of varying quantities of acetone, ethyl and methyl alcohols to the milk. From the results obtained, which are tabulated, the author draws the conclusion that it is not possible to conclude that milk caseinogen and milk albumin have distinct individuality. S. B. S.

Combination of Lactic Acid and Casein. W. VAN DAM (*Chem. Weekblad*, 1910, **7**, 1013—1019).—By means of Bredig's ethyl diazoacetate method, the author has determined the reduction in the concentration of the hydrogen ions in solutions of lactic acid produced by addition of increasing amounts of casein. In solutions containing a large excess of hydrogen ions, the casein combines with a constant amount of lactic acid, 4·25%. Assuming that 1 molecule of lactic acid combines with 1 molecule of casein, the molecular weight of the protein is 2118. On the assumption that 1 molecule of potassium hydroxide neutralises 1 molecule of casein, Robertson (Abstr., 1910, ii, 679) gives 556 as the molecular weight. It follows that one basic group is present for every four replaceable hydrogen atoms in the casein molecule. A. J. W.

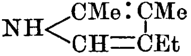
Electrochemistry of Proteins. III. Dissociation of Salts of Ovimucoid in Solutions of Varying Alkalinity and Acidity. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1910, **14**, 709—718. Compare Abstr., 1910, ii, 679).—Mörner's ovimucoid, that part of the white of egg proteins which is not precipitated by boiling dilute acetic acid, but is precipitated by concentrated alcohol (Abstr., 1894, i, 264), was obtained as a dry white powder. It has been investigated by the method previously used with caseinogen.

Unlike caseinogen and globulin, ovimucoid dissolves readily, and is more basic than acidic. One gram requires $7·0 \times 10^{-5}$ gram-equivalents of hydrogen chloride to produce a solution which is neutral to litmus, and solutions containing less acid are alkaline. In very dilute potassium hydroxide solutions, ovimucoid tends to combine with the whole of the alkali, but the proportion of potassium hydroxide combined decreases with concentration, until in strongly alkaline solution the ovimucoid attains a maximum combining capacity of 50×10^{-5} gram-equivalents of alkali per gram.

The combining capacity for acid also increases, and tends to attain a constant value in presence of large excess of acid. The constant was never attained, but is probably greater than 100×10^{-5} gram-equivalents of acid per gram. The addition of ovimucoid to alkali or acid of concentration less than $N/10,000$ increases the conductivity by reason of the considerable conductivity of the free protein. The conductivity of stronger solutions is considerably diminished by the protein. The depression in conductivity, λ, brought about by addition of 1% of ovimucoid to solutions of potassium hydroxide at 30° is expressed by $\lambda = 0{\cdot}2085b - 12{\cdot}5b^2 - 0{\cdot}000356$, and in the case of hydrogen chloride by $\lambda = 0{\cdot}4199a - 8{\cdot}527a^2 - 0{\cdot}000414$, where b and a are the concentrations of alkali and acid respectively. A similar expression was deduced in the case of caseinogen, in which, however, the factor c, the concentration of the protein, was introduced.

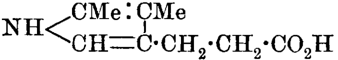
The author endeavours to trace a theoretical connexion between the constants 0·2085 and 0·4199 in the above equations, and the values 0·218 and 0·384 of the conductivities of potassium hydroxide and hydrogen chloride respectively at infinite dilution. R. J. C.

The Constitution of the Coloured Constituent of the Pigment of Blood. OSKAR PILOTY [with EUGEN QUITMANN and PAUL EPPINGER] (*Annalen*, 1910, **377**, 314—369. Compare Abstr., 1909, i, 539).—The acid previously termed hæmopyrrolecarboxylic acid is not derived from hæmopyrrole, but from an isomeride, and hence the name *phonopyrrolecarboxylic acid* is suggested; by the elimination of carbon dioxide from this acid, a dimethylethylpyrrole (*phonopyrrole*) is obtained, which is not identical with hæmopyrrole. Both compounds must be represented as dimethylethylpyrroles with a methyl group in position 2, and methyl and ethyl groups in positions 3 and 4 or 4 and 3. As phonopyrrolecarboxylic acid shows no tendency to yield an indole derivative, it is improbable that the methyl and $\cdot CH_2\cdot CH_2\cdot CO_2H$-groups are in the relative positions 2 and 3. This conclusion is confirmed by the fact that hæmatopyrrolidinic acid (Abstr., 1909, i, 540), which is formed by the union of molecular quantities of phonopyrrolecarboxylic acid and hæmopyrrole, on decomposition loses propionic acid from the phonopyrrolecarboxylic acid portion of the molecule, and yields 2 : 3-dimethylpyrrole. Phonopyrrole and its carboxylic acid must therefore have the two methyl groups in positions 2 and 3, and must be represented by the formulæ:



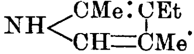
$$NH<\begin{matrix}CMe{:}CMe\\ CH{=}CEt\end{matrix}$$

and



$$NH<\begin{matrix}CMe{:}CMe\\ CH{=}C\cdot CH_2\cdot CH_2\cdot CO_2H\end{matrix}$$

and hæmopyrrole as 2 : 4-dimethyl-3-ethylpyrrole,

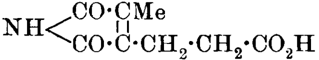


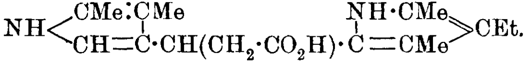
$$NH<\begin{matrix}CMe{:}CEt\\ CH{=}CMe\end{matrix}.$$

An ethereal solution of phonopyrrolecarboxylic acid reacts with a $0{\cdot}2N$-solution of benzenediazonium chloride, yielding a dark red *azo-dye*, $C_{15}H_{18}O_2N_3Cl$, m. p. 145—146° (decomp.). Phonopyrrolecarboxylic acid is scarcely affected when fused with potassium hydroxide at 300° for half an hour, or when distilled under very low pressures, but at atmospheric pressure it loses carbon dioxide at 250—330°, and gives a 28% yield of *phonopyrrole*, which is best purified by steam distillation. After distillation over barium oxide it has b. p. 96—98°/19 mm., and is readily distinguished from the isomeric hæmopyrrole, as it yields an oily *picrate*, which does not solidify when placed in a freezing mixture, and reacts with nitrous acid, yielding a small amount of a syrupy maleinimide derivative (compare Abstr., 1910, i, 133).

Full details for the reduction of hæmatoporphyrin with tin and hydrochloric acid are given, and also for the preparation of hæmatopyrrolidinic acid free from tin. The acid is soluble in water to an appreciable extent, but yields precipitates with many salts and alkalis; these precipitates appear to be adsorption products. Hæmopyrrole forms an unstable compound with the acid. When the zinc derivative of the acid is fused with potassium hydroxide (compare Abstr., 1910, i, 857), water and the loosely-combined hæmopyrrole are evolved at 170—200°; at 270° a dark oil is formed, and the temperature is kept at 270° by dropping water gradually into the retort, but towards the end the temperature is raised to 320°.

The products isolated from the distillates are hæmopyrrole and 2 : 3-dimethylpyrrole, and from the residue, potassium acetate. The acetic acid must come from the portion of the hæmatopyrrolidinic acid which yields the 2 : 3-dimethylpyrrole, as the zinc compound of Kuster's hæmatic acid yields the acid $\mathrm{NH}\Big<\begin{matrix}\mathrm{CO\cdot CMe}\\ \|\\ \mathrm{CO\cdot C\cdot CH_2\cdot CH_2\cdot CO_2H}\end{matrix}$ on oxidation, and this cannot be derived from hæmopyrrole. The formula suggested for hæmatopyrrolidinic acid is therefore



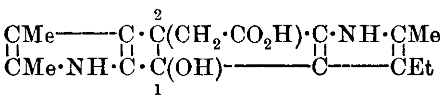


$$\mathrm{NH}\Big<\begin{matrix}\mathrm{CMe{:}CMe} & & \mathrm{NH\cdot CMe}\\ | & & |\\ \mathrm{CH{=}C\cdot CH(CH_2\cdot CO_2H)\cdot} & \mathrm{C} & \mathrm{{=}CMe}\end{matrix}\Big>\mathrm{CEt}.$$

The constitution of the 2 : 3-dimethylpyrrole has been proved by the following method. The base yields methylmaleinimide, m. p. 105°, when oxidised by Willstätter and Asahina's method (Abstr., 1910, i, 499), and cannot therefore be an ethylpyrrole, 2 : 5-dimethyl- or 3 : 4-dimethyl-pyrrole, and, as it does not yield a crystalline azo-dye, cannot be 2 : 4-dimethylpyrrole (Marchlewski and Robel, Abstr., 1910, i, 206).

It is suggested that hæmin and hæmatin contain a group somewhat similar to that of hæmatopyrrolidinic acid (annexed formula).

On reduction, the 6-carbon ring can become ruptured at carbon atom No. 1 or 2. In the first case hæmatopyrrolidinic acid would be formed, and in the latter an isomeric acid. It is probable that the small yield of hæmatopyrrolidinic acid obtained when hæmatoporphyrin is fused with potassium hydroxide is due to the formation of this isomeric acid.



The authors agree with Küster that the hæmins obtained from different sources have the same composition, and the product described by von Zeyneck (Abstr., 1900, i, 711) as having the composition $C_{34}H_{34}O_4N_5FeCl$ is shown to be impure hæmin, and, after purification by Schalféeff's method, has the composition of hæmin. The formula suggested is $C_{34}H_{33}O_4N_4FeCl$. The conversion of hæmin into hæmatin by means of alkali is usually regarded as due to the replacement of chlorine by hydroxyl. In further support of this view, it is now shown that hæmatin can be quantitatively transformed back into hæmin by adding a solution of the latter in chloroform containing quinine to a hot glacial acetic acid solution of sodium chloride and stirring; after repeating the above operations, steel-blue, glistening crystals of pure hæmin are obtained (compare also Siewert, Abstr., 1908, i, 486), and as hæmin can be obtained from hæmatin prepared from hæmin or from oxyhæmoglobin, it follows that the products obtained from the two sources are identical.

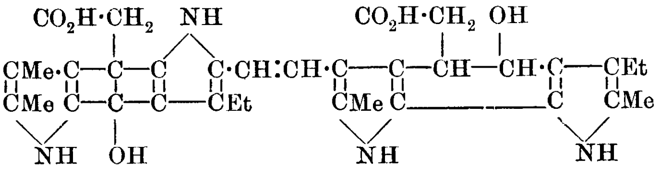
According to Nencki and Zaleski (Abstr., 1900, i, 709), hæmin contains two phenolic hydroxyl groups, as it can give dialkyl ethers which are insoluble in alkalis; these hydroxyl groups are also present in hæmatin, although, so far, hæmatin ethers have not been prepared. Hæmatin contains a third hydroxyl group, which is readily replaced by chlorine. This hydroxyl group is removed when the iron is withdrawn from the hæmatin molecule, and is, therefore, presumably attached to the iron atom. Hæmatin and hæmin do not appear to contain free carboxyl groups, but when the iron is removed from hæmin, the product, hæmatoporphyrin, is both distinctly acidic and basic, as it dissolves readily in both dilute acids and alkalis and forms well-defined salts. The development of basic properties is attributed to the removal of the iron which was previously attached to nitrogen, and the production of basic imino-groups. The iron in the hæmin molecule is thus in the tervalent condition, and when removed by the aid of hydrogen bromide, it is removed as ferric salt only, provided the temperature is not allowed to rise.

Küster's statement that a ferrous salt is formed is due to the fact that he used comparatively high temperatures, and the ferrous salt obtained was a secondary product formed by the reduction of the ferric salt. The authors used a modification of Nencki and Sieber's method for transforming hæmin into hæmatoporphyrin. Iron hæmatoporphyrin is regarded as the ferric salt of a carboxylic acid, and analyses agree fairly well with the formula $(C_{34}H_{35}O_5N_4)_3Fe$.

In the conversion of hæmin into hæmatoporphyrin, it is suggested that the carboxylic groups which were latent in hæmin become active. The presence of ethylene linkings in hæmatoporphyrin is proved by the readiness with which it is reduced by sodium amalgam, one molecule of the compound taking up 6 or 8 atoms of hydrogen; the solution of the leuco-base thus obtained reduces Fehling's solution and ammoniacal silver nitrate, and on the addition of acids yields a white precipitate of the leuco-base, which immediately turns brown on exposure to the air. The leuco-base cannot be obtained pure, but on oxidising the reduced solution by means of atmospheric oxygen and then acidifying, a product is formed which is apparently identical with deoxyhæmatoporphyrin. The production of this compound from hæmatoporphyrin probably takes place according to the equations: $C_{34}H_{38}O_6N_4 + 8H = C_{34}H_{44}O_5N_4 + H_2O$ and $C_{34}H_{44}O_5N_4 + 3O = C_{34}H_{38}O_5N_4 + 3H_2O$.

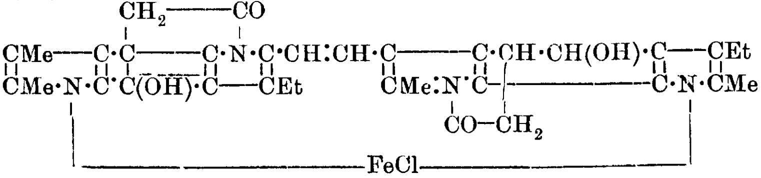
Schalféeff's method for the preparation of hæmin has been modified in several details, and a yield of 7·33 grams has been obtained from 1 litre of blood.

The following structural formulæ are suggested for hæmatoporphyrin (I), mesoporphyrin (II), and hæmin (III).



(I.)

(II.) Similar formula with 2H atoms for the two OH groups.



(III.)

Attention is drawn to the fact that these formulæ cannot be regarded as established beyond question, as they are based to a large extent on the reactions of hæmatopyrrolidinic acid, a compound which it is impossible to obtain in a pure state. J. J. S.

Hæmin Dimethyl Ether. William Küster (*Ber.*, 1910, 43, 2960—2962).—Hæmin dimethyl ether (Nencki and Zaleski, Abstr., 1900, i, 710) is easily prepared in quantity by adding hæmin dissolved in chloroform containing a little pyridine to a boiling mixture of methyl alcohol and strong hydrochloric acid. It is a black powder consisting of aggregates of microscopic needles, and dissolves in pyridine, probably with the formation of a dimethyl ether of hæmin-pyridinium chloride. On the addition of water, a colloidal solution is formed, from which the dye is precipitated by a few drops of nitric acid, chlorine remaining in the solution. E. F. A.

The Decomposition of Blood-pigment. F. Bardachzi. **Compounds of Pyridine in Blood-pigment.** Ernst Kalmus. **Pyridine Compound of Hæmochromogen.** Richard von Zeynek (*Zeitsch. physiol. Chem.*, 1910, 70, 205—216, 217—223, 224—229).—On heating oxyhæmoglobin with 10% alkali, the fluid first shows the spectrum of alkali-hæmatin, and on prolonged heating, of hæmochromogen. Proofs are adduced that this is really hæmochromogen, and not an alkali compound of that substance. In carbon monoxide hæmochromogen, the gas is less firmly combined than it is in carboxyhæmoglobin; it can be removed in a vacuum at room temperature by boiling, or by a stream of pure hydrogen. An apparatus is also described for obtaining the gases evolved on the heat coagulation of blood-pigment.

The two last papers agree in regarding the crystals obtained by the action of pyridine on blood-pigment as a pyridine compound of hæmochromogen, and not as Kobert and Dilling state, as hæmochromogen itself. Dilling's statement that hæmochromogen does not give the guaiacum reaction is also said to be incorrect. W. D. H.

Valency of the Metal in Blood-pigments, and the Estimation of the Gas Combining Power. A Critical Study. WILHELM MANCHOT (*Zeitsch. physiol. Chem.*, 1910, **70**, 230—249).—Kuster states that hæmoglobin and hæmochromogen are ferrous compounds, and bases his conclusion partly on Hüfner's investigations on the uptake of nitric oxide by solutions of metallic salts. The bulk of the present paper is occupied in showing that Hüfner's method is not trustworthy, that hæmoglobin is a ferric compound, and that in hæmocyanin the copper is probably present in the cupric state.

W. D. H.

Yeast Nucleic Acid. III. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, **43**, 3150—3163. Compare Abstr., 1909, i, 620, 686).—On hydrolysing yeast nucleic acid with mineral acids, the following components have been obtained: adenine, guanine, cytosine, uracil, *d*-ribose, and phosphoric acid, but it was not certain whether cytosine and uracil are primary decomposition products or formed by the decomposition of the purine bases.

It is now shown that cytosine is not derived from the purine bases, and that it is not fixed in the nucleic acid molecule as a pentoside. On partial hydrolysis of nucleic acid with ammonia, *cytidine*,

$$C_9H_{13}O_5N_3,$$

is obtained; it forms crystalline derivatives; thus the *picrate* has m. p. 185—187°, the *sulphate*, m. p. 233°, the *hydrochloride*, m. p. 218°. The free base has $[\alpha]_D^{20}$ $+19{\cdot}14°$, the *sulphate* having $[\alpha]_D^{30}$ $+29{\cdot}7°$.

Cytidine is hydrolysed to cytosine only by concentrated acids or by heating under pressure; neither pentose nor lævulic acid is formed, yet cytidine gives a faint orcinol reaction.

A crystalline acetyl derivative could not be obtained. The *tribenzoyl* derivative crystallises in long, prismatic needles, m. p. 205°; it could not be acetylated.

Nitrous acid effects the quantitative elimination of the amino-group from cytidine, and *uridine* is obtained, crystallising in long, prismatic needles, m. p. 165°, $[\alpha]_D^{30}$ $+5{\cdot}15°$.

The relation of amino-acid nitrogen to the total nitrogen in nucleic acid is 3 : 15; this figure confirms the presence of uracil in the molecule, since uracil does not contain an amino-group, whilst the other three bases each contain one, so that were uracil absent the relation should be 3 : 13.

By the action of nitrous acid, adenosine is converted into inosine identical with that obtained from carnine. Similarly, guanosine gave xanthosine.

E. F. A.

Triticonucleic Acid. PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*Ber.*, 1910, **43**, 3164—3167).—It is probable that yeast nucleic acid and the triticonucleic acid discovered in wheat embryos by Osborne and Harris (compare also Osborne and Heyl, Abstr., 1908, i, 376) are identical. Triticonucleic acid on partial hydrolysis gives the nucleosides guanosine and adenosine, and also cytidine, that is, the same complexes as were obtained by Levene and Jacobs (Abstr., 1909, i, 620, 686) from yeast nucleic acid.

E. F. A.

The Pentose from the Pancreas. PHŒBUS A. LEVENE and WALTER A. JACOBS (*Ber.*, 1910, **43**, 3147—3150).—Polemical. The authors (Abstr., 1909, i, 447, 620) have shown that the pentose in inosic acid, guanylic acid, and yeast nucleic acid is *d*-ribose, the optical antipode of the *l*-ribose synthesised by Alberda van Eckenstein and Blanksma. Rewald (Abstr., 1909, i, 858) identifies the pentose as xylose. Nucleoprotein prepared from the pancreas by Salkowski's method is now shown to give ribose and no trace of xylose (compare Neuberg, Abstr., 1909, i, 686). E. F. A.

The Pentose from the Pancreas. CARL NEUBERG (*Ber.*, 1910, **43**, 3501—3502).—In reply to Levene and Jacobs' criticism (preceding abstract) of his work (Abstr., 1909, i, 686), the author points out that their process does not determine whether different nucleic acids and pentoses occur in the pancreas, and also calls attention to the many contradictory statements of Levene concerning the pancreas nucleic acid. C. S.

The Pentose from the Pancreas. BRUNO REWALD (*Ber.*, 1910, **43**, 3502—3503).—Levene's identification of the pentose from the nucleic acid of the pancreas, guanylic acid, and similar nucleic acids as *d*-ribose depends on the rotation of a very dilute solution of its osazone (Levene and Jacobs, above). In the author's experiments (Abstr., 1909, i, 858) more than a gram of material was used. C. S.

Prolylglycineanhydride Formed by the Tryptic Digestion of Gelatin. PHŒBUS A. LEVENE (*Ber.*, 1910, **43**, 3168—3170).—Prolylglycineanhydride, $[\alpha]_D$ $-55°$, was obtained by the tryptic digestion of gelatin extending over eight months (Levene and Beatty, Abstr., 1906, i, 718), whereas the same peptide obtained synthetically by Fischer and Reif (Abstr., 1908, i, 1007) had $[\alpha]_D$ $-217°$. A product obtained after twenty-four days' tryptic digestion had $[\alpha]_D$ $-169°$, and the conclusion is drawn that the peptide becomes racemised during the prolonged action of the enzyme. E. F. A.

The Sulphur and Cystine in the Keratin of Birds. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1910, **69**, 310—312).—Keratin from goose feathers contains 3·15% sulphur and 6·3% cystine; from hen's claws, 2·28% sulphur and 2·14% cystine; from the epidermic scales of hen's toes, 2·2% sulphur and 1·88% cystine. Hofmann and Pregl (Abstr., 1907, i, 884) state that the horny material from the bird's stomach, which they term koilin, contains no cystine; in the present research it was found to contain rather more than 0·5%. W. D. H.

Iodoproteins. HENRY L. WHEELER and LAFAYETTE B. MENDEL (*Biochem. Zeitsch.*, 1910, **29**, 417—419). CARL NEUBERG (*ibid.* 420—421).—Polemical (compare Abstr., 1910, i, 704, ii, 143). S. B. S.

The Dissociation Constants of Tryptophan. ARISTIDES KANITZ (*Biochem. Zeitsch.*, 1910, **29**, 126—129).—These have been calculated from the data given for specific rotation of the amphoteric substance, and for the hydrochloride and sodium salts in acid and alkaline solutions. From these, $K_b = 1{\cdot}1 \times 10^{-13}$, and $K_s = 1{\cdot}3 \times 10^{-11}$.

S. B. S.

The Inactivation of Ferments and the Production of Anti-Ferments in vitro in the Presence of Artificial Membranes. A. E. Porter (*Quart. J. exp. Physiol.*, 1910, **3**, 375—390. Compare Abstr., 1910, i, 601).—Certain enzymes can be inactivated by contact with artificial membranes, especially those made of collodion. At the same time the solution acquires inhibitive properties. Possibly in the body, the living membranes act in the same way. Only traces of the enzyme can be recovered from the membrane, the inactivating power of which increases with use. The inhibitive power is only in part due to substances previously in the solution, and the question arises whether the anti-enzyme which appears combines with the enzyme or acts on the substrate as Cramer and Bearn suggest for their zymoids; the latter explanation is adopted as the main one. W. D. H.

Influence that the Reaction [of the Medium] Exerts on Certain Properties of Malt Macerations. Auguste Fernbach and M. Schœn (*Compt. rend.*, 1910, **151**, 894—897. Compare Abstr., 1906, i, 327; Maquenne and Roux, *ibid.*, i, 327).—The resistance of malt diastases to the action of heat is closely connected with the reaction of the medium in which they are present. If this is rendered neutral to methyl-orange, the amylolytic power of the malt is increased, but the resistance to heat is diminished. On the other hand, the stability is greater in a medium neutral to phenolphthalein, but hydrolytic activity is diminished. Auto-activation is at a maximum when the malt macerations are neutral to phenolphthalein.

W. O. W.

Influence of Different Temperatures on Ferments and on the Regeneration of Fermentative Properties. M. J. Gramenitzki (*Zeitsch. physiol. Chem.*, 1910, **69**, 286—300).—Taka diastase in aqueous solutions loses its fermentative properties at 80°, but recovers at temperatures below 45°, slowly at the ordinary temperature, and more quickly at 40°. Similar results were obtained after heating to 115°, the ferment not being destroyed, but only losing temporarily its fermentative power.

The oxydase maltin retains its oxidising power to a slight extent after being heated for ten minutes at 100°. Longer heating (fifteen to twenty minutes) results in complete loss of power for a time; the oxydase recovers its properties, however, after a certain time. When subjected to higher temperatures, the oxydase loses its properties beyond recovery.

At 80° the oxydase not only loses (temporarily) its oxidising properties, but acquires the power of deoxidising.

Solutions of maltin, after being heated for ten minutes at 100°, retain the power of dissolving starch, but no longer produce sugar.

N. H. J. M.

Influence of Temperature on the Activity of Cellase. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1910, **151**, 1076—1079. Compare Abstr., 1910, i, 212, 290).—The optimum temperature for the hydrolysis of cellose by cellase prepared from sweet almonds is about 46°. The fatal temperature, at which the enzyme is rapidly destroyed, is about 75—76°, but the preparation loses its activity more slowly at lower temperatures. W. O. W

Hydrolysis of Amygdalin by Emulsin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1910, **248**, 534—535).—The hydrolysis of amygdalin by emulsin occurs in three stages, each of which is caused by a particular enzyme. The amygdalin, under the influence of amygdalase, first yields α-dextrose and mandelonitrileglucoside (Auld, Trans., 1908, **93**, 1276); the latter is then decomposed by a β-glucosidase into β-dextrose and *d*-benzaldehydecyanohydrin, which is split by δ-*d*-oxynitrilase into benzaldehyde and hydrogen cyanide.

The new facts on which these statements are based are the following. A 5% solution of emulsin, after being heated for ten hours at 60—65°, hydrolyses *d*-benzaldehydecyanohydrin, but not amygdalin; conversely, the filtrate obtained after saturating a solution of emulsin with magnesium sulphate, hydrolyses amygdalin, but not *d*-benzaldehydecyanohydrin.

The primary formation of *d*-benzaldehydecyanohydrin in the hydrolysis of amygdalin is proved by the fact that the filtrate mentioned above, which cannot contain oxynitrilase or the synthetic enzyme, produces a considerable amount of *d*-benzaldehydecyanohydrin by its action on amygdalin. The view that *d*-benzaldehydecyanohydrin is also produced in a secondary reaction (Abstr., 1910, i, 403) is supported by the fact that *d*-benzaldehydecyanohydrin is produced by the action of emulsin on prulaurasin, a glucoside of the corresponding *i*-nitrile. C. S.

Synthetical Enzyme Action. II. JACOBUS H. VAN'T HOFF (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, **48**, 963—970. Compare Abstr., 1909, ii, 988).—The behaviour of glucosides of tertiary alcohols towards emulsin in presence of their solid products of hydrolysis, and moistened with solutions saturated with these products, has been studied by means of volume changes. Hydrolysis, on account of the taking up of water, is accompanied by contraction; synthesis of the glucoside causes expansion. A small dilatometer was employed. In the case of the hydrolysis of the natural glucosides salicin, arbutin, and æsculin by emulsin, contraction was observed of a magnitude corresponding with the complete hydrolysis of the glucoside. With tertiary alcohol glucosides, emulsin has no synthetic action. This is analogous to the behaviour of the tertiary alcohols on etherification.

Primary alcohols are readily etherified. No glucoside of a solid primary alcohol was available for investigation, but a mixture of dextrose hydrate, glycerol, and emulsin, set aside at 31°, showed a diminution in the amount of dextrose from 0·305 to 0·211 dextrose per gram of the mixture after twenty-five days, and the quantity increased on diluting with an emulsin solution or heating with dilute hydrochloric acid for an hour. With anhydrous dextrose instead of the hydrate, no condensation was observed. The best results were obtained with a mixture of 2 parts of dextrose hydrate, 4 parts of glycerol, 1 part of water. When used in molecular proportions, about 70% of glycerol and dextrose are converted into glucoside. The rate of synthetic action was proportional to the quantity of enzyme. Of two different enzyme preparations, the most active synthetically was also that most active in promoting hydrolysis. E. F. A.

Isomerisation of Some Phosphorus Compounds. II. ALEXANDER E. ARBUSOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 549—561. Compare Abstr., 1910, i, 802).—The thiophosphinites of the type $PR_2{\cdot}SR'$ under the catalytic influence of alkyl iodides undergo similar processes of isomerisation into the sulphides PSR_2R' to the corresponding oxygen compounds, but in the former the reaction is complicated by the formation of by-products.

Ethyl diphenylthiophosphinite, $PPh_2{\cdot}SEt$, obtained by the action of sodium mercaptide on diphenylphosphoryl chloride, has b. p. 196·5—197°/13 mm., D_0^0 1·1330, and gives double salts with the copper halides, of which the *copper iodide* compound is described. When treated with ethyl iodide in a sealed tube at 100°, it yields *diphenylethylphosphine sulphide*, $PSEtPh_2$, which crystallises in colourless, rhombic tablets, m. p. 65·5—66°; diphenyldiethylphosphonium iodide, PPh_2Et_2I, m. p. 207—208°, the platinichloride of which has m. p. 202—203° (Michaelis, *Annalen*, 1881, **207**, 215, gives m. p. 218°); *ethyl diphenyloxythiophosphinate*, $PPh_2O{\cdot}SEt$, m. p. 72—73°; diphenylphosphinic acid, crystallising in bright prisms, m. p. 194—195°, and probably *ethyl diphenylthiophosphinate*, $PPh_2S{\cdot}SEt$. iso*Butyl diphenylthiophosphinite*, $PPh_2{\cdot}S{\cdot}C_4H_9$, was prepared by the action of sodium *iso*butylmercaptide on diphenylphosphoryl chloride. It is a colourless liquid, b. p. 200·5—201°/8 mm., D_0^0 1·0892, and forms a crystalline *additive* compound with copper iodide. Under the catalytic influence of *iso*butyl iodide at 115°, it is converted almost quantitatively into *diphenyl*iso*butylphosphine sulphide*, $PSPh_2{\cdot}C_4H_9$, forming rhombic crystals, m. p. 80—81°, but if the mixture be subjected to prolonged gentle heating at 80°, *diphenyldi*iso*butylphosphonium iodide*,

$$PPh_2(C_4H_9)_2I,$$

m. p. 183—184°, is obtained. Sodium *iso*amylmercaptide when treated with diphenylphosphoryl chloride forms iso*amyl diphenylthiophosphinite*, $PPh_2{\cdot}S{\cdot}C_5H_{11}$, b. p. 219—220°/12 mm., D_0^{17} 1·0645, which, with *iso*amyl iodide at 120°, yields chiefly *diphenyl*iso*amylphosphine sulphide*, $PSPh_2{\cdot}C_5H_{11}$, large, bright, rhomboid crystals, m. p. 63·5°.

Sodium propylmercaptide with diphenylphosphoryl chloride yields only a small quantity of *propyl diphenylthiophosphinite*, $PPh_2{\cdot}SPr$, b. p. 229—230°/28 mm., which with propyl iodide is rapidly isomerised at 99° into *diphenylpropylphosphine sulphide*, $PSPh_2Pr$, crystallising in thin tablets, m. p. 97—98°. Z. K.

Organic Chemistry.

Formation of Hydrocarbons from Carbon Monoxide. LÉO VIGNON (*Bull. Soc. chim.*, 1911, [IV], **9**, 18—20).—Various observers have shown that when carbon monoxide is passed over heated sodium or potassium hydroxide, soda-lime, or calcium hydroxide, a formate is produced, and that on further heating hydrogen is evolved. In the present investigation it is shown that with lime and carbon monoxide between 350° and 400° considerable quantities of methane, ethylene, and hydrogen are formed, and that from 400° to 600° the quantity of hydrogen increases at the cost of the hydrocarbons. The reactions taking place are probably represented by the following equations :

$$2CO + Ca(OH)_2 = (H{\cdot}CO{\cdot}O)_2Ca = C_2O_2(O)_2Ca + H_2\ ;$$
$$2(H{\cdot}CO{\cdot}O)_2Ca + CaO = 3CaCO_3 + CH_4\ ;$$
$$4(H{\cdot}CO{\cdot}O)_2Ca + 2CaO = 6CaCO_3 + C_2H_4 + 2H_2,$$

and experiments in heating calcium formate or oxalate alone and mixed with lime have confirmed this explanation of the origin of the hydrocarbons. Carbon monoxide may be converted into hydrogen and hydrocarbons to the extent of 99·5% by passage over hot lime several times, and it is suggested that in this way illuminating gas might be freed from this toxic constituent. T. A. H.

A Secondary Heptane in Roumanian Petroleum. N. COSTACHESCU (*Ann. sci. Univ. Jassy*, 1910, **6**, 294—301).—The fraction of petroleum from Colibasi having b. p. 87·5—93·5° contains β-methylhexane with 1 : 3-dimethyl*cyclo*pentane and a small quantity of isomeric heptanes. When the fraction is heated with nitric acid (D 1·4) at 60° in sealed tubes, the β-methylhexane is converted mainly into a *nitro*-derivative, $C_7H_{15}O_2N$, b. p. 86—86·5°/21·5 mm, D^0_0 0·9961, n_D 1·43855 ; the other hydrocarbons, however, undergo oxidation to oxalic acid and carbon dioxide. W. O. W.

Dimorphism of Iodoform. BRUNO BARDACH (*Chem. Zeit.*, 1911, **35**, 11—12).—The thin, yellow needles obtained previously (Abstr., 1909, i, 645) by the action of iodine and potassium iodide on acetone solutions of anhydrides and anhydride-forming compounds are now found to consist of iodoform. The crystals have m. p. 121°, and, on distilling in steam or crystallising from alcohol, are transformed into the ordinary hexagonal form. F. B.

Estimation of Active Hydrogen in Organic Compounds by means of Magnesium Methyl Iodide. TH. ZEREWITINOFF *Ber.*, 1910, **43**, 3590—3595. Compare Abstr., 1907, ii, 509 ; 1908, i, 593).—The method previously described for the determination of replaceable hydrogen atoms is applicable also to the alkaloids. Those alkaloids which contain active hydrogen react with magnesium methyl iodide at the ordinary temperature, and yield methane quantitatively.

When heated, no additional methane is formed, showing the alkaloids to contain no amino-group. The rapidity of the method and the fact that only small quantities of substance are required are important features. A number of the commoner alkaloids were tested.

Pseudo-acids from nitromethane, nitroethane, etc., react as if they contained one hydroxyl, although the amount of methane obtained is somewhat less than the calculated, but it increases on warming. The experiments were made both in amyl ether and in pyridine solution; xylene, mesitylene, and anisole may equally well be used.

E. F. A.

[Pinacolin Derivatives] Corrections. MAURICE DELACRE (*Bull. Soc. chim.*, 1911, [iv], 9, 41—43).—Polemical in reply to Richard (this vol., i, 6), claiming priority as regards the synthesis of the alcohol $CMe_3{\cdot}CHMe{\cdot}OH$ (Abstr., 1906, i, 477) and other matters.

T. A. H.

Preparation of Octan-γη-dione-α-ol and its Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 227177).—The condensation of unsaturated ketones, by which 1:5-diketones are obtained, is a reaction about which very little is known; the diketo-alcohols now described are of technical importance in pharmacological preparations.

Octan-γη-dione-α-ol, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 142—143°/22 mm., a colourless, odourless oil, miscible with water in all proportions, is prepared as follows: methyleneacetone (Abstr., 1910, i, 652) is mixed with water (15 parts), either alone or in the presence of a small quantity of potassium carbonate, and allowed to remain until the odour of methyleneacetone has disappeared; the solution is acidified with tartaric acid, saturated with ammonium sulphate, and the product extracted with ether, dried, and fractionated, when a considerable amount of butan-γ-on-α-ol, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b. p. 84—85°/23 mm., is also obtained.

βζ-Dimethyloctan-γη-dione-α-ol is prepared by boiling methyl methylene-ethyl ketone with aqueous formic acid during forty to fifty hours, unchanged methyl methylene-ethyl ketone is removed by steam, and the solution rendered alkaline, whereby any *formyldimethyloctandionol* is hydrolysed. The product, a viscous, odourless, colourless oil, b. p. 145·5°/16 mm., 148°/18 mm., and 264—268° under atmospheric pressure, can also be obtained by either boiling dimethyloctendione (this vol., i, 114) with water, or by shaking it with cold dilute formic or with sulphuric acid; the *semicarbazone* has m. p. 209—210°.

F. M. G. M.

Preparation of Narcotics [Glyceryl Ethers]. C. F. BOEHRINGER and SÖHNE (D.R.-P. 226454).—Glyceryl triethyl ether is not a narcotic, but when mixed alkyl residues are introduced, this property is developed; these compounds are colourless, mobile fluids.

Glyceryl αγ-dimethyl β-ethyl ether, $C_7H_{16}O_3$, b. p. 65°/20 mm., D^{20} 0·917, was prepared by the ethylation of the αγ-dimethyl ether in benzene solution with the necessary quantity of sodium ethoxide and ethyl bromide. *Glyceryl αγ-dimethyl β-propyl ether*, $C_8H_{18}O_3$, was similarly obtained with propyl chloride; it has b. p. 76—77°/17 mm., and D^{20} 0·908. *Glyceryl β-methyl αγ-diethyl ether*, $C_8H_{18}O_3$, has b. p. 75°/17 mm., D^{20} 0·902.

Glyceryl αβ-dimethyl γ-ethyl ether, $C_7H_{16}O_3$, b. p. 49°/7—8 mm., D^{20} 0·919, was prepared from glycerol ethyl ether, methyl iodide, and sodium methoxide in benzene solution.

Glyceryl αγ-diethyl β-propyl ether, $C_{10}H_{22}O_3$, has b. p. 77—78°/9—10 mm., and D^{20} 0·882.

Glyceryl αβ-dimethyl γ-propyl ether, $C_8H_{18}O_3$, b. p. 66—67°/9—10 mm., D^{20} 0·910, was obtained from *glycerol propyl ether*, b. p. 122°/12 mm., D^{22} 1·024, which was prepared by the action of sodium propoxide on glycerol monochlorohydrin.

Glyceryl α-methyl βγ-diethyl ether, $C_8H_{18}O_3$, b. p. 57°/7—8 mm., D^{20} 0·901, was prepared from *glycerol methyl ether*, b. p. 108—109°/8—10 mm., D^{20} 1·115. *Glyceryl β-benzyl αγ-dimethyl ether*, $C_{12}H_{18}O_3$, has b. p. 149—150°/17—18 mm., and D^{20} 1·023. *Glycerol α-ethyl γ-propyl ether*, b. p. 86·5°/10 mm., D^{20} 0·935, was prepared from the sodium derivative of glycerol ethyl ether and propyl bromide, and yielded on methylation *glyceryl β-methyl α-ethyl γ-propyl ether*, $C_9H_{20}O_3$, b. p. 71·5—72°/7—8 mm., D^{20} 0·893. F. M. G. M.

A Very Basic Chromic Acetate. Ernst Gussmann (*Zeitsch. anorg. Chem.*, 1911, **69**, 217—220).—In the preparation of hexa-acetatotripyridinetrichromi-diacetate (Abstr., 1910, i, 503) it was found that the mother liquors contained a violet basic acetate, $Cr_2(OAc)_3(OH)_3,9H_2O$. This is best obtained as follows: To a solution of 10 grams of hexa-acetatotrichromium diacetate (Abstr., 1909, i, 757) in 15 grams of water are added 10 grams of pyridine, and the solution heated for half a day. After separating the crystals of the above-mentioned diacetate of the tripyridine base, the mother liquor is allowed to evaporate at room temperature. After several weeks the crystals are collected, and washed with cold water to remove the admixed diacetate of the tripyridine base. Rapid concentration of the solution is not favourable to the formation of crystals.

The violet acetate forms violet, four-sided double pyramids, and loses $9H_2O$ over sulphuric acid. It readily dissolves in dilute acids, giving a violet solution, which makes it probable that the hydroxyl groups possess an hydroxo- and not an ol-character. In phenol it gives a normal molecular weight. It is also formed when a solution of the diacetate of the trichromium base is repeatedly evaporated, or when a solution of freshly cold-precipitated chromium hydroxide in acetic acid is allowed to evaporate at room temperature.

A green, amorphous basic acetate has also been obtained by drying the diacetate of the hexa-acetatotrichromium base at 100—110°. It is less basic than the violet acetate. A formula cannot be given for it at present. T. S. P.

Behaviour of Acetic Anhydride at a High Temperature. Eugen Bamberger (*Ber.*, 1910, **43**, 3517—3520).—According to the author, the first stage in the formation of acetone, by the distillation of calcium acetate, is the dissociation of the salt into calcium oxide and acetic anhydride, which at the high temperature necessary for its production decomposes into carbon dioxide and acetone. With a view to confirming this supposition, the behaviour of acetic anhydride at high temperatures has been studied. On heating the anhydride for several hours at 290—300°, small quantities of acetone and acetylacetone were found amongst the products. Whether the formation of the last-named substance is due to the direct acetylation of acetone by means of acetic anhydride, or to the intermediate formation of keten, has not been determined.

These experiments also support the contention of Schmidlin and Bergmann (Abstr., 1910, i, 816) that the first stage in the synthesis of keten from acetic anhydride (Wilsmore, Trans., 1907, **91**, 1938) consists in the decomposition of the latter into carbon dioxide and acetone.

The reaction $O(COMe)_2 = CO_2 + COMe_2$ is probably reversible, but the amounts of carbon dioxide and acetone are very small, when equilibrium is attained.

The fact that acetone is produced in large quantity by the distillation of calcium acetate is not in opposition to this view, for the dissociation products, carbon dioxide and acetone, are continuously removed during the reaction, the latter by distillation, the former by union with the calcium oxide, produced by the decomposition of the acetate.

Various by-products obtained in the manufacture of acetone were examined for acetylacetone, but no indication of its presence was obtained. F. B.

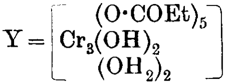
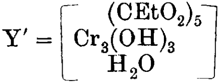
Salts of a Green and of a Violet Propionatochromium Base.

Rudolf F. Weinland and Karl Hoehn [with M. Fiederer] (*Zeitsch. anorg. Chem.*, 1910, **69**, 158—178. Compare Abstr., 1908, i, 847).—Salts of the *green hexapropionatotrichromium* base, $Y(OH)_3$, where $Y = \left[Cr_3{}^{(O\cdot COEt)_6}_{(OH_2)_2}\right]$. To prepare the *dichromate propionate*, $Y(O\cdot COEt)(Cr_2O_7),H_2O$, 2 grams of chromium trioxide are warmed with 20 c.c. of propionic acid. After filtering from the undissolved chromium trioxide, the solution, on keeping, deposits four-sided, brownish-green plates of the salt in question. Molecular weight determinations in acetophenone gave 961—801, as against 937·6. The *sesquichromate propionate*, $Y(O\cdot COEt)(HCrO_4)(\frac{1}{2}CrO_4)$, is obtained by warming chromium trioxide and chromium hydroxide, in the proportion of 2 mols. of the former to 1 mol. of the latter, with propionic acid. On concentrating the solution, dark olive crystals are obtained. Molecular weight in acetophenone was 753—878, as against 877·5. When a mixture of chromium trioxide and chromium hydroxide in the molecular proportion of 1 : 3 is dissolved in propionic acid and the solution concentrated, green, six-sided plates of the *chromate propionate*, $Y(O\cdot COEt)(CrO_4),1\cdot5H_2O$, are obtained. It may also be obtained by dissolving 1 gram of chromium trioxide in 50 c.c. of propionic acid and concentrating the solution.

When less than ten parts of propionic acid to one part of chromium trioxide are taken and the mixture heated, chromates are obtained which contain less propionic acid in the anion than the above-mentioned salts. Whether a dichromate or a lower chromate of the base is obtained depends on the time of heating; the longer the heating, the poorer is the resulting chromate in chromic acid.

Whenever the dichromate propionate is recrystallised from a little water, propionic acid is lost from the anion, and pure *sesquichromate*, $Y(CrO_4)(\frac{1}{2}CrO_4),2H_2O$, is obtained. Even when the chromate propionates are recrystallised from a solution of propionic acid, some of the latter is split off from the anion.

The *chloride chromate*, $Y(CrO_4)Cl,H_2O$, is obtained as yellowish-green, six-sided plates by the addition of concentrated hydrochloric acid to strong solutions of any of the above salts. The *monopropionate*, $Y(O{\cdot}COEt),2H_2O$, is prepared from the chromate propionates by removing the chromic acid with lead propionate, or from the chloride (Abstr., 1908, i, 935) by treatment with silver propionate: it forms pale green, rod-like crystals.

Salts of a *violet pentapropionatotrichromium* base, $Y(OH)_2$, where  $Y=\left[\begin{matrix}(O{\cdot}COEt)_5\\ Cr_3(OH)_2\\ (OH_2)_2\end{matrix}\right]$. The *dipropionate*, $Y(O{\cdot}COEt)_2$, forms the starting point for the preparation of the other salts. It is best prepared by dissolving 1 mol. of freshly-prepared chromium hydroxide, which has been washed with cold water, in 3 mols. of propionic acid at the room temperature. The solution is then heated in a sealed tube for five hours at 140—160°; on cooling, violet crystals of the dipropionate are found on the walls of the tube. After purification by a somewhat complicated method they are obtained as flat prisms, which may be 1 cm. long. Molecular weight in acetophenone was 615, as against 737·7. The *monopropionate*, $Y'(O{\cdot}COEt),3H_2O$, where  $Y'=\left[\begin{matrix}(CEtO_2)_5\\ Cr_3(OH)_3\\ H_2O\end{matrix}\right]$, is obtained by saturating the aqueous solution of the dipropionate with sodium chloride or nitrate; light violet crystals. The *sesquipropionate*, $Y(O{\cdot}COEt)_2,Y'O{\cdot}COEt,H_2O$, results on evaporating a solution of one part of the dipropionate with five parts of sodium propionate; violet, flat prisms. The *sulphate propionate*, $(YO{\cdot}COEt)_2SO_4,4H_2O$, crystallises in violet plates on the addition of concentrated sulphuric acid to the saturated solution of the dipropionate. The *bromide propionate*, $Y(O{\cdot}COEt)Br,4H_2O$, forms violet prisms, as also does the *chloride*, $Y'Cl,Y'O{\cdot}COEt,10H_2O$; they are formed from the dipropionate by precipitation with concentrated hydrobromic and hydrochloric acid respectively.

All the salts of the violet base are readily soluble in ether and chloroform; those of the green base are insoluble in ether. The salts of the violet base cannot be recrystallised from water.

From the solution of chromium chloride hydrate, $CrCl_3,6H_2O$, in a solution of sodium propionate, violet crystals are obtained having the composition $Cr(O{\cdot}COEt)_2{\cdot}OH,H_2O$. They are insoluble in ether, in contradistinction to the violet pentapropionatotrichromium salts.

T. S. P.

Condensation of $\alpha\beta$-Dibromopropaldehyde with Malonic Acid. ROBERT LESPIEAU (*Compt. rend.*, 1910, **151**, 1359—1361. Compare Spenzer, Abstr., 1905, i, 204).—$\alpha\beta$-Dibromopropaldehyde acts on malonic acid to form *$\beta\gamma\delta$-tribromovaleric acid*, m. p. 128—130°; the *ethyl* ester has b. p. 160—161°/12—13 mm. Both the acid and the ester, on treatment with zinc and alcohol, furnish *ethyl Δ^{β}-pentenoate*, $CHMe{:}CH{\cdot}CH_2{\cdot}CO_2Et$, b. p. 145—146°/760 mm. On brominating the corresponding acid, a substance is obtained probably identical with $\alpha\beta$-dibromovaleric acid. W. O. W.

The Oil and Wax of Coffee Beans. HANS MEYER and ALFRED ECKERT (*Monatsh.*, 1910, 31, 1227—1251).—Unroasted coffee beans, from which the greater part of the caffeine had been extracted, were dried, powdered, and digested with benzene. The oil thus obtained had a brownish-yellow colour, was nearly odourless, and had the consistency of olive oil. On hydrolysis it gave 21·2% of non-saponifiable matter. For isolating the acids formed on hydrolysis, it was found advisable to saponify with lithium hydroxide solution (compare Partheil and Ferié, Abstr., 1904, i, 4), but this method did not give a complete separation of saturated from unsaturated acids. The sparingly soluble lithium salts gave the following acids: Carnaubic acid, 10% (Stürcke, Abstr., 1884, 1280; Darmstädter and Liefschütz, 1896, i, 346; Dunham and Jacobson, 1910, i, 215); daturic acid, 1—1·5% (Gerard, Abstr., 1890, 1396; Kreis and Hafner, 1903, i, 788; Holde, Ubbelohde, and Marcusson, 1905, i, 318); palmitic acid, 25—28%, and decoic acid, 0·5%.

In order to obtain the carnaubic acid pure, the least soluble fraction of the lithium salts was transformed into chloride by means of thionyl chloride and then into ester; the processes of conversion into lithium salt, chloride, and ester were repeated, when the *methyl* ester was obtained in the form of glistening plates, m. p. 54—55°, and this on hydrolysis gave the acid with m. p. 74° (not 70° or 72·5°). The *lead* salt has m. p. 109—110°, and is soluble in toluene. The acid resembles stearic acid in many respects, but its ethyl ester is not so soluble in alcohol. The detection of glyceryl esters of this acid in fats is readily accomplished by warming the fat with absolute alcohol and a little sulphuric acid, when the sparingly soluble ethyl carnaubate mixed with a little palmitate and stearate is deposited.

Methyl daturate, $C_{16}H_{33}{\cdot}CO_2Me$, has m. p. 30°, and the *magnesium* salt, m. p. 137—142°.

The more soluble lithium salts were converted into lead salts, and the saturated and unsaturated acids separated by extraction with benzene. The acids isolated were palmitic, oleic 2%, and linoleic 50%. The unsaturated acids were identified by oxidation with 2% permanganate solution in the cold, when dihydroxystearic and sativic acids were obtained, and by bromination, when tetrabromostearic acid was isolated.

The wax contained a small amount of alkaloid, which was removed by steam distillation and solution in glacial acetic acid. When finely divided and made into an emulsion with potassium hydroxide solution, the wax was oxidised by 4% permanganate to carnaubic acid, and when hydrolysed with alcoholic potassium hydroxide solution at 150—170°, it gave carnaubic acid (50%) and a compound with the properties of a tannol. This latter has not been obtained crystalline; it has no definite m. p., but is soluble in alkali solutions and can be benzoylated. The wax is therefore a tannol resin. J. J. S.

Preparation of Compounds of Unsaturated Acids with Aldehydes, Ketones, and Formic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 226222 and 226223).—It is found that unsaturated fatty acids of high molecular weight combine (in the presence of acid condensing agents) with ketones or aldehydes to form a new series of oily compounds. The free acid may be replaced by the oil, which under the experimental conditions becomes almost entirely hydrolysed. The substances employed were acetone, formaldehyde, acetaldehyde, benzaldehyde, dextrose, lævulose, sucrose, and maltose, which were severally heated with castor oil, ricinoleic acid, oleic acid, and cottonseed oil in the presence of either sulphuric acid, zinc chloride, or phosphoryl chloride. The second patent states that formic acid may be employed in this reaction instead of formaldehyde, and details are given of its condensation with ricinoleic acid.

F. M. G. M.

Preparation of Acyl Derivatives of Castor Oil [Ricinoleic Acid]. VEREINIGTE CHININFABRIKEN ZIMMER & CO. (D.R.-P. 226111. Compare Abstr., 1909, i, 696).—The aromatic acyl derivatives of ricinoleic acid have not previously been prepared; it is now found that aromatic acid chlorides reacting with the hydroxyl group of the acid yield the corresponding acyl derivative; these are usually tasteless, odourless oils.

The *benzoyl* ester was prepared by boiling castor oil in benzene solution with benzoyl chloride in the presence of pyridine during half an hour; the *anisoyl* ester was obtained in a similar manner. The *salicyl* ester was prepared by heating castor oil and salol together at a temperature of 200° during three hours, and distilling off the separated phenol in a vacuum. F. M. G. M.

Ester Condensations with Chloroacetic Ester. WILHELM WISLICENUS (*Ber.*, 1910, 43, 2528—2533).—In the Claisen condensation, ethyl chloroacetate can function as the ester component and also as the methylene compound.

The interaction of ethyl chloroacetate, ethyl oxalate, and sodium ethoxide in ethereal solution yields ethyl chloro-oxalacetate,

$$CO_2Et\cdot CO\cdot CHCl\cdot CO_2Et,$$

b. p. 150—152°/56 mm. (compare Peratoner, Abstr., 1893, i, 11; Roubleff, Abstr., 1891, 223); this forms a green *copper* salt, and yields oxamide when treated with ammonia; at 240° it loses only half the theoretical amount of carbon monoxide; in alcoholic solution it gives an intense red ferric chloride reaction.

When equal molecular quantities of ethyl formate and ethyl chloroacetate are introduced into a cold alcoholic ethereal solution of potassium methoxide, a *potassium* salt is formed, from which, by acidification, *ethyl α chloroformylacetate*, $CHO \cdot CHCl \cdot CO_2Et$, is obtained as an oil giving an intense violet ferric chloride reaction. On repeated distillation in a vacuum, it is obtained in colourless leaflets, m. p. 88—90°; the latter give only a faint violet coloration with ferric chloride, and yield with copper acetate a green *copper* salt; after fusion, the crystalline ester gives the original, intense violet ferric chloride reaction. The isomerism here exhibited has not been further investigated, but there is little doubt that the liquid ester has the enolic structure, $OH \cdot CH{:}CCl \cdot CO_2Et$.

The *benzoyl* derivative, $OBz \cdot CH{:}CCl \cdot CO_2Et$, prepared from the above-mentioned potassium salt, crystallises from alcohol in large, colourless plates, m. p. 90—91°. With phenylhydrazine, both the ester and the potassium salt react to form the osazone of ethyl β-hydroxypyruvate, $CH({:}N \cdot NHPh) \cdot C({:}N \cdot NHPh) \cdot CO_2Et$ (compare Will, Abstr., 1892, 356).

The condensation of two molecules of ethyl chloroacetate has also been effected (compare Erlenbach, Abstr., 1892, 953); ethyl chloroacetate (2 mols.) and sodium ethoxide (1 mol.), free from alcohol, are allowed to react in ethereal solution at a low temperature; on acidifying the *sodium* salt thus produced, *ethyl α-γ-dichloroacetoacetate*, $CH_2Cl \cdot CO \cdot CHCl \cdot CO_2Et$, is obtained in an impure condition. It is purified by converting it into the copper salt and decomposing this with hydrochloric acid; it forms a colourless oil with a penetrating odour, b. p. 118—120°/15 mm., and solidifies on cooling, m. p. 18—20°; it gives an intense cherry-red coloration with ferric chloride, and is hydrolysed by boiling with dilute sulphuric acid to *s*-dichloroacetone; the *copper* salt, $(CH_2Cl \cdot CO \cdot CCl \cdot CO_2Et)_2Cu$, crystallises in microscopic, green needles, melting at 149° (decomp.) to a turbid yellow liquid. F. B.

Ethyl γ Chloroacetoacetate. ROBERT LESPIEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 31—33. Compare Abstr., 1899, i, 243; 1905, i, 406; Picha, Abstr., 1907, i, 178).—Polemical with Schlotterbeck (Abstr., 1909, i, 550) on the physical properties of this ester.

T. A. H.

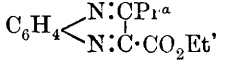
Condensation of Ethyl Acetate with its Higher Homologues. ANDRÉ WAHL (*Compt. rend.*, 1911, **152**, 95—98).—It has hitherto been found impossible to prepare β-ketonic esters by condensing ethyl acetate with its higher homologues. This condensation has now been effected by adding alternately to the higher ester, small, carefully weighed portions of ethyl acetate and sodium. In this way the formation of ethyl acetoacetate and of the compound

$$R \cdot CO \cdot CHR \cdot OH$$

is prevented or diminished; the yield, however, is small, 5—6% in the case of ethyl propionylacetate for the pure compound, and 18—20% in the case of ethyl butyrylacetate. The latter forms a green *copper* derivative, $Cu(C_8H_{13}O_3)_2$, m. p. 125—126°; on boiling with methyl alcohol it changes into a blue *basic* salt, $C_8H_{13}O_3 \cdot CuOMe$.

Ethyl butyrylacetate is converted by oxides of nitrogen into *ethyl butyrylglyoxylate*, $CH_2Et \cdot CO \cdot CO \cdot CO_2Et$, an orange-yellow liquid, b. p.

87—88°/13 mm., becoming colourless on the addition of water or alcohol, with which it combines; the diketone condenses with *p*-phenylenediamine, forming *ethyl 2-propylquinoxaline-3-carboxylate*,



$$C_6H_4<\begin{array}{l}N:CPr^{\alpha}\\ \quad\;\, | \\ N:C\cdot CO_2Et\end{array}$$

long needles, m. p. 63—64°. W. O. W.

γ-Ethoxy-α-alkylacetoacetic Esters. MARCEL SOMMELET (*Bull. Soc. chim.*, 1911, [iv], **9**, 33—38. Compare Abstr., 1907, i, 21, 107).—The considerable differences in the boiling points ascribed by Isbert to the compounds he regarded as α-ethoxybutanone and α-ethoxypentanone (Abstr., 1886, 1009) from those found by the author for his preparations of these substances has led him to re-investigate esters having the constitution assigned by Isbert to the esters from which his ketones were prepared. The author finds that they do not correspond with Isbert's descriptions, and that on hydrolysis they furnish ketones identical with those he has described already (*loc. cit.*).

Ethyl γ-ethoxy-α-methylacetoacetate, $OEt\cdot CH_2\cdot CO\cdot CHMe\cdot CO_2Et$, D_4^0 1·033, D_4^{17} 1·017, b. p. 112—114°/14 mm., 116·5—118·5°/19 mm., obtained by condensing ethoxyacetonitrile with ethyl α-bromopropionate in presence of zinc (compare Blaise, Abstr., 1901, i, 252), is a faintly yellow liquid, which reduces ammoniacal silver nitrate in the cold, and gives a violet coloration with ferric chloride. On hydrolysis with potassium hydroxide solution, the ester yields α-ethoxybutanone, and with hydrazine hydrate gives a *pyrazolone*, m. p. 135—137°, which crystallises from boiling water.

Ethyl γ-ethoxy-α-ethylacetoacetate, $D_4^{14\cdot5}$ 1·0157, b. p. 125—128°/18 mm., similarly obtained, resembles its lower homologue, and on hydrolysis gives α-ethoxypentanone, and with hydrazine hydrate furnishes a *pyrazolone*, m. p. 99—99·5°, which crystallises from boiling water in hard prisms.

Ethyl γ-ethoxy-$\alpha\alpha$-dimethylacetoacetate, D_4^0 1·065, D_4^{17} 1·047, b. p. 114—116°/17 mm., 111—113°/14 mm., obtained by condensing ethyl bromo*iso*butyrate with ethoxyacetonitrile in presence of zinc, is a pale yellow liquid, reduces ammoniacal silver nitrate, and on alkaline hydrolysis furnishes *ethoxymethyl* iso*propyl ketone*, $OEt\cdot CH_2\cdot COPr^{\beta}$, b. p. 160° (approx.), which gives a *semicarbazone*, m. p. 128—129·5°. Along with the ester there is formed in this condensation a small quantity of a *substance*, $C_{12}H_{19}O_4N$, m. p. 90—91·5°, which crystallises in needles or prisms, is soluble in strong acids, becomes yellow in contact with alkali, and gives no coloration with ferric chloride. Heated with alkali in a closed tube, it evolves ammonia and furnishes a trace of *iso*butyric acid and an unidentified oily product.

T. A. H.

Iso- and Hetero-poly-acids. II. Oxalato-tellurates. ARTHUR ROSENHEIM and M. WEINHEBER (*Zeitsch. anorg. Chem.*, 1911, **69**, 261—265. Compare this vol., ii, 116).—Concentration of a solution containing molecular proportions of telluric acid and an alkali oxalate leads to the deposition of crystals of the oxalato-tellurates. The potassium, rubidium, and cæsium salts have the general formula

$M_2C_2O_4,H_6TeO_6$, where M = K, Rb, or Cs, and crystallise in stellar aggregates of needles. The effect of heat on these salts shows that the water is firmly combined, so that telluric acid hydrate, H_6TeO_6, and not the anhydride, TeO_3, is probably contained in the complex anion. These compounds should therefore be formulated as

$$M_2[H_6TeO_6C_2O_4].$$

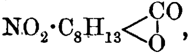
Their solubilities increase from the potassium, through the rubidium, to the cæsium salt, this being the opposite order to what generally obtains with salts of these metals. Comparison of the solubility of the potassium salt with the solubilities of potassium tellurate and oxalic acid shows that a great diminution in solubility has taken place, pointing to complex formation. This could not be verified by conductivity measurements, however, owing to the hydrolysis which takes place.

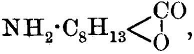
Homogeneous ammonium or sodium oxalato-tellurates could not be obtained. T. S. P.

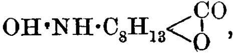
Molecular Rearrangements in the Camphor Series. VI. *iso*Campholactone.

WILLIAM A. NOYES and A. W. HOMBERGER (*J. Amer. Chem. Soc.*, 1910, **32**, 1665—1669).—In an earlier paper (Abstr., 1909, i, 133) the authors described a compound obtained by the action of nitric acid on *iso*campholactone, which they regarded as a dilactone of the composition $C_8H_{13}O_4$. It has now been found that this substance is, in reality, a nitrolactone.

*iso*Campholactone, prepared by Noyes and Taveau's method (Abstr., 1904, i, 807), gave $[\alpha]_D^{28}$ $-63{\cdot}1°$ in an 8·8% solution in alcohol; Noyes and Taveau found $[\alpha]_D$ $-60{\cdot}7°$ in a 5% solution.

On heating *iso*campholactone with ammonium hydroxide in a sealed tube at 100°, it yields the *ammonium* salt of the corresponding acid, m. p. 137°, which is re-converted into the lactone when left in the air. When the lactone is heated with nitric acid (D 1·27), a mixture of products is obtained, the chief of which is *nitro*iso*campholactone*,  $NO_2\cdot C_8H_{13}<\begin{smallmatrix}CO\\|\\O\end{smallmatrix}$, m. p. 122°, b. p. 272°, which crystallises in needles, and has $[\alpha]_D$ $-85{\cdot}4°$ in a 5·5% solution in alcohol. A monobasic lactonic *acid*, $C_9H_{12}O_4$, m. p. 138°, was isolated from the mother liquor, which has $[\alpha]_D$ $-42{\cdot}05°$ in a 6% solution in alcohol; its *barium* salt was prepared; the *amide* has m. p. 164°.

*Amino*iso*campholactone*,  $NH_2\cdot C_8H_{13}<\begin{smallmatrix}CO\\|\\O\end{smallmatrix}$, m. p. 84°, obtained by reducing nitro*iso*campholactone with tin and hydrochloric acid, forms small crystals, and is decomposed by sodium hydroxide with formation of a compound, m. p. 152°. *Hydroxylamino*iso*campholactone*,



$$OH\cdot NH\cdot C_8H_{13}<\begin{smallmatrix}CO\\|\\O\end{smallmatrix},$$

m. p. 144°, prepared by treating nitro*iso*campholactone with zinc dust and acetic acid, forms small, stellate crystals, is slightly basic, and readily reduces Fehling's solution.

When nitro*iso*campholactone is shaken with 0·5*N*-sodium hydroxide until completely dissolved, and afterwards acidified with hydrochloric acid, an *acid*, $C_5H_8O_2N\cdot CO_2H$, m. p. 73—74°, is produced; its *barium* salt crystallises in needles containing $2\frac{1}{2}H_2O$. By the action of ammonium hydroxide on nitro*iso*campholactone, the corresponding *amide*, m. p. 96—97°, is obtained. E. G.

Molecular Rearrangements in the Camphor Series. VII. Derivatives of *iso*Camphoric Acid; *l*-Hydroxydihydrocampholytic Acid. William A. Noyes and Luther Knight (*J. Amer. Chem. Soc.*, 1910, 32, 1669—1674).—*d*- and *l*-*iso*Camphoric acids are usually regarded as *cis*- and *trans*-isomerides. As, however, the evidence of this structure does not seem altogether conclusive in the case of the latter compound, the present work was undertaken in order to throw some light on the question. Assuming that *iso*camphoric acid is stereoisomeric with camphoric acid, α is used in this paper to denote the secondary carboxyl, and β the tertiary carboxyl, group.

By boiling *iso*camphoric acid with methyl alcohol and sulphuric acid, the α-methyl and dimethyl esters are obtained. The *dimethyl* ester, $C_8H_{14}(CO_2Me)_2$, b. p. 146°/27 mm., has D^{20} 1·073, D^{25} 1·069, and $[\alpha]_D^{21}$ $-65·2°$; a 10% solution in alcohol has $[\alpha]_D$ $-63·6°$. The α-*methyl* ester, m. p. 88°, crystallises in needles, and gives $[\alpha]_D$ $-57·9°$ in a 10% alcoholic solution; its *amide*, m. p. 157°, crystallises in plates, and has $[\alpha]_D$ $-60·05°$ in a 10% alcoholic solution.

β-iso*Camphoramic acid*, $CO_2H\cdot C_8H_{14}\cdot CO\cdot NH_2$, m. p. 165—166°, obtained by hydrolysing the α-methyl ester amide with sodium hydroxide, crystallises in needles. When its sodium salt is treated with sodium hypobromite solution, *amino*iso*dihydrocampholytic acid*, $CO_2H\cdot C_8H_{14}\cdot NH_2$, m. p. 225—227°, is produced; its *hydrochloride* and *lead* salt are described. When this acid is heated at 250—300°, it is converted into an *anhydride*, which furnishes a *nitroso*-compound, m. p. 194°. If amino*iso*dihydrocampholytic acid hydrochloride is treated with a solution of sodium nitrite, there are produced a hydrocarbon, a lactone, *d*-campholytic acid, and l-*hydroxydihydrocampholytic acid*, $CO_2H\cdot C_8H_{14}\cdot OH$, m. p. 132°, which forms granular crystals and gives $[\alpha]_D$ $-70·04°$ in an aqueous solution containing 1·45%. The formation of this compound, instead of hydroxydihydro*iso*campholytic acid, which was expected, renders it probable that the former is the more stable, and that part of the hydroxydihydro*iso*campholytic acid is converted into it by the action of the nitrous acid, or else that *d*-campholytic acid is formed as an intermediate product and unites with water to produce *l*-hydroxydihydrocampholytic acid. E. G.

Saccharinic Acids. Heinrich Kiliani (*Ber.*, 1911, 44, 109—113).—A reply to Nef (Abstr., 1910, i, 714). The phenylhydrazide of α-metasaccharin has m. p. 145°, as previously found, and not 113—115°, as stated by Nef.

The trihydroxyadipic acid described by Kiliani and Eisenlohr (Abstr., 1909, i, 553) is not identical with the old trihydroxy-acid; it has m. p. 159—160°, whereas a mixture of the two melts at 142—145°. The silver salt also does not crystallise in the small plates characteristic of the silver salt of the old acid. The presence of a compound with a branched chain in parasaccharin has been confirmed by reduction to α-ethylbutyrolactone, and the isolation of this in the form of Chanlaroff's calcium salt, $3Ca(C_6H_{11}O_3)_2,2H_2O$ (Abstr., 1885, 374). The yield of calcium salt, however, is small, and large quantities of syrupy salts are formed.

By oxidising parasaccharin with nitric acid to parasaccharone (Abstr., 1904, i, 975) and reducing this with hydriodic acid, a small amount of *n*-adipic acid has been obtained. These results indicate that parasaccharin must be a mixture.

Nef's parasaccharin (α-*d*-galactometasaccharin) does not appear to be hygroscopic, whereas the author's preparations are excessively hygroscopic.

The acid obtained by the oxidation of barium parasaccharinic acid is not hydroxycitric acid, as stated previously (Abstr., 1904, i, 976), but *l*-tartaric acid. J. J. S.

Glucodeconic Acids. L. H. PHILIPPE (*Compt. rend.*, 1910, **151**, 1366—1367. Compare this vol., i, 12).—On evaporating an aqueous solution of β-glucodeconic acid, a mixture of two compounds is obtained: (1) the hydrated β-*lactone*, $C_{10}H_{18}O_{10},H_2O$, crystallising in hemihedral needles, m. p. 135° (anhydrous, m. p. 193°), $[\alpha]_D^{17} - 41{\cdot}2°$; (2) an *anhydride*, $C_{20}H_{38}O_{21}$, separating in microscopic granules resembling those of starch, m. p. 216—218°, $[\alpha]_D$ about $-10°$. The lactone is the chief constituent in dilute solutions, whilst the anhydride predominates in concentrated solutions. The β-lactone is also formed when the α-lactone is heated at 140° in pyridine.

Sodium β-glucodeconate is gummy, but the *barium*, *cadmium*, and *strychnine* salts are crystalline. The β-*phenylhydrazide* crystallises in needles, m. p. 246°, and is ten times more soluble in water than the α-compound. W. O. W.

Derivatives of Aldol and Crotonaldehyde. RUDOLF WEGSCHEIDER and ERNST SPÄTH (*Monatsh.*, 1910, **31**, 997—1029).—The authors have examined the behaviour of aldol towards acetylating agents under various conditions, and find that acetylation is accompanied by the formation of condensation products; loss of water and rupture of the aldol molecule also occur.

When aldol is boiled with acetic anhydride in the presence of a little sulphuric acid, ethylidene acetate and *aldol triacetate*,

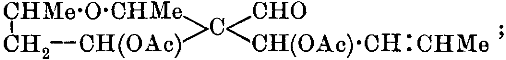
$$OAc{\cdot}CHMe{\cdot}CH_2{\cdot}CH(OAc)_2,$$

are produced. The latter substance is a colourless oil, b. p. 138—140°/12 mm., which yields crotonaldehyde when boiled with water or alkalis; when treated with bromine in chloroform solution, it is converted into bromocrotonaldehyde.

Gentle acetylation of aldol with acetic anhydride and sulphuric acid in benzene or chloroform solution yields, amongst other products, *aldol monoacetate*, $OAc{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$; it is a colourless oil, b. p. 87—89°/18 mm., and is also obtained by the action of acetic acid and a little sulphuric acid on aldol at the ordinary temperature.

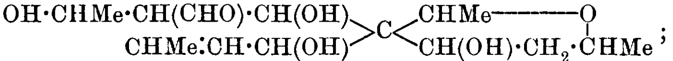
By heating aldol with acetic anhydride alone, Wurtz (this Journ., 1872, 808) obtained two substances, which he considered to be crotonaldehyde diacetate and acetylaldol. The authors have repeated Wurtz's experiments, and find that his crotonaldehyde diacetate consists of a mixture of aldol triacetate and a compound $C_{12}H_{18}O_5$, whilst the substance described as acetylaldol is identical with crotonaldehyde diacetate. The *compound*, $C_{12}H_{18}O_5$, is probably the diacetyl derivative of dialdan, $C_8H_{14}O_3$, a substance obtained by Wurtz by the action of acids on aldol; it is produced by gently acetylating aldol with acetic anhydride and sulphuric acid, either alone or in chloroform and benzene solution, and also by the action of acetic and sulphuric acids on aldol at the ordinary temperature; the b. p. varies from 144—147°/13 mm. to 152—154°/12 mm., according to the method of preparation, but whether this variation is due to impurity or the presence of two dialdan diacetates has not been decided. The constitution of the compound is discussed, and arguments advanced in favour of the formula OAc·CHMe·CH(CHO)·CH(OAc)·CH:CHMe.

The following condensation products were also isolated and examined: a *diacetate* of $C_{12}H_{20}O_2$, colourless oil, b. p. 201—203°/10 mm., produced by acetylating aldol with acetic anhydride in the presence of a little sulphuric acid, and probably having the structure



$$\begin{array}{l}\mathrm{CHMe{\cdot}O{\cdot}CHMe}\\ |\\ \mathrm{CH_2{-}{-}CH(OAc)}\end{array}\!>\!\mathrm{C}\!<\!\begin{array}{l}\mathrm{CHO}\\ \\ \mathrm{CH(OAc){\cdot}CH{:}CHMe}\end{array}$$

; a *substance*, $C_{18}H_{30}O_7$, b. p. 228—233°/13 mm., obtained by the action of a mixture of acetic and sulphuric acids on aldol, and represented as a monoacetyl derivative of



$$\begin{array}{r}\mathrm{OH{\cdot}CHMe{\cdot}CH(CHO){\cdot}CH(OH)}\\ \mathrm{CHMe{:}CH{\cdot}CH(OH)}\end{array}\!>\!\mathrm{C}\!<\!\begin{array}{l}\mathrm{CHMe{-}{-}{-}{-}{-}{-}{-}O}\\ \mathrm{CH(OH){\cdot}CH_2{\cdot}CHMe}\end{array}$$

; a mixture of the monoacetyl derivatives of $C_8H_{14}O_3$ and $C_8H_{16}O_4$, produced by acetylating aldol with acetic anhydride and sulphuric acid in chloroform solution.

Acetyl chloride reacts with aldol in benzene solution, forming α-chlorocrotyl acetate, CHMe:CH·CHCl·OAc, b. p. 76—77°/18 mm.; the same substance is also produced by the addition of acetyl chloride to crotonaldehyde. When aldol is acetylated by means of acetic anhydride in the presence of sodium acetate, the main product is crotonaldehyde diacetate.

Aldolphenylhydrazone is obtained in an impure condition by the action of phenylhydrazine on aldol in ethereal solution; it is a viscid oil, b. p. 196°/10 mm.; the p-*nitrophenylhydrazone* crystallises in reddish-yellow needles, m. p. 109—111°, with previous sintering at 107°; *aldoloxime* has b. p. 117—118°/11 mm.

Crotonaldehydephenylhydrazone, prepared by the action of phenylhydrazine on crotonaldehyde in alcoholic solution at 35—42°, is a yellow oil, b. p. 156—158°/11 mm. (compare Trener, Abstr., 1901, i, 232); the p-*nitrophenylhydrazone* crystallises in brown needles, m. p. 184—185°.

The authors also describe two new condensation products of acetaldehyde. A specimen of crotonaldehyde, which had been kept for three and a-half months in a closed glass vessel filled with carbon dioxide, yielded on distillation an *oil*, $C_{10}H_{18}O_4$, b. p. 88—95°/16 mm., and a viscid *liquid*, $C_{16}H_{28}O_6$, b. p. 156—161°/16 mm. It is suggested that these two substances are produced by the condensation of acetaldehyde, derived from the para-aldehyde (with which the original crotonaldehyde was probably contaminated) according to the equations: $C_{10}H_{18}O_4 = 5C_2H_4O - H_2O$ and $C_{16}H_{28}O_6 = 8C_2H_4O - 2H_2O$. F. B.

Preparation of Octendione and its Homologues. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 227176).—The methylene ketones employed in the following reactions were recently described (Abstr., 1910, i, 652); it is now found that they polymerise readily, yielding octendiones (and higher polymerides) of considerable therapeutic importance.

Δ_{α}*-Octen-*$\gamma\eta$*-dione*, b. p. 75—76°/21 mm., a colourless oil, sparingly soluble in water, and with a penetrating odour, is prepared by the long boiling of methyleneacetone under reflux, and subsequent fractional distillation of the products: its *semicarbazone* has m. p. 199°.

$\beta\zeta$*-Dimethyl-*Δ^{α}*-octen-*$\gamma\eta$*-dione*, $COMe\cdot CHMe\cdot CH_2\cdot CH_2\cdot CO\cdot CMe\colon CH_2$, is prepared in a similar manner from methyl methylene-ethyl ketone, but owing to the higher temperature employed more of the higher polymerides are simultaneously produced; it is a colourless, highly refractive oil, b. p. 187—194° or 83—85°/17 mm., with pine-like odour, immiscible with water, and slowly decomposed by boiling at atmospheric pressure into its progenitors; its *semicarbazone* has m. p. 183°. Dimethyloctendione can also be obtained by the slow distillation in a vacuum of $\beta\zeta$-dimethyloctan-$\gamma\eta$-dione-α-ol (see this vol., i, 102) with an equal weight of hydrogen potassium sulphate, or by boiling it with acetic anhydride.

F. M. G. M.

The Influence of Inactive Substances on the Rotation of Lævulose. NEUMANN WENDER (*Biochem. Zeitsch.*, 1911, **30**, 357—373).—The addition of inorganic acids to a solution of lævulose was found in most cases to increase the specific rotation, the increase varying with the degree of acidity of the solution. Inorganic salts as well as organic acids varied in their behaviour, causing in some cases a rise, in others a decrease, in the rotation. Alcohols and acetone produced a marked diminution in the rotation, which was proportional to the amount added. W. J. Y.

Mercerised Cellulose. CHARLES F. CROSS (*Ber.*, 1911, **44**, 153—154).—In connexion with Miller's results (this vol., i, 17) it is pointed out that bleached cotton is not a homogeneous cellulose, and that by the action of sodium hydroxide solution the β-celluloses are dissolved. Previous heating at 90—100° renders the β-celluloses still more reactive towards alkalis. The increase in weight of the cellulose on hydration is compensated by the loss in weight due to the removal of the β-celluloses (compare Cross and Bevan, "Cellulose," pp. 4 and 28).

The author upholds the view that a definite series of hydrated celluloses exists, and that these are stable within the limits 0° to 50°.

J. J. S.

Mercerised Cellulose. CARL G. SCHWALBE (*Ber.*, 1911, **44**, 151—152. Compare preceding abstract).—Attention is drawn to the fact that during treatment with sodium hydroxide solution a portion of the cellulose is dissolved.

Previous experiments (Abstr., 1908, ii, 627) have shown that mercerised cellulose does not contain water (compare also Ost and Westhoff, Abstr., 1909, i, 210).

According to Liebermann (*Dingler's polyt. J.*, 1886, **181**, 133) an aqueous solution of rosaniline base does not dye cotton-cellulose. For behaviour of mercerised cotton towards substantive dyes, compare Knecht (*J. Soc. Dyers*, 1908, **24**, 68), and Hübner and Pope (*J. Soc. Chem. Ind.*, 1904, **23**, 401). J. J. S.

Cellulose. II. Hydrocellulose. H. JENTGEN (*Zeitsch. angew. Chem.*, 1911, **24**, 11—12. Compare Abstr., 1910, i, 654).—In support of the view that acid in the molecular condition brings about the conversion of cellulose to hydrocellulose (compare Schwalbe, Abstr., 1910, i, 817), the following facts are given: (1) A 1% aqueous acid solution has practically no hydrolysing effect; (2) Methyl or ethyl alcoholic solutions act slowly, and the action depends on the amount of dissociation; (3) 1% solutions of acids in non-ionising media hydrolyse readily. The compounds of cellulose with the molecular acids are regarded as catalysts. The hydrolysis observed by Schwalbe during acetylation is regarded as a secondary or tertiary process.

J. J. S.

Hydrocellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, **24**, 12—13. Compare Abstr., 1910, i, 817).—Mainly polemical in reply to Jentgen (preceding abstract). J. J. S.

Acyl Derivatives of Guanidine. WILHELM TRAUBE (*Ber.*, 1910, **43**, 3586—3590).—Guanidine interacts with the esters of monobasic acids, forming simple acyl guanidines.

Formylguanidine, $NH_2\cdot C(NH)\cdot NH\cdot CHO$, separates in crystalline granules, m. p. 178° (decomp.). On shaking with bromine, *formylbromoguanidine* results; it crystallises in almost colourless needles, which decompose violently at 125°.

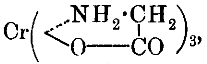
Acetylguanidine separates in colourless, rhombic crystals, m. p. 185° to a clear liquid; on further heating, it solidifies, and the new compound, after crystallisation from water, has m. p. 261°. Acetylguanidine hydrochloride has m. p. 145° (Korndörfer found 142°, *Arch. Pharm.*, 1903, **241**, 449).

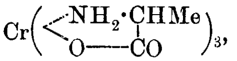
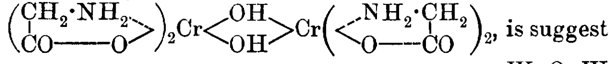
Chloroacetylguanidine crystallises in slender, colourless needles, m. p. 125°. *Trichloroacetylguanidine* forms small, colourless crystals, m. p. 183°; the *hydrochloride* crystallises in platelets.

Benzoylguanidine forms short, colourless crystals, m. p. 160°; the hydrochloride separates in lustrous needles, m. p. 207° (Korndörfer found 210°, *loc. cit.*).

m-*Nitrobenzoylguanidine* crystallises in stellate needles, m. p. 195—197°. E. F. A.

Complex Salts of Certain Amino-acids. LEO TSCHUGAEFF and E. SERBIN (*Compt. rend.*, 1910, **151**, 1361—1363).—α-Amino-acids form stable, complex, internal salts with certain heavy metals, in this respect differing from the β-, γ-, and δ-acids, which appear unable to do so. The following salts are sparingly soluble, and were prepared in each case by boiling an aqueous solution of the amino-acid with somewhat less than the calculated amount of purpureochromium chloride.

The *glycine* salt,  $\mathrm{Cr}\left(<\begin{matrix}\mathrm{NH_2\cdot CH_2}\\ \mathrm{O\text{——}CO}\end{matrix}\right)_3$, crystallises in small, bright red prisms; it is stable at 300°, and is not decomposed by boiling with alkalis or dilute acids.

The *alanine* salt,  $\mathrm{Cr}\left(<\begin{matrix}\mathrm{NH_2\cdot CHMe}\\ \mathrm{O\text{——}CO}\end{matrix}\right)_3$, has a similar constitution, and shows the same properties; it crystallises in rosy needles. The *asparagine* derivative, $Cr(C_4H_7O_3N_2)_3$, is less soluble, and separates in microscopic, rose-violet needles. α-Amino*iso*butyric acid, α-amino*iso*valeric acid, and leucine form similar compounds. The salts can also be prepared, but in a less pure state, by boiling the amino-acids with an aqueous, ammoniacal solution of chromic chloride. When glycine is treated in this way, a basic salt is obtained, for which the constitution  $\left(\begin{matrix}\mathrm{CH_2\cdot NH_2}\\ \mathrm{CO\text{——}O}\end{matrix}>\right)_2\mathrm{Cr}<\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}>\mathrm{Cr}\left(<\begin{matrix}\mathrm{NH_2\cdot CH_2}\\ \mathrm{O\text{——}CO}\end{matrix}\right)_2$, is suggested.

W. O. W.

Action of Carbon Disulphide on Amino-acids.

MAX SIEGFRIED and O. WEIDENHAUPT (*Zeitsch. physiol. Chem.*, 1910, **70**, 152—160).—Carbon disulphide combines with amino-acids in the presence of barium hydroxide or other alkalis in much the same manner that carbon dioxide does (compare Abstr., 1905, ii, 332; 1906, i, 324; 1908, i, 379), yielding dithiocarboxylic derivatives of the amino-acids; for example, glycol yields a salt of

$$CO_2H\cdot CH_2\cdot NH\cdot CS\cdot SH.$$

Most of the salts are readily soluble, but, when treated with benzyl chloride, yield sparingly soluble acid benzyl esters of the type $CO_2H\cdot CH_2\cdot NH\cdot CS\cdot S\cdot CH_2Ph$, by means of which the dithiocarboxylic acids can be isolated with great ease.

Benzyl hydrogen glycinedithiocarboxylate, $C_{10}H_{11}O_2NS_2$, crystallises from water in long, broad, colourless needles with a silvery lustre, and has m. p. 165°; 100 c.c. of an aqueous solution saturated at the ordinary temperature contains 0·0096 gram of ester. The *barium* salt, $(C_{10}H_{10}O_2NS_2)_2Ba$, crystallises from hot water in broad needles.

The yield of ester is 50% when the theoretical amount (2 mols.) of potassium hydroxide (78·6% solution) is used, but falls to nil when 1·5 times the theoretical amount is used.

Benzyl hydrogen dl-*alaninedithiocarboxylate*,

$$CO_2H\cdot CHMe\cdot NH\cdot CS_2\cdot CH_2Ph,$$

crystallises from water in short, colourless, glistening needles, m. p. 136°. Its solubility at 20° is 0·0102.

Benzyl hydrogen phenylglycinedithiocarboxylate,

$$CO_2H\cdot CH_2\cdot NPh\cdot CS_2\cdot CH_2Ph,$$

crystallises from water in slender needles, m. p. 171°. Its solubility in water at 20° is 0·0038, and it is only sparingly soluble in hot water.

The acid *benzyl* ester of *dithiocarboxyphenylaminoacetic acid*, $CO_2H{\cdot}CHPh{\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph$, crystallises from aqueous alcohol in needles, m. p. 88°; the *barium* salt, $(C_{16}H_{14}O_2NS_2)_2Ba$, crystallises in slender needles.

Benzyl hydrogen sarcosinedithiocarboxylate,

$$CO_2H{\cdot}CH_2{\cdot}NMe{\cdot}CS_2{\cdot}CH_2Ph,$$

crystallises from hot water in colourless needles, m. p. 125°, and has solubility 0·0153 at 20°. The *barium* salt forms rhombs. *Benzyl hydrogen asparaginedithiocarboxylate*,

$$CO_2H{\cdot}C_2N_3(CO{\cdot}NH_2){\cdot}NH{\cdot}CS_2{\cdot}CH_2Ph,$$

has m. p. 180°, and yields a *barium* salt, which crystallises in slender needles.

Similar compounds have not been obtained from arginine, lysine, histidine, aspartic acid, and glutamic acid; the leucine derivative is oily.

The formation of the sparingly soluble benzyl ester affords a simple method for the separation of glycine from aspartic or glutamic acids. J. J. S.

Syntheses of Bases of the Sugar Group. EMIL FISCHER and KARL ZACH (*Ber.*, 1911, **44**, 132—135).—*Aminomethylglucoside hydrobromide*, $C_7H_{15}O_5N,HBr$, is formed when triacetylmethylglucoside bromohydrin (Fischer and Armstrong, Abstr., 1902, i, 263) reacts with ammonia at the ordinary temperature. The acetyl derivative (10 grams) is sealed up with 12—15 c.c. of solid ammonia. The temperature is allowed to rise gradually to the ordinary temperature, at which it is kept for seven days, and the tube then opened after the ammonia has been again solidified. After removal of the excess of ammonia, the syrup is extracted with absolute alcohol, the alcohol evaporated under reduced pressure, and the residue extracted with warm, dry ethyl acetate, which removes acetamide and leaves a mixture of ammonium bromide and the hydrobromide of the aminoglucoside; the latter is obtained from the mixture in a crystalline form by dissolving in a little warm methyl alcohol and adding much ethyl acetate. To remove the last traces of ammonium bromide, the compound is dissolved in absolute alcohol. The yield is 56% of the theoretical. The salt has not a well-defined m. p., but melts and decomposes at about 205° (corr.). It has $[\alpha]_D^{20}$ $-21{\cdot}2°$. The *hydrochloride* has m. p. 215° (decomp., corr.) and $[\alpha]_D^{20}$ $-25{\cdot}1°$, and both salts dissolve readily in water. The free base dissolves in methyl alcohol, but is precipitated as a flocculent mass on the addition of ether. When heated with *N*-hydrochloric acid in a sealed tube at 100°, the hydrochloride yields the salt of an amino-sugar. This reduces Fehling's solution, but is not identical with glucosamine hydrochloride, since it dissolves more readily in water and concentrated hydrochloric acid, and is decomposed much more readily than glucosamine by concentrated hydrochloric acid. The osazone, which it yields with sodium acetate and phenylhydrazine hydrochloride, is not identical with phenylglucosazone. J. J. S.

Preparation of Double Compounds of Carbamide with Alkaline-earth Bromides. GEHE & Co. (D.R.-P. 226224).—The action of carbamide on the alkaline-earth bromides yields compounds of therapeutic value in heart complaints.

Calcium bromocarbamide, m. p. 186°, is prepared by heating calcium bromide (250 parts) with carbamide (225 parts) in the presence of a small quantity of alcohol or water during three hours under a reflux condenser; it crystallises from alcohol or ether.

F. M. G. M.

Preparation of Substituted Carbamic Acid Esters. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 225712).—*a-Methyl-β-trichloroethyl allophanate*, $C_5H_7O_3N_2Cl_3$, prisms, m. p. 186°, is prepared by heating trichloro*iso*propyl alcohol (1 mol.) with carbamic chloride (2 mols.) on the water-bath.

Tetrachloroethyl allophanate, $C_4H_4O_3N_2Cl_4$, is obtained by substituting chloral for the alcohol in the foregoing preparation and allowing the mixture to remain at the ordinary temperature during two days; it forms colourless crystals, which decompose at about 160°. When molecular proportions of trichloro*iso*propyl alcohol and *p*-ethoxyphenylcarbimide are heated together at 185°, *trichloro*iso*propyl* p-*ethoxyphenylcarbamate*, $C_{12}H_{14}O_3NCl_3$, is obtained as a syrup, which after crystallisation from petroleum has m. p. 86°. F. M. G. M.

Preparation of Esters of Allophanic Acid. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 226228).—Tertiary alcoholic esters which are therapeutically important are not readily prepared by the ordinary methods, and allophanic tertiary alcoholic esters have not previously been obtained.

Amyl allophanate, $CMe_2Et\cdot O\cdot CO\cdot NH\cdot CO\cdot NH_2$, colourless needles, m. p. 149—150°, is prepared by treating a cooled solution of amylene hydrate in an indifferent solvent with cyanic acid and evaporating in a vacuum; it is sparingly soluble in water, ether, or benzene, readily so in alcohol, and is decomposed by hot alkalis. F. M. G. M.

Preparation of α-Bromo-α-ethylbutyrylcarbamide. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 225710).—*α-Bromo-α-ethylbutyrylcarbamide*, $CBrEt_2\cdot CO\cdot NH\cdot CO\cdot NH_2$, colourless, tasteless, odourless crystals, m. p. 114—118°, and of therapeutic value, is prepared (1) by heating α-bromo-α-ethylbutyryl bromide (obtained by the action of bromine on α-ethylbutyric anhydride) with carbamide at 100°; (2) by the action of sulphuric acid on α-bromoethylbutyrylcyanamide (prepared from cyanamide and α-bromoethylbutyryl chloride); (3) from the interaction of ammonium acetate with *phenyl α-bromo-α-ethylbutyrylcarbamate*, which forms colourless crystals, and is prepared from α-bromo-α-ethylbutyryl bromide and the sodium derivative of phenyl carbamate; (4) by the oxidation of α-bromo-α-ethylbutyrylthiocarbamide with potassium permanganate, or (5) the direct bromination of α-ethylbutyrylcarbamide. F. M. G. M.

Calcium Cyanamide. NIKODEM CARO (*Zeitsch. angew. Chem.* 1910, **23**, 2405—2417).—[With B. SCHÜCK]—When solutions contain ing dicyanodiamide and silver nitrate, in the mol. proportions 1 : 1, 2 : 1, and 3 : 1 are mixed, the compounds $AgNO_3,C_2H_4N_4$, $AgNO_3,2C_2H_4N_4$, and $AgNO_3,3C_2H_4N_4$ are produced. The first of these substances is converted by sodium hydroxide into the compound $C_2H_3N_4Ag$, whilst the second yields a mixture of the same compound and silver oxide.

Silver dicyanodiamide decomposes when boiled, first into silver cyanamide; when the boiling is more prolonged, the latter is further decomposed with production of cyanamide.

Cyanamide, dicyanodiamide, and carbamide are estimated as follows: Calcium cyanamide (7 grams) is shaken for two and a-half hours with 400 c.c. of water, and the solution made up to 500 c.c. A portion of the solution (250 c.c.) is treated with ammonia and silver acetate, diluted to 400 c.c., filtered, and the precipitate washed. The nitrogen (cyanamide) is then estimated by the Kjeldahl method. A part of the filtrate (300 c.c.) is boiled with potassium hydroxide, diluted to 400 c.c., and the nitrogen in the precipitate (dicyanodiamide) estimated as before. A part of the filtrate (300 c.c.) is evaporated down, the silver precipitated with hydrogen sulphide, and the excess of the latter expelled by carbon dioxide. It is then diluted to 400 c.c., and the nitrogen (carbamide) estimated in 100 c.c.

[With RICHARD JACOBY and B. SCHÜCK.]—When calcium carbide is heated in absence of air with 10% sodium cyanide for three hours at 900°, nearly the whole of the cyanide is converted into cyanamide. The same change occurs when barium cyanide is heated in a current of acetylene diluted with hydrogen.

[With B. SCHÜCK.]—When calcium cyanamide is heated in a current of dry carbon dioxide, the carbide present is completely decomposed, and the calcium cyanamide is decomposed with production of carbon.

[With R. JACOBY and B. SCHÜCK.]—As regards the alleged production of nitrides by the action of nitrogen on a mixture of alumina and carbide, it was found that neither nitrides nor cyanamide are produced at 800—1200°, products being obtained containing not more than 0·8% per cent. N at the lower temperature, and generally no nitrogen at temperatures of 1000° or more. Calcium carbide when heated with alumina in an inert atmosphere yields a black substance containing neither calcium nor aluminium carbide.

[With B. SCHÜCK.]—Pure cyanamide can be prepared by slowly adding sodium cyanamide to well cooled, strong hydrochloric acid, and distilling off the water in a vacuum. The cyanamide is then dissolved in ether.

It can also be obtained by adding a concentrated solution of aluminium sulphate to an aqueous extract of calcium cyanamide. The filtrate is distilled in a vacuum and extracted with ether. Cyanamide forms colourless crystals, m. p. 41—42°, readily soluble in water, alcohol, and ether. When heated, it is at once converted into dicyanodiamide (m. p. 204°); the same change takes place when it is exposed to air.

[With R. JACOBY.]—The temperature at which nitrogen acts on mixtures of baryta and carbon is reduced by adding fluorides; the action takes place at a temperature below the m. p. of the fluoride. When a mixture of barium carbonate, carbon, and calcium (or barium) fluoride is heated without nitrogen at the temperatures employed for nitrogen fixation, there is a production of carbide. No carbide is formed at this temperature in absence of fluoride. N. H. J. M.

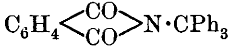
Preparation of Phenylnitromethane [ω-Nitrotoluene] by the Action of Mercurous Nitrite on Benzyl Chloride. Pañchánan Neogi and Birendra Bhusan Adhicáry (*Zeitsch. anorg. Chem.*, 1911, **69**, 270—272).—ω-Nitrotoluene is readily obtained by the interaction of mercurous nitrite and benzyl chloride, the reaction mixture being fractionally distilled under diminished pressure. The yield is much better than when silver nitrite is used. T. S. P.

Preparation of Diphenylmethane and its Homologues. Ernst von Meyer (*J. pr. Chem.*, 1910, [ii], **82**, 538—540).—The hydrocarbon obtained by the action of phosphoric oxide on benzyl ethyl ether in benzene solution, and regarded by Schickler as an isomeride of stilbene, is shown to be diphenylmethane, not only by the fact that it is not formed when light petroleum is used as the solvent, but also by its oxidation to benzophenone by chromic and acetic acids, and by its nitration to 4 : 4′-dinitrodiphenylmethane and tetranitrodiphenylmethane.

Phenyl-*p*-tolylmethane and phenyl-α-naphthylmethane are obtained in a similar manner by replacing the benzene by toluene and naphthalene respectively; *p*-chlorodiphenylmethane is obtained by using *p*-chlorobenzyl ethyl ether instead of benzyl ethyl ether, and triphenylmethane by employing diphenylmethyl ethyl ether.

C. S.

Triphenylmethyl Chloride, Diphenylcarbamyl Chloride, and Cyanuric Bromide Acting as Acid Halogenides. Ernst von Meyer (*J. pr. Chem.*, 1910, [ii], **82**, 521—538).—A comparative study of transformations in which triphenylmethyl chloride, diphenylcarbamyl chloride, and cyanuric bromide function as acid halogenides.

[With P. Fischer.]—Triphenylmethyl chloride reacts with carbamide, methylcarbamide, and phenylcarbamide in pyridine to form s-*ditriphenylmethylcarbamide*, $CO(NH{\cdot}CPh_3)_2$, s-*triphenylmethylmethylcarbamide*, $NHMe{\cdot}CO{\cdot}NH{\cdot}CPh_3$, m. p. 263°, and s-*phenyltriphenylmethylcarbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}CPh_3$, m. p. 242°, respectively, and with thiocarbamide to form *triphenylmethylthiocarbamide*, $NH_2{\cdot}CS{\cdot}NH{\cdot}CPh_3$, m. p. 217°. Triphenylmethyl chloride reacts with potassium phthalimide at 200° to form *triphenylmethylphthalimide*,  $C_6H_4<^{CO}_{CO}>N{\cdot}CPh_3$, m. p. 172°, with pyrrole and with piperidine, yielding *triphenylmethylpyrrole*, $C_4NH_4{\cdot}CPh_3$, m. p. 258°, and *triphenylmethylpiperidine*, $C_5NH_{10}{\cdot}CPh_3$, m. p. 153°, respectively, and with pyridine or quinoline in benzene solution readily forms the crystalline additive compounds, C_5NH_5,CPh_3Cl, m. p. 171°, and C_9NH_7,CPh_3Cl, m. p. 163°, which are decomposed by water or alcohol, and form intensely yellow solutions in hot pyridine. When fused with phenol or with resorcinol, triphenylmethyl chloride yields *p*-hydroxytetraphenylmethane and *dihydroxy*-

tetraphenylmethane, $CPh_3{\cdot}C_6H_4(OH)_2$, m. p. 268°, respectively; with mercaptans in benzene or ethereal solution, however, the chloride acts as an acid chloride, yielding thio-ethers: *triphenylmethyl methyl sulphide*, m. p. 105°, from methyl mercaptan, *triphenylmethyl ethyl sulphide*, m. p. 125°, from ethyl mercaptan, and *phenyl triphenylmethyl sulphide*, m. p. 105°, from phenyl mercaptan. Triphenylmethyl chloride reacts with alcoholic *p* toluene-sulphinic acid at 130° to form acetaldehyde and triphenylmethane by the decomposition of the initially formed triphenylmethyl ethyl ether, and yields with sodium *p*-toluenesulphinate, in benzene, p-*tolyltriphenylmethylsulphone*, $CPh_3{\cdot}SO_2{\cdot}C_6H_4Me$, m. p. 173°, which is decomposed by water into triphenylcarbinol and *p*-toluenesulphinic acid. Triphenylmethyl chloride reacts in ether with magnesium benzyl chloride to form *triphenylbenzylmethane*, m. p. 140°, with magnesium *p*-chlorobenzyl chloride to form *triphenyl*-p-*chlorobenzylmethane*, m. p. 172°, and with magnesium phenyl bromide to form diphenyl and triphenylmethyl, the latter being obtained in the form of its peroxide.

[With A. NICOLAUS.]—Diphenylcarbamyl chloride and pyridine yield an additive compound, $C_5NH_5,NPh_2{\cdot}COCl$, m. p. 107°, which forms a *platinichloride*, decomp. 170°, *picrate*, m. p. 161°, and *iodide*, m. p. 182°. The formation of esters from diphenylcarbamyl chloride and alcohols only occurs very slowly; easily, however, in the presence of a little alkali or potassium cyanide; ethyl diphenylcarbamate has m. p. 72°, the corresponding *methyl* and *isopropyl* esters, 86° and 117° respectively.

Triphenylsemicarbazide (s-*Diphenylcarbamylphenylhydrazide*),

$$NHPh{\cdot}NH{\cdot}CO{\cdot}NPh_2$$

(*acetyl* derivative, m. p. 165°; *nitroso*-compound, m. p. 131°), is obtained readily from phenylhydrazine (2 mols.) and diphenylcarbamyl chloride in benzene, and is oxidised by alcoholic ferric chloride to *diphenylcarbamylazophenyl*, $NPh{:}N{\cdot}CO{\cdot}NPh_2$, m. p. 138°, red needles, which develops a deep red coloration with concentrated sulphuric acid. The interaction of diphenylcarbamyl chloride and aliphatic amino-acids is accomplished best by employing the latter in the form of their esters or sodium salts, acetone being used as solvents; thus α-*diphenylcarbamidopropionic acid*, $CO_2H{\cdot}CHMe{\cdot}NH{\cdot}CO{\cdot}NPh_2$, m. p. 149°, is obtained from alanine, and α-*diphenylcarbamidohexoic acid*,

$$CH_2Me{\cdot}[CH_2]_2{\cdot}CH(CO_2H){\cdot}NH{\cdot}CO{\cdot}NPh_2,$$

m. p. 52°, from leucine.

Ethyl o-*diphenylcarbamidobenzoate*, $CO_2Et{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NPh_2$, m. p. 108°, obtained by heating equal molecular quantities of ethyl anthranilate and diphenylcarbamyl chloride with an excess of zinc dust at about 100°, yields the free *acid*, m. p. 178°, by hydrolysis. The halogen in diphenylcarbamyl chloride is readily replaced by an alkyl or aryl group by the Grignard reaction; thus with magnesium ethyl iodide it yields *diphenylpropionamide*, m. p. 58°, with magnesium propyl bromide, *diphenylbutyramide*, m. p. 47°, and with magnesium phenyl bromide, *diphenylbenzamide*, m. p. 176°. *Diphenylcarbamyl cyanide*, $NPh_2{\cdot}CO{\cdot}CN$, m. p. 126°, obtained from the chloride and an excess of potassium cyanide at 180—200°, yields diphenylamine, hydrogen cyanide, and carbon dioxide by hydrolysis with alcoholic potassium hydroxide; it forms an *amido-oxime*, $NPh_2 \cdot CO \cdot C(NH_2) \colon NOH$, m. p. 222·5°, with alcoholic hydroxylamine at 60—80°, and is converted in alcoholic solution into the *thioamide*, $NPh_2 \cdot CO \cdot CS \cdot NH_2$, m. p. 220°, by hydrogen sulphide in the presence of aqueous ammonia.

[With FRAULEIN NÄBE.]—Cyanuric bromide is obtained in 70—80% yield by the action of nascent hydrogen bromide on a benzene solution of cyanogen bromide. Cyanuric bromide forms cyanuric trihydrazide with 10% hydrazine, cyanuric triphenylhydrazide with ethereal phenylhydrazine, and in boiling benzene reacts (*a*) with *o*-chloroaniline to form *cyanuric tri-o-chloroanilide* (*trichlorophenylmelamine*),

$$(CN)_3(NH \cdot C_6H_4Cl)_3,$$

m. p. 161°; (*b*) with 2 : 4-dichloroaniline to form *cyanuric tri-2 : 4-dichloroanilide*, m. p. 261°; (*c*) with *m*-nitroaniline to form *trinitrophenylmelamine*, $(CN)_3(NH \cdot C_6H_4 \cdot NO_2)_3$; (*d*) with *a*-naphthylamine to form *tri-a-naphthylmelamine*, $(CN)_3(NH \cdot C_{10}H_7)_3$, m. p. 225°; (*e*) with methylaniline to form *triphenyltrimethylmelamine*, $(CN)_3(NMePh)_3$, m. p. 115°; (*f*) with benzylaniline to form *triphenyltribenzylmelamine*, m. p. 120°; (*g*) with *p*-aminophenol to form *cyanuric di-p-hydroxyanilide bromide*, $(CN)_3(NH \cdot C_6H_4 \cdot OH)_2Br$, m. p. 275° (decomp.); (*h*) with *p*-anisidine to form a corresponding *anisidide*,

$$(CN)_3(NH \cdot C_6H_4 \cdot OMe)_2Br,$$

m. p. 250° (decomp.), and (*i*) with anthranilic acid to form the *substance*, $(CN)_3(NH \cdot C_6H_4 \cdot CO_2H)_2Br$, m. p. 197°. Cyanuric bromide and carbamide (3 mols.) at 130—140° yield *tricarbamylmelamine*,

$$(CN)_3(NH \cdot CO \cdot NH_2)_3,$$

m. p. above 300°.

Cyanuric bromide reacts in the normal way with aluminium chloride and an aromatic hydrocarbon in the presence of carbon disulphide, forming substances of the type: $(CN)_3Ar_3$; $Ar = Ph$, m. p. 231°; $Ar = p\text{-}C_6H_4Me$, m. p. 275—276°; $Ar = 3:4\text{-}C_6H_3Me_2$, m. p. 210°; $Ar = 2:4\text{-}C_6H_3Me_2$, m. p. 155°; $Ar = p\text{-}C_6H_4 \cdot OMe$, m. p. 115°; $Ar = a\text{-}C_{10}H_7$, m. p. 190—200°; the constitutions of these compounds (excluding the first) are determined by the fact that hydrolysis by hydrochloric acid at 200—220° yields *p*-toluic, 3 : 4-dimethylbenzoic, 2 : 4-dimethylbenzoic, anisic, and *a*-naphthoic acids respectively. The analogous triethyl compound, $(CN)_3Et_3$, obtained by Otto and Voigt from dichloropropionitrile is also produced by the interaction of cyanuric bromide and ethereal magnesium ethyl iodide. C. S.

Triarylmethyls. V. WILHELM SCHLENK and ANNA HERZENSTEIN (*Ber.*, 1910, **43**, 3541—3546. Compare Abstr., 1909, i, 791; 1910, i, 236, 237, 469).—According to the authors, the sole objection to the hexaphenylethane formula for the colourless form of triphenylmethyl lies in the comparative stability of the closely related pentaphenylethane. Investigation of the behaviour of the latter compound in high boiling solvents shows, however, that the remarkable power of dissociation characteristic of "colourless" triphenylmethyl is also shared by pentaphenylethane, although in a less marked degree.

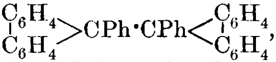
Solutions of pentaphenylethane in anisole or ethyl benzoate, on being heated rapidly to boiling, acquire the deep yellowish-brown colour of a hot solution of triphenylmethyl; on quickly cooling, the colour diminishes to a light yellow. The solution decolorises iodine, and at once becomes colourless when shaken with air; the colour, however, rapidly reappears, and finally vanishes only by repeated shaking with air. This behaviour so closely resembles that of triphenylmethyl solutions that there can be no doubt that triphenylmethyl is one of the products of dissociation of pentaphenylethane, $Ph_3C{-}|{-}CHPh_2$. The second dissociation product, diphenylmethyl, polymerises to tetraphenylethane, which can be readily isolated by boiling pentaphenylethane in ethyl benzoate solution in an atmosphere of nitrogen.

On passing oxygen through a boiling solution of pentaphenylethane in ethyl benzoate, the diphenylmethyl is oxidised to tetraphenylethylene.

A new method of formation of hexa-arylethanes is also described. When a concentrated benzene solution of molecular quantities of 4-phenyl-triphenylmethane and 4-phenyl-triphenylmethyl chloride is exposed to sunlight, it acquires a reddish colour, due to the formation of 4-phenyl-triphenylmethyl: $C_6H_4Ph\cdot CPh_2H + ClCPh_2\cdot C_6H_4Ph \rightleftarrows C_6H_4Ph\cdot CPh_2\cdots CPh_2\cdot C_6H_4Ph + HCl$.

The reaction is, however, reversible, the amount of 4-phenyltriphenylmethyl being very small when equilibrium is attained.

In a similar manner phenylbisdiphenylmethyl, $CPh(C_6H_4Ph)_2$, is obtained from phenylbisdiphenylmethane and phenylbisdiphenylmethyl chloride.

Diphenylbisdiphenylene-ethane,  $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>CPh\cdot CPh<\!\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}$, on account of its stability towards hydrochloric acid, is produced in quantitative yield by exposing a concentrated benzene solution of phenyldiphenylenemethyl chloride and phenyldiphenylenemethane (phenylfluorene) to the action of sunlight. F. B.

Hydrogenations in Presence of Palladium. Applications to Phenanthrene.

Pierre Breteau (*Compt. rend.*, 1910, **151**, 1368—1369).—By passing a mixture of phenanthrene vapour and hydrogen over spongy palladium at 160°, a mixture of the tetra- and octa-hydride is obtained; when hydrogenation is carried out at the ordinary temperature, in presence of palladium black suspended in *cyclo*hexane, only the tetrahydride is formed. Precipitated palladium, prepared by treating a solution of the chloride in hydrochloric acid with zinc, also yields the tetrahydride when brought into contact with phenanthrene in alcoholic solution. W. O. W.

Action of Concentrated Sulphuric Acid on Some Aromatic Nitroamines. II. Derivatives of Methylaniline, Methyl-*p*-anisidine, and Methyltoluidines.

Frédéric Reverdin (*Bull. Soc. chim.*, 1911, [iv], **9**, 43—49. Compare Abstr., 1910, i, 255).—Further instances are given of the reduction of the nitro- to the nitroso-group by sulphuric acid in certain aromatic nitro-derivatives, and it is shown that this reaction explains why such nitro-derivatives respond to Liebermann's test.

2 : 4 : 6-Trinitrophenylmethylnitroamine, on treatment with sulphuric acid at atmospheric temperature, furnishes picramide and some nitrosomethylpicramide (Bamberger and Müller, Abstr., 1900, i, 217). The latter is also produced if alcohol is used along with sulphuric acid,

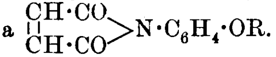
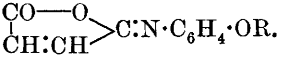
but in this case the principal product of the reaction is trinitromethylaniline.

Dimethyl-*p*-anisidine, on nitration in the cold, furnishes the N-*nitroso*-derivative of dinitromethyl-*p*-anisidine, m. p. 111—112°, but with hot nitric acid gives the N-*nitro*-derivative, m. p. 125°, which may also be obtained by the further action of nitric acid on the nitrosoamine, and, conversely, the latter is reproduced by the action of sulphuric acid on the nitroamine. Further, when the nitroamine is heated with phenol or the nitrosoamine is heated with hydrochloric acid, *dinitromethyl*-p-*anisidine*, m. p. 129°, is formed. By boiling the nitroamine with sodium hydroxide solution, a small yield of Weselsky and Benedikt's dinitroquinol methyl ether (Abstr., 1881, 1139) is obtained. The fact that this nitroamine, like that obtained from dimethyl-*o*-anisidine (Abstr., 1910, i, 255), gave the Liebermann reaction, led the author to examine nitroamines obtained from alkyltoluidines, and for this purpose 3 : 5-dinitro-*o*-tolylmethylnitroamine and its *p*-isomeride were prepared by the method described by van Romburgh (*Rec. trav. chim.*, 1884, **3**, 392). As secondary products in these preparations some 3 : 5-dinitro-2-nitromethylaminobenzoic acid and its 4-isomeride were obtained (Abstr., 1908, i, 167). These melted at 187° and 204° respectively. Both nitroamines gave Liebermann's reaction. The first on treatment with sulphuric acid at atmospheric temperature gives Stoermer's 3 : 5-dinitro-*o*-tolylmethylnitrosoamine (Abstr., 1899, i, 44), but is recovered unchanged from sulphuric acid at $-10°$. 3 : 5-Dinitro-*o*-tolylmethylnitroamine, with sulphuric acid at atmospheric temperature, furnishes 3 : 5-dinitro-2-nitromethylaminobenzoic acid (see above) and a *substance* crystallising in colourless needles and decomposing above 300°, but with sulphuric acid at $-10°$ it gives the same acid with, as chief product, 3 : 5-dinitro-*p*-tolylmethylnitrosoamine, m. p. 127—128° (compare van Romburgh, Abstr., 1896, i, 478). T. A. H.

The Reaction of Cellulose Nitrate with Dimethylaniline.

JOHANN WALTER (*Zeitsch. angew. Chem.*, 1911, **24**, 62—64).—Guncotton and celluloid absorb dimethylaniline, the colour gradually deepening through green and blue to violet. The coloration becomes darker on exposure to light, and is not removed by solvents. Strongly-coloured specimens have an odour of phenylmethylnitrosoamine. Other aromatic amines produce similar colorations, but less rapidly and of less intensity. C. H. D.

Velocities of Addition of Bromine to the Imides of Some Substituted Maleinamic Acids. II.

ARNALDO PIUTTI and G. CALCAGNI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], **16**, 255—261. Compare Abstr., 1909, i, 360).—Continuing their investigations on this subject, the authors have measured the velocities of addition of bromine to the following imides (compare Abstr., 1910, i, 672): hydroxyphenylmaleinimide (white form), methoxyphenylmaleinimide (white and yellow forms), ethoxyphenylmaleinimide (white and yellow forms). The velocity is very slow in all these cases; for the white imides, the reaction is complete in about fifty days, for the yellow forms in about seventy-five days. Since Bauer has shown that substance of this type the power of adding on bromine diminishes with increase in the number of negative groups, this forms an additional argument for assigning to the yellow form the symmetrical formula  $\left.\begin{array}{l}\mathrm{CH\cdot CO}\\ \mathrm{CH\cdot CO}\end{array}\right>\mathrm{N\cdot C_6H_4\cdot OR}$. The white isomerides behave as weak bases, and that is consonant with their having the constitution  $\left.\begin{array}{l}\mathrm{CO{-}O}\\ \mathrm{CH{:}CH}\end{array}\right>\mathrm{C{:}N\cdot C_6H_4\cdot OR}$. R. V. S.

Preparation of Alkali and Ammonium Salts of Nitrosoarylhydroxylamines. OSKAR BAUDISCH (D.R.-P. 227659).—Nitrosoarylhydroxylamines are known, but their salts have not previously been obtained; they are now prepared by either the oxidation of an amine or the reduction of a nitro-compound in alkaline solution in the presence of sodium nitrite, or an alkyl nitrite.

Ammonium nitrosophenylhydroxylamine, prepared from nitrobenzene, concentrated ammonium hydroxide, zinc dust, and amyl nitrite, crystallises in silvery leaflets, m. p. 163—164°, and sublimes readily.

The *sodium* salt, $C_6H_5\cdot N(NO)\cdot ONa$, and the *potassium* salt form snow-white needles; the *iron* salt crystallises in garnet-red needles or rosettes, with a blue, metallic lustre; it is insoluble in water, but soluble in the ordinary organic solvents; the *copper* salt forms dark grey crystals, and has similar properties. *Ammonium a-nitrosonaphthylhydroxylamine*, colourless leaflets, is rather unstable, turning pink in the light; it dissolves in water, and is converted on boiling into a-nitrosonaphthalene; the *sodium* and *potassium* salts are colourless; the *copper* salt, $(C_{10}H_7O_2N_2)_2Cu$, forms glistening, bluish-grey needles insoluble in water.

The formation of complex double salts of ammonium with copper, nickel, cobalt, or iron is also discussed. F. M. G. M.

Separation of *p*- and *m*-Nitro-*o*-anisidine. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 228357).—The nitration of aceto-*o*-anisidide yields a mixture of two isomeric nitroaceto-*o*-anisidides; these have previously been separated by the more ready hydrolytic dissociation of *p*-nitro-*o*-anisidine, which is precipitated by the addition of water to an acid solution of the mixed sulphates, whilst *m*-nitro-*o*-anisidine sulphate remains in solution.

It is now found that a separation can be effected by fractional crystallisation of the mixed sulphates; the mixture of *m*- and *p*-nitroaceto-*o*-anisidides is hydrolysed by heating with 70% sulphuric acid, and the mixture then diluted with hot water until the concentration of the sulphuric acid is reduced to 40%; on cooling, pure p-*nitro*-o-*anisidine sulphate* separates in colourless crystals, and the *m*-nitro-*o*-anisidine is precipitated from the filtrate by the addition of alkali.

F. M. G. M.

Preparation of Phenyl Ortho-oxalates. SCHÜLKE and MAYR (D.R.-P. 226231).—When dehydrated oxalic acid is mixed with fused phenol (2 mols.) at a temperature of about 40°, and then heated to 90—100° with continual stirring, pure *diphenyl ortho-oxalate*,

$OPh\cdot C(OH)_2\cdot C(OH)_2\cdot OPh$,

is obtained in quantitative yield; it crystallises from acetic acid, and has m. p. 126°. F. M. G. M.

Synthesis of Alcohols in the *cyclo*Hexane Series. Alphonse Mailhe and Marcel Murat (*Bull. Soc. chim.*, 1910, [iv], 7, 1083—1089). —The condensation of 1-methyl*cyclo*hexan-3-one with various magnesium alkyl haloids has been studied, and the alcohols obtained, and some of their derivatives are described (compare Sabatier and Mailhe, Abstr., 1906, i, 254; Murat, Abstr., 1909, i, 146).

1-Methyl-3-ethyl*cyclo*hexan-3-ol, D^0 0·9201, D^{20} 0·9013, n_D 1·459, b. p. 88°/20 mm., obtained by condensing 1-methyl*cyclo*hexan-3-one (Abstr., 1905, i, 275) with ethyl magnesium bromide, is a colourless liquid, with a feebly camphoraceous odour (compare Zelinsky, Abstr., 1901, i, 661); the *phenylurethane*, m. p. 98°, crystallises in colourless prisms; the *acetate*, D^0 0·9493, D^{20} 0·9303, n_D 1·441, b. p. 98—100°/20 mm., has a fruity odour. The alcohol is readily dehydrated, yielding 1-*methyl*-3-*ethyl*cyclo*hexene*, D^0 0·8366, D^{20} 0·8296, n_D 1·454, b. p. 149—151°/760 mm., a mobile, colourless liquid of pleasant odour; it gives a greenish coloration with sulphuric acid and alcohol, furnishes a *nitrosochloride*, m. p. 124—126°, and on reduction yields 1-*methyl*-3-*ethyl*cyclo*hexane*, D^0 0·8320, D^{20} 0·8213, n_D 1·460, b. p. 145—146°. 1-Methyl-3-propyl*cyclo*hexan-3-ol, D^0 0·9063, D^{15} 0·8961, n_D 1·461, b. p. 96—98°/20 mm., is a colourless, viscous liquid (Zelinsky, *loc. cit.*); it yields a *phenylurethane*, m. p. 112°, and an *acetate*, D^0 0·9367, D^{20} 0·9248, n_D 1·454, and b. p. 108—110°/20 mm., which is colourless and has a fruity odour. The alcohol is readily dehydrated, yielding 1-*methyl*-3-*propyl*cyclo*hexene*, D^0 0·8375, D^{15} 0·8302, n_D 1·456, and b. p. 168—171°/760 mm., which absorbs bromine and gives a yellowish-green colour with alcohol and sulphuric acid, furnishes a *nitrosochloride*, m. p. 128—131° (decomp.), and on reduction gives 1-*methyl*-3-*propyl*cyclo*hexane*, b. p. 164—165°.

1-*Methyl*-3-iso*butyl*cyclo*hexan*-3-*ol*, D^0 0·9011, D^{19} 0·8972, n_D 1·465, b. p. 107—109°/20 mm., is best obtained by condensing magnesium *iso*butyl chloride with methyl*cyclo*hexanone, although the secondary reaction already described (Abstr., 1905, i, 706) occurs and occasions some loss. The alcohol is viscous and dehydrates easily, giving an *ethylenic hydrocarbon*, b. p. 192—195°, having a somewhat alliaceous odour.

1-*Methyl*-3-iso*amyl*cyclo*hexan*-3-*ol*, D^0 0·8982, D^{22} 0·8856, n_D 1·464, b. p. 126—127°/20 mm., is a viscous, colourless, pleasant-smelling liquid; the *phenylurethane*, m. p. 128°, is crystalline, and the *acetate*, D^{20} 0·9146, n_D 1·457, b. p. 140°/20 mm., is a thick liquid with a pleasant odour. The alcohol on dehydration gives 1-*methyl*-3-iso*amyl*cyclo*hexene*, D^0 0·8301, D^{20} 0·8190, n_D 1·459, b. p. 209—211°/760 mm., which gives a greenish coloration with sulphuric acid and alcohol, yields a *nitrosochloride*, m. p. 136°, and on reduction furnishes 1-*methyl*-3-iso*amyl*cyclo*hexane*, b. p. 205°, a colourless liquid with an odour recalling that of petrol.

3-cyclo*Hexyl*-1-*methyl*cyclo*hexan*-3-*ol*, D^0 0·9815, D^{18} 0·9685, n_D 1·495, b. p. 153—155°/20 mm., is a viscous liquid of agreeable aroma, yields a *phenylurethane*, m. p. 141°, gives an intense blue coloration with bromine in chloroform, and on dehydration furnishes 3-cyclo*hexyl*-1-*methyl*cyclo*hexene*, D^0 0·9634, D^{18} 0·9138, n_D 1·492, b. p. 240°/760 mm., a mobile liquid which is scarcely coloured by sulphuric acid and alcohol, but gives a *nitrosochloride*, m. p. 142—146°, which is possibly a mixture of isomerides.

3-*Phenyl*-1-*methyl*cyclo*hexan*-3-*ol*, m. p. 61°, b. p. 153°/20 mm. (decomp.), crystallises in monoclinic prisms, yields a *phenylurethane*, m. p. 143°, and on dehydration furnishes 3-*phenyl*-1-*methyl*cyclo*hexene*, D^0 0·9859, D^{20} 0·9702, n_D^{20} 1·555, and b. p. 145°/20 mm., as a colourless, mobile liquid, which absorbs bromine, and with sulphuric acid and alcohol gives a rose-red coloration.

3-*Benzyl*-1-*methyl*cyclo*hexan*-3-*ol*, D^0 1·0032, D^{17} 0·9873, n_D 1·532, b. p. 165°/18 mm. (decomp.), is a colourless liquid, having a lemon-like odour, and is obtained in small yields by condensing methyl*cyclo*hexanone with benzyl magnesium chloride, the chief product being dibenzyl. 3-*Benzyl*-1-*methyl*cyclo*hexene*, D^0 0·9693, D^{20} 0·9591, n_D 1·547, b. p. 156°/20 mm. or 271°/760 mm., is colourless, and has a disagreeable odour. T. A. H.

A Solid Molecular Compound of Hexamethylenetetramine and Guaiacol. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 225924).—The preparation of a hexamethylenetetraminetriguaiacol has been previously described (Abstr., 1910, i, 378). A compound obtained in a similar manner and with identical properties is now found to have tho composition of a hexamethylenetetraminediguaiacol, and it is suggested that the former compound was possibly not an individual substance. F. M. G. M.

Fermentation of Tyrosine to *p*-Hydroxyphenylethanol (Tyrosol). FELIX EHRLICH (*Ber.*, 1911, **44**, 139—146. Compare Abstr., 1907, ii, 384).—A 60—80% yield of *p*-hydroxyphenylethanol, $OH\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot OH$, can be obtained by the fermentation of tyrosine with large amounts of yeast in the presence of much sugar and of nutritive salts. Small amounts of acids are also formed; these are soluble in ether, and give Millon's reaction. The hydroxy-alcohol is termed *tyrosol*. It crystallises in long, glistening needles and rods of rhombic habit; it has m. p. 93° and b. p. 310°. It has a bitter taste, does not reduce Fehling's solution, and gives a Bordeaux-red coloration when warmed with concentrated sulphuric acid. With ferric chloride solution it gives an indigo-blue coloration, and with Millon's reagent, and also with diazobenzenesulphonic acid, dark red colorations. It does not give the Piria reaction, but develops an intense yellowish-green coloration with formaldehyde and sulphuric acid. It is oxidised by alkaline permanganate solutions, reacts with phosphorus pentachloride, yielding a yellow oil, and also forms an oily acetyl derivative. The *dibenzoyl* derivative, $C_{22}H_{18}O_4$, prepared by the Schotten-Baumann method, crystallises from alcohol in felted needles, m. p. 111°.

The formation of tyrosol is brought about by either top or bottom yeasts. It is also formed in appreciable amounts when a sterilised solution of tyrosine and sugar is inoculated with pure cultures of yeast, and in small amounts during the fermentation of pure sugar solutions by pure yeasts. Its formation in the latter case is due to the autolysis of the dead yeast cells and the formation of tyrosine, which is used as nitrogenous nutritive material by the living cells and transformed into tyrosol. It is not formed in the absence of sugars.

Tyrosol thus appears to be a by-product in most processes of fermentation by yeast, and is present in all fermented liquors, especially in beer and wine, the flavours of which are due, in part, to the presence of the hydroxy-alcohol. J. J. S.

Preparation of Nitrobenzoic Acids from the Corresponding Nitrotoluenes. GUSTAV LÜTTGEN (D.R.-P. 226225).—The oxidation of nitrotoluenes to the corresponding nitrobenzoic acids with nitric and sulphuric acids is not satisfactory; it is now found that the reaction proceeds smoothly in nitric acid solution with potassium chlorate as the oxidising agent. 2 : 4 : 6-Trinitrotoluene was dissolved in concentrated nitric acid (48 Bé), and warmed to 90—95°; potassium chlorate (2 parts) was gradually stirred in, the temperature being maintained meanwhile at 100—120°; pure trinitrobenzoic acid separated from the reaction mixture on cooling. F. M. G. M.

Synthesis of Compounds of the Normal Amyl Series from Piperidine. JULIUS VON BRAUN and W. SOBECKI (*Ber.*, 1910, **43**, 3596—3599).—Although benzo-ϵ-chloroamylamide, derived from piperidine, is very stable, the corresponding benzoiodoamylamide is relatively easily reduced. It is prepared from the chloro-compound by boiling this with sodium iodide in alcohol, and is dissolved in much concentrated hydrochloric and acetic acid, cooled, and stirred with zinc dust for a number of hours.

Benzo-n-amylamide separates as an oil, and is purified by distillation; b. p. 208—210°/15 mm. It is readily hydrolysed to *n*-amylamine, or when distilled with phosphorus pentachloride or pentabromide is converted into *n*-amyl chloride or bromide respectively. To prove that the normal carbon-chain structure had remained intact, the bromide was boiled with potassium cyanide and converted into the nitrile of *n*-hexoic acid. E. F. A.

Secondary Anthranilic Acids and the Transformation of their Nitroso-derivatives into a Peculiar Class of Intensely Red Substances, Soluble in Water. JOSEF HOUBEN and TH. ARENDT (*Ber.*, 1910, **43**, 3533—3541. Compare Abstr., 1908, i, 27; 1909, i, 645, 794).—Previous attempts to nitrosylate methyl dimethylanthranilate failed. The authors now find that the action of sodium nitrite and fuming hydrochloric acid on the ester yields 5-nitroso-*N*-methylanthranilic acid, one of the methyl groups being split off from the nitrogen atom.

When 5-nitroso-*N*-methylanthranilic acid is dissolved in sodium carbonate and shaken with acetic anhydride, a red substance is formed, which is very soluble in water. Similar red products have been obtained by the action of various acid chlorides and anhydrides, either in aqueous or pyridine solution, on a large number of nitroso-derivatives of secondary anthranilic acids and their esters, and also on quinoneoximecarboxylic acid, but only in one instance has the product been isolated.

When 5-nitroso-*N*-methylanthranilic acid is shaken with pyridine and acetic anhydride, a red solution is formed, from which, by the addition of ether, a brownish-red *pyridine* salt, $C_{15}H_{15}O_4N_3$, is precipitated; the salt is very soluble in water, forming blood-red solutions, and melts with decomposition to a dark red liquid.

[With L. Ettinger.]—N-*Acetonylanthranilic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot COMe,$$

prepared by dissolving anthranilic acid in the equivalent quantity of potassium carbonate and boiling the solution with chloroacetone, has m. p. 169—170°; the *nitrosamine*, which forms white crystals, m. p. 115—116° (decomp.), could not be transformed into 5-nitroso-*N*-acetonylanthranilic acid by the action of hydrochloric acid; the *semicarbazone*, $CO_2H\cdot C_6H_4\cdot NH\cdot CH_2\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2$, obtained from the *sodium bisulphite* compound of acetonylanthranilic acid, has m. p. 240—241° (decomp.).

Methylacetonylanthranilic acid, $CO_2H\cdot C_6H_4\cdot NMe\cdot CH_2\cdot COMe$, prepared from methylanthranilic acid and chloroacetone, crystallises in small, light grey needles, m. p. 123—126°.

2 : 4-*Dinitrodiphenylmethylamine-2′-carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot NMe\cdot C_6H_3(NO_2)_2,$$

is obtained by boiling 4-chloro-1 : 3-dinitrobenzene with methylanthranilic acid in aqueous potassium carbonate; it forms clusters of yellow needles, m. p. 178°. F. B.

Action of Ethereal Salts on the Monosodium Derivative of Phenylacetonitrile. F. Bodroux (*Compt. rend.*, 1910, **151**, 1357—1359. Compare Abstr., 1910, i, 623).—Ethyl benzoate condenses with the sodium derivative of phenylacetonitrile to give a 75% yield of cyanophenylacetophenone, $CN\cdot CHPh\cdot COPh$, lamellæ, m. p. 93—94° (compare Walther and Schickler, Abstr., 1897, i, 522). Ethyl carbonate in the same way forms ethyl cyanophenylacetate, $CN\cdot CHPh\cdot CO_2Et$, b. p. 163—165°/19 mm., D^{17} 1·085, the yield being 55%. Ethyl oxalate yields a small quantity of ethyl cyanophenylpyruvate. The foregoing cyano-derivatives are sufficiently acidic to be capable of titration, using phenolphthalein as indicator.

W. O. W.

Crystallographic Examination of Some Nitrophenylmethylacrylic Derivatives. Francesco Ranfaldi (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], **16**, 225—234).—β-*o*-Nitrophenyl-α-methylacrylic acid, $NO_2\cdot C_6H_4\cdot CH{:}CMe\cdot CO_2H$, forms monoclinic, prismatic crystals [$a:b:c = 1·3446 : 1 : 1·4562$; $\beta = 92°24'51''$]. β-*m*-Nitrophenyl-α-methylacrylic acid forms colourless, acicular crystals, which could not be obtained in a measurable form. β-*p*-Nitrophenyl-α-methylacrylic acid forms triclinic, pinacoidal crystals [$a:b:c = 1·2867 : 1 : 1·4602$; $\alpha = 84°42'8''$; $\beta = 83°31'31''$, $\gamma = 87°35'18''$]. Sodium β-*o*-nitrophenyl-

a-methylacrylate forms rhombic, disphenoidal crystals [$a:b:c = 1\cdot3940:1:2\cdot0544$]. R. V. S.

Preparation of Glycol Monosalicylate. C. F. BOEHRINGER & SÖHNE (D.R.-P. 225984. Compare Abstr., 1908, i, 176).—The esterification of salicylic acid with ethylene chlorohydrin yields *β-chloroethyl salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2Cl$, which on careful hydrolysis with mild reagents gives the therapeutically valuable *glycol salicylate*, $OH\cdot C_6H_4\cdot CO_2\cdot CH_2\cdot CH_2\cdot OH$.

The hydrolytic agents described as suitable are (1) sodium acetate and dilute acetic acid; (2) disodium phosphate and water, or (3) sodium salicylate and water, a sealed tube being employed and a temperature of 130° maintained in each case. F. M. G. M.

Pyrogenetic Decomposition of *cyclo*Gallipharic Acid. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Arch. Pharm.*, 1910, **248**, 695—709. Compare Abstr., 1904, i, 587; 1910, i, 458, 677).—The decomposition of *cyclo*gallipharic acid when heated alone or with various dehydrating agents has been studied, and the results correlated with those recorded in previous papers (*loc. cit.*).

When heated with potassium hydrogen sulphate, the acid furnishes unsaturated gaseous hydrocarbons, acraldehyde, *cyclo*gallipharol, and 4-hydroxy-*m*-xylene.

Sulphuric acid is without action on *cyclo*gallipharic acid in the cold, but on heating with this reagent, it is converted into the keto-anhydride of *cyclo*gallipharic acid at 125—130°; at 150—160° some *cyclo*gallipharol is formed, and at 180° this substance is the sole product of the reaction.

When heated alone, the temperature being gradually raised from 130° to 250°, the amounts of carbon dioxide evolved indicate that the acid undergoes the same progressive decomposition as with sulphuric acid, the same stages, however, being reached at somewhat higher temperatures. Above 250° complete decomposition into carbon dioxide and volatile hydrocarbons takes place. In conclusion, a summary of the results recorded in this and the two preceding papers of the series is given. T. A. H.

Preparation of Carvacrolphthalein. CURT EHRLICH (D.R.-P. 225983).—*Carvacrolphthalein*, colourless, transparent needles, m. p. 246—247°, is prepared by heating phthalic anhydride (1 part) with carvacrol (2 parts) and stannic chloride (2 parts) at 100° during two hours. It is insoluble in water, soluble in sodium hydroxide with a deep blue colour, and compares very favourably with phenolphthalein as an indicator. F. M. G. M.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXIII. Trimellitic Acid. RUDOLF WEGSCHEIDER, HEINRICH FELIX PERNDANNER, and OTTO AUSPITZER (*Monatsh.*, 1910, **31**, 1253—1301).—The formation of acid esters of trimellitic acid (benzene-1 : 2 : 4-tricarboxylic acid) by different methods has been studied in order to determine whether the rules previously laid down for dibasic acids hold good. The investigation was complicated by the fact that the three carboxyl groups differ but little from one another, and therefore mixtures of acid esters are obtained by each method; these mixtures cannot be separated readily into their constituents. They do not crystallise well, and several of them tend to form mixed crystals. The 1 : 4- and 2 : 4-dimethyl esters crystallise extremely slowly, and are usually obtained as syrups, although from their constitutions their m. p.'s should be relatively high. The constitution of the 4-methyl ester,

$$CO_2Me \cdot C_6H_3 \cdot (CO_2H)_2\ [(CO_2H)_2 \colon CO_2Me = 1:2:4],$$

follows from the fact that it is formed by the addition of water to the methyl ester of the anhydro-acid, $CO_2Me \cdot C_6H_3 \colon (CO)_2O$, and the constitutions of the two isomeric monomethyl esters were determined by conversion into the corresponding amidedicarboxylic acid and then by means of bromine and potassium hydroxide, transforming the amides into amino*iso*- and aminotere-phthalic acids. The constitution of the dimethyl esters was determined by the elimination of carbon dioxide from their potassium salts in the presence of lime.

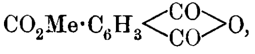
The products formed by the esterification of the acid, both by the direct and by the catalytic method, could not be obtained pure, with the exception of small amounts of the 1- and 2-monomethyl esters, but the fact that the syrups obtained yield appreciable amounts of the methyl ester of anhydrotrimellitic acid points to the conclusion that by these methods the carboxyl groups in position 4, that is, the carboxyl group least affected by "steric hindrance," is first esterified. The 1- and 2-monomethyl esters, under similar conditions, yield the 1 : 4- and 2 : 4-dimethyl esters, and but little 1 : 2-dimethyl ester. By partial hydrolysis of the normal ester with potassium hydroxide, the 1 : 2-dimethyl ester is first formed, and, by further hydrolysis, the 2-monomethyl ester, with smaller amounts of the isomeric 1-ester. By the addition of methyl alcohol to the acid anhydride, both the 1- and 2-monomethyl esters are formed, but, at the same time, the carboxylic group in position 4 is esterified to a slight extent. The mono-silver salt with methyl iodide yields mainly 1-methyl, together with the 2-methyl ester, and the disilver salt yields mainly 1 : 2-dimethyl ester. These results agree on the whole with the generalisation that in the formation of acid esters from the acid by esterification, or from neutral esters by hydrolysis, steric hindrance is the determining factor, whereas in the formation from the anhydride or from the acid metallic salts, the relative strengths of the carboxyl groups are of first importance.

Full details of the methods used for separating the mixtures obtained in each experiment are given.

Methyl hydrogen *iso*phthalate has m. p. 167—169°, and not 126° as stated by Meyer (*Monatsh.*, 1901, **22**, 437).

A 20% yield of trimellitic acid can be obtained by the action of nitric acid on French colophony (compare Scheder, *Ann. Chem. Pharm.*, 1874, **172**, 94), provided the mother liquors are worked up. It has not been found possible to prepare the acid from naphthol yellow-*S* by Ree's method (Trans., 1886, **49**, 510), but Schultz' method (Abstr., 1909, i, 897) gives fairly good yields if the chromic anhydride is added gradually. The m. p. depends on the method of heating; when dipped into a bath at 200°, it has m. p. 215—217° in an open tube or 229—234° in a closed tube. A 2% solution of the normal ammonium salt gives precipitates with solutions of mercuric, cadmium, lead, ferric, aluminium, uranyl, and silver salts.

The following acid salts have been prepared: $CO_2H\cdot C_6H_3(CO_2Ag)_2$, slender needles from hot water; $CO_2Ag\cdot C_6H_3(CO_2H)_2$; $C_9H_4O_6Ba,H_2O$, insoluble in water.

The 1-*monomethyl* ester, $C_{10}H_8O_6$, is most readily prepared from the mono-silver salt, and is most conveniently separated from the free acid by precipitating the latter in the form of its barium salt; it may be purified by the addition of benzene to its ethereal solution, and has m. p. 203·5—205·5°, but frequently melts to a certain extent at 177°, resolidifies at 179°, and then melts at the higher temperature given. The two m. p.'s are probably due to dimorphism. When mixed with the isomeric 2-*monomethyl* ester, its m. p. is not appreciably affected. The latter ester is best prepared by the partial hydrolysis of the 1 : 2-dimethyl ester; it is sparingly soluble in water, whereas the 1-ester dissolves readily, and crystallises from this medium as a colourless powder, m. p. 208°. The 4-methyl ester is most readily obtained by the addition of water to the methyl ester of the anhydro-acid, and crystallises from water in compact plates, m. p. 145—147°. The *anhydro*-ester,  $CO_2Me\cdot C_6H_3<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O$, has m. p. 94—99°, is transformed into a syrup by the addition of a little alcohol, and when kept for some time, even in a desiccator, yields the 4-monomethyl ester. The 1 : 2-*dimethyl* ester, $C_{11}H_{10}O_6$, crystallises from carbon tetrachloride, or better from a mixture of ether and light petroleum, in nodular masses of needles, m. p. 115·5—117° after softening at 108°; when slowly heated above the m. p., the ester resolidifies, and then has m. p. 121°. It has b. p. 200°/12 mm. The 1 : 4- and the 2 : 4-dimethyl esters are both syrups, and the solution of the ammonium salt of the former gives a precipitate with concentrated solutions of copper sulphate, whilst that of the latter is precipitated even in dilute solution. The trimethyl ester has b. p. 194°/12 mm. (corr.), and solidifies in a freezing mixture at −13° to a vitreous mass.

The 1-*amide*, $NH_2\cdot CO\cdot C_6H_3(CO_2H)_2$, is obtained by heating the corresponding ester with a concentrated solution of ammonia in methyl alcohol at 100° for one and a-half hours, then acidifying, removing trimellic acid by extracting with ether, and extracting several times with amyl alcohol. After removal of the amyl alcohol and recrystallising the residue from a mixture of methyl alcohol and benzene, the amide is obtained pure, and has m. p. 185—186°. The isomeric 2-*amide*, obtained by a similar method, has m. p. 199—200°. The 1-amide reacts with bromine and alkali, yielding 4-amino-*iso*phthalic acid, which was isolated in the form of its methyl ester (m. p. 130°). The 2-amide under similar conditions yields aminoterephthalic acid, which was isolated as its methyl ester, m. p. 123—126° (Cahn-Speyer, Abstr., 1907, i, 849, gives m. p. 133°). By the action of a methyl-alcoholic solution of ammonia on the anhydro-acid, a mixture of the 1- and 2-amides is obtained. J. J. S.

Ring Synthesis of Pyromellitic Acid. FRANZ FEIST (*Ber.*, 1911, **44**, 135—138).—Small amounts of pyromellitic acid (14% yield) are formed according to the equation: $2CO_2Et\cdot CH_2\cdot CHBr\cdot CHBr\cdot CO_2Et + 8KOH = C_6H_2(CO_2K)_4 + 4KBr + 4EtOH + 4H_2O + H_2$ when ethyl $\alpha\beta$-dibromoglutarate is mixed with alcoholic potassium hydroxide solution. The acid is isolated by acidifying the potassium salt and extracting eighteen times with ether. It is accompanied by large quantities of oily impurities, which can be removed by stirring with a small amount of ether in which the impurities dissolve. The anhydrous acid has m. p. 275°, and the tetramethyl ester, m. p. 141·5°.

J. J. S.

Preparation of Diglycollyldisalicylic Acid. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (D.R.-P. 227999).—*Diglycollyldisalicylic* [o-*diglycollyloxybenzoic*] *acid*, $O(CH_2\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H)_2$, glistening leaflets, m. p. 168—170°, is readily prepared by boiling salicylic acid (or a salicylate) in benzene solution with diglycollic anhydride in the presence of an indifferent base (such as pyridine); it is of therapeutic importance, and compares favourably with acetylsalicylic acid in this respect.

F. M. G. M.

An *o*-Hydroxyaldehyde of Triphenylcarbinol. AUGUST BISTRZYCKI and MARTIN FELLMANN (*Ber.*, 1910, **43**, 3579—3586).—Salicylaldehyde can be condensed with benzylic acid, forming 4-hydroxy-3-aldehydotriphenylacetic acid (Abstr., 1910, i, 321), and this by the elimination of carbon dioxide is readily converted into 4-hydroxy-3-aldehydotriphenylcarbinol, which is the third aldehyde of the triphenylmethane series to be described.

4-Hydroxy-3-aldehydotriphenylacetic acid, prepared by the condensation of the components in benzene in presence of tin tetrachloride, crystallises, $+\frac{1}{2}C_7H_8$, in microscopic prisms or needles, m. p. 198—200° (from toluene), or in stellar aggregates of prisms, $+\frac{1}{2}C_6H_6$, m. p. 197—198° (from benzene).

The *azine*, $N_2[:CH\cdot C_6H_3(OH)\cdot CPh_2\cdot CO_2H]_2$, derived from the action of hydrazine sulphate and sodium carbonate, is a yellow powder (decomp., 270—280°); the *sodium* salt crystallises in slender, yellow needles. The *oxime* crystallises in microscopic, colourless needles, which turn yellow at 110°, m. p. 226° (decomp.). The *semicarbazone* forms bunches of microscopic, slender, prismatic needles, m. p. 198—199° (decomp.). The *aniline* derivative is a granular, yellow powder, m. p. 85—86° (decomp.).

Methyl 4-*methoxy*-3-*aldehydotriphenylacetate*, prepared by the action of methyl sulphate in cold sodium hydroxide solution, crystallises in bunches of faintly yellow-coloured, four-sided prisms, m. p. 148—149°.

4-*Benzoxy*-3-*aldehydotriphenylacetic acid* crystallises in concentrically-grouped, colourless needles, m. p. 195·5—196·5°.

4-Hydroxy-3-aldehydotriphenylcarbinol (*loc. cit.*), prepared by the action of concentrated sulphuric acid on the aldehydo-acid, crystallises in aggregates of light yellow, prismatic plates, m. p. 123—124°, decomp. at 170°. The solution in concentrated sulphuric acid is orange-red; a second isomeric form could not be obtained. The *acetyl* derivative crystallises in reniform aggregates of colourless prisms, m. p. 131—132°, the fused mass being orange-yellow. The *phenylhydrazone* forms rounded aggregates of microscopic prisms, decomp. 177°. The *oxime* separates in bunches of colourless, flat prisms; on heating, it becomes yellow and softens at 95°, becomes colourless, and solid again at 102°, m. p. 151° (decomp. 175°). The *semicarbazone* crystallises in colourless, microscopic needles, which become yellow at 140° and decompose at 164°, with an intense red coloration.

On heating the hydroxyaldehydocarbinol in a stream of dry air in a sulphuric acid bath at 190—200°, the anhydride, 2-*aldehydodiphenylquinomethane*, $CPh_2{:}C_6H_8O\cdot CHO$, is obtained as a brown powder. This darkens in colour at 100°, and begins to melt indefinitely at a somewhat higher temperature. E. F. A.

Hexahydroacetophenone [*cyclo*Hexyl Methyl Ketone] and Hexahydrobenzoylacetone. MARCEL GODCHOT (*Compt. rend.*, 1910, **151**, 1131—1134).—Adipic acid is the sole product of the oxidation of *cyclo*hexyl methyl ketone by alkaline potassium permanganate. *cyclo*Hexyl methyl ketone (Bouveault, Abstr., 1904, i, 61) forms an *oxime*, b. p. 145—150°/20 mm., m. p. 60°; no isomeric form was detected. It undergoes the Beckmann change, forming *acetylamino*cyclo*hexane* (*hexahydroacetanilide*), $C_6H_{11}\cdot NHAc$, crystallising in needles, m. p. 103°, identical with the product obtained by acetylating *cyclo*hexylamine.

Hexahydrobenzoylacetone, $C_6H_{11}\cdot CO\cdot CH_2\cdot COMe$, is obtained in the form of its *sodium* salt by the addition of sodium ethoxide to a mixture of *cyclo*hexyl methyl ketone and ethyl acetate. The diketone has b. p. 103—105°/25 mm., D^{15} 0·9933, and was prepared in the pure state from its *copper* derivative, which crystallises in pale green needles m. p. 210°; the phenylhydrazone and oxime appear to be oily. W. O. W.

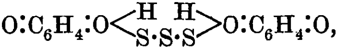
Ketones Derived from *o*-, *m*-, and *p*-Toluic Acids. JEAN B. SENDERENS (*Compt. rend.*, 1911, **152**, 90—92. Compare Abstr., 1909, i, 286, 627; 1910, i, 11, 179, 489).—The under-mentioned ketones have been prepared by passing the vapour of an aromatic and an aliphatic acid over thorium oxide at 460—470°. A single distillation of the product usually suffices to yield the aromatic ketone in a state of purity. The new ketones are liquids; their odour resembles that of citrons in the case of the ortho-compounds, and of fennel in the case of the para-derivatives; the odour of the meta-compounds is not characteristic. The b. p.'s given are corrected.

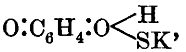
o-Tolyl methyl ketone, b. p. 211°/745 mm., D^0_4 1·0262; *semicarbazone*, m. p. 192°. *m*-Tolyl methyl ketone, b. p. 221°/745 mm., D^0_4 1·0165; *semicarbazone*, m. p. 188° (decomp.). *p*-Tolyl methyl ketone, b. p. 224·5°/745 mm., D^0_4 1·0150; *semicarbazone*, m. p. 200°. *o*-Tolyl ethyl ketone, b. p. 224°/745 mm., D^0_4 1·0119; *semicarbazone*, m. p. 169°. *m*-Tolyl ethyl ketone, b. p. 234°/745 mm., D^0_4 1·0059; *semicarbazone*, m. p. 166°. *p*-Tolyl ethyl ketone, b. p. 238°/745 mm., D^0_4 1·0053; *semicarbazone*, m. p. 180°. *o-Tolyl propyl ketone*, b. p. 238·5°/758 mm.,

D_4^0 0·9936; *semicarbazone*, m. p. 176°. m-*Tolyl propyl ketone*, b. p. 247°/758 mm., D_4^0 0·9882; *semicarbazone*, m. p. 152°. p-*Tolyl propyl ketone*, b. p. 251·5°/758 mm., D_4^0 0·9774; *semicarbazone*, m. p. 190°. o-*Tolyl* iso*propyl ketone*, b. p. 230°/758 mm., D_4^0 0·9858; the *semicarbazone* is an oil. m-*Tolyl* iso*propyl ketone*, b. p. 238°/758 mm., D_4^0 0·9841; *semicarbazone*, m. p . 120°. p-Tolyl *iso*propyl ketone, b. p. 243°/758 mm., D_4^0 0·9778; *semicarbazone*, m. p. 101°. o-*Tolyl* iso*butyl ketone*, b. p. 247·5°/758 mm., D_4^0 0·9744; *semicarbazone*, m. p. 166°. m-*Tolyl* iso*butyl ketone*, b. p. 254°/758 mm., D_4^0 0·9712; *semicarbazone*, m. p. 172°. p-*Tolyl* iso*butyl ketone*, b. p. 259°/758 mm., D_4^0 0·9707; *semicarbazone*, m. p. 212°.
W. O. W.

Quinones. HERMANN HAAKH (*J. pr. Chem.*, 1910, [ii], **82**, 546—551).—A theoretical paper in which an attempt is made to account for the recent numerous examples of the formation of highly-coloured additive compounds of *p*-benzoquinone with inorganic acids and salts, aromatic hydrocarbons, and other substances. The author assumes that the comparatively feebly-coloured *p*-benzoquinone itself has Graebe's peroxide constitution, in which the oxygen atoms have no residual affinity; when it forms highly-coloured additive compounds, the quinone acquires the Fittig constitution, addition occurring by means of the residual affinity of the oxygen atoms.
C. S.

Oxonium Hydrosulphides of *p*-Benzoquinone. M. M. RICHTER (*Ber.*, 1910, **43**, 3599—3603).—On mixing hydropersulphide and *p*-benzoquinone in anhydrous solvents at the ordinary temperature, a voluminous, brilliantly blue compound is obtained, which is labile in character and under certain conditions changes to a faintly yellow substance. The blue compound is obtained in presence of an excess of benzoquinone, the yellow with an excess of hydropersulphide.

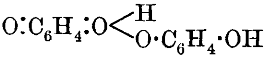
The amorphous indigo-blue substance, *bis*-p-*benzoquinoneoxonium hydrotrisulphide*,  $\mathrm{O{:}C_6H_4{:}O}{<}\substack{\mathrm{H\ \ H}\\ \mathrm{S{\cdot}S{\cdot}S}}{>}\mathrm{O{:}C_6H_4{:}O}$, decomposes at 115°, or when exposed to moisture. It dissolves in anhydrous solvents with an orange coloration, but is more or less decomposed.

By the action of *p*-benzoquinone dissolved in carbon disulphide and potassium hydrosulphide in absolute alcohol in a stream of hydrogen, p-*benzoquinoneoxonium hydrosulphide*,  $\mathrm{O{:}C_6H_4{:}O}{<}\substack{\mathrm{H}\\ \mathrm{SK}}$, is obtained as a dark greenish-black powder, extremely sensitive to traces of moisture.

Trisquinhydroneoxonium hydrosulphide, $C_{36}H_{32}O_{12}S$, is obtained by passing dry hydrogen sulphide through a solution of quinone in formic acid. It is a microcrystalline, almost black powder, decomp. 140°. The same compound is obtained on passing dry hydrogen sulphide over fused *p*-benzoquinone.

Hydropersulphide does not combine with substituted quinones; the entry of substituents, particularly of strongly negative groups, into the quinone molecule weakens the basic properties of oxygen and prevents salt formation.
E. F. A.

Constitution of Quinhydrone-like Substances. M. M. Richter (*Ber.*, 1910, **43**, 3603—3611).—The characteristics of oxonium salts, namely, simple addition of the components in their formation, ready decomposition in solution or when sublimed, and marked increase in the intensity of the colour, are also those of the quinhydrones. It is suggested that quinhydrones, phenoquinones, alloxantin, etc., are all to be regarded as oxonium compounds, and their dissociative and colour properties are due to quadrivalent oxygen and quinquevalent nitrogen. *p*-Benzoquinone has been shown (compare Siegmund, Abstr., 1909, i, 109; Meyer, *ibid.*, i, 395) to combine both with one and with two molecules of mono- and di-hydroxyphenols.

The evidence in favour of the formula  $\mathrm{O{:}C_6H_4{:}O}{<}\begin{matrix}\mathrm{H}\\ \mathrm{O\cdot C_6H_4\cdot OH}\end{matrix}$ for quinhydrone is discussed.

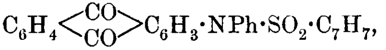
Two more must be added to the characteristics of the quinhydrones already enumerated, namely, they are composed of quinonoid and benzenoid sections, and they have the power of forming salts. The entry of substituting groups, particularly those of a strongly negative nature, into the quinone molecule materially lessens the basic properties of the oxygen atom, and in consequence prevents salt and quinhydrone formation.

Thirteen compounds are enumerated of six main types which are quinhydrone compounds of *p*-phenylenediamine, benzidine, and *p*-benzoquinonedichlorodi-imine.

It is considered that the simple oxygen atom generally behaves as a quadrivalent atom. E. F. A.

Preparation of *N*-Alkyl- and *N*-Arylaryl-sulphaminoanthraquinones. Fritz Ullmann (D.R.-P. 227324).—By the action of alkylsulphonamides of the general formula $R\cdot NH\cdot SO_2\cdot R_1$ (R = alkyl or aryl; R_1 = aryl) on halogenated anthraquinones, condensation products are obtained.

1-p*Toluenesulphonylphenylaminoanthraquinone*,



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_3\cdot NPh\cdot SO_2\cdot C_7H_7,$$

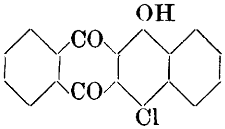
is prepared by heating together *p*-toluenesulphonylanilide and α-chloroanthraquinone in nitrobenzene solution in the presence of copper acetate and sodium carbonate; it crystallises from acetic acid in glistening, yellow crystals, m. p. 193°.

1-p-*Toluenesulphonylmethylaminoanthraquinone*, yellow needles, m. p. 192°, is prepared in a similar manner from *p*-toluenesulphonylmethylamide and α-chloroanthraquinone. By treatment with concentrated sulphuric acid, it yields α-methylaminoanthraquinone. F. M. G. M.

Preparation of 6-Chloro-1-hydroxynaphthacenequinone, and of 6-Chloro-1-hydroxynaphthacenequinone-4-sulphonic Acid. Anilinfarben and Extract-Fabriken vorm. J. R. Geigy (D.R.-P. 226230).—The work of Weizmann and others has shown that *o*-1-hydroxy-β-naphthoylbenzoic acid when heated with concentrated sulphuric acid and boric acid is converted quantitatively into 1-hydroxynaphthacenequinone (Trans., 1906, **90**, 116; 1907, **91**, 411;

1909, **93**, 279); this reaction has now been extended to 4′-chloro-1′-hydroxy-β-naphthoyl-*o*-benzoic acid (Abstr., 1910, i, 746) and its sulphonic acids.

6-*Chloro*-1-*hydroxynaphthacenequinone* (annexed formula) was prepared by dissolving crystallised boric acid (6 parts) in 80 parts of concentrated sulphuric acid (25% SO_3), slowly adding the 4′-chloro-1′-hydroxy-β-naphthoylbenzoic acid (20 parts), and heating at 70° until sodium hydroxide ceased to produce a yellow coloration. The product after crystallisation from benzene formed long, reddish-yellow needles, m. p. 307°, and seems not to be identical with the 6-chloro-1-hydroxynaphthacenequinone, m. p. 290—293° (Trans., 1907, **91**, 418). The *sodium* salt is insoluble in water.



6-*Chloro*-1-*hydroxynaphthacenequinone*-4-*sulphonic acid* was isolated in the form of its *monosodium* salt, a brick-red powder, by boiling with a saturated solution of sodium chloride; it is soluble in water with a yellow coloration; the *disodium* salt was obtained as a dark red gelatinous precipitate soluble in water with a blue coloration.

F. M. G. M.

Preparation of Alkyloxyacetyl Derivatives of Menthols. Alfred Einhorn (D.R.-P. 225821).—The interaction of ethoxyacetic acid and mentholcarboxyl chloride in a cooled ethereal solution yields *menthol ethoxyacetate*, a colourless oil, b. p. 144°/14 mm. The reaction is a general one for the alkyloxyacetic acids and mentholcarboxyl halides.

F. M. G. M.

Preparation of Santalyl Alkylaminoacetates. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 226229).—It is found that santalyl alkylaminoacetates of therapeutic importance can be prepared by treating chloroacetylsantalol with a secondary amine. *Chloroacetylsantalol*, a viscous, yellow oil, was prepared by treating santalol with chloroacetyl chloride in the presence of pyridine, or with chloroacetic acid, pyridine, and carbonyl chloride. This product was isolated, mixed with a solution of dimethylamine in benzene, and left during twenty-four hours; the *santalyl dimethylaminoacetate* was extracted with hydrochloric acid, and, on rendering the solution alkaline with sodium carbonate, separated as a yellow, odourless oil, which hydrolyses readily with alkalis into its components. It forms well characterised salts; the *hydrochloride* crystallises from acetone in odourless, colourless needles, m. p. 154°. Analogous compounds can be prepared with diethylamine or piperidine.

F. M. G. M.

Catalytic Reactions at High Temperatures and Pressures. XXII. Reduction of Terpenes. Wladimir Ipatieff (*Ber.*, 1910, **43**, 3546—3553. Compare Sabatier and Senderens, Abstr., 1901, i, 459; Vavon, Abstr., 1910, i, 52, 400).—By reducing *l*-limonene with hydrogen at 280—300° under 110—120 atmospheres' pressure, using cupric oxide as the catalyst, an unsaturated hydrocarbon, $C_{10}H_{18}$, b. p. varying from 172° to 176°, is obtained. The same hydrocarbon is also produced when copper is used, but a higher temperature is necessary. Further reduction of this hydrocarbon leads to the formation of *p*-menthane.

[With DRACHUSSOFF.]—French *l*-pinene in the presence of iron is not reduced, but undergoes isomerisation to dipentene. At 265° with cupric oxide as catalyst, it is reduced to a hydrocarbon, $C_{10}H_{18}$, whilst repeated reduction at 280—290° yields a hydrocarbon, $C_{10}H_{20}$, b. p. 163—170°, D^{20} 0·7949. Similar results were also obtained with metallic copper. With nickel oxide, the reduction takes place with great rapidity and at a lower temperature than with cupric oxide, $C_{10}H_{20}$ being formed.

It is considered probable that the hydrocarbon, $C_{10}H_{20}$, obtained from *l*-pinene consists of a mixture of *o*- and *p*-menthanes.

For the purpose of comparison, menthane was prepared from cymene by reducing with hydrogen, nickel oxide being used as a catalyst; it had b. p. 167—170°, D^{20} 0·8038. F. B.

Peppermint Oil Prepared from Dry Leaves of Mentha piperita. J. MURAOUR (*Bull. Soc. chim.*, 1911, [iv], **9**, 66—67).—Dry leaves, which had fallen naturally from mint plants during cultivation, gave a yield of from 400 to 500 grams of oil per 100 kilos. of leaves. This oil was yellow, and had an odour recalling that of Japanese peppermint oil. Two samples gave the following constants: D^{15} 0·911 to 0·913, $a_D = -38°18'$ to $-40°4'$, solubility 1 in 1·5 to 2·5 vols. of alcohol at 80°, and contained 33·16 to 40·31% of esters and 43·99 to 45·67% of total menthol. The results of examination of commercial peppermint oils indicated that some of these products consisted of true peppermint oil of French origin mixed with oil from the fallen leaves. T. A. H.

Essential Oils. I. Orange Flower Oil. II. Schinus molle Oil. G. LALOUE (*Bull. Soc. chim.*, 1910, [iv], **7**, 1101—1107, 1107—1109).—A more detailed account of work already published (Abstr., 1910, i, 755; 1909, i, 817). Gildemeister and Stephan's observation (Abstr., 1897, i, 81) that *Schinus molle* oil contains pinene and phellandrene is confirmed, and there is probably also about 20% of sesquiterpenes present. Oil distilled from branches and leaves, obtained at Grasse, was richer in pinene than oil from leaves and branches obtained in Algeria. T. A. H.

Milk Sap of Antiaris toxicaria. HEINRICH KILIANI (*Ber.*, 1910, **43**, 3574—3579. Compare Abstr., 1897, i, 91).—Seligmann (Abstr., 1903, ii, 314) obtained from the juice of *A. toxicaria* procured from Sarawak an antiarin differing from that previously described. It is now found with juice obtained from Java that two antiarins exist, the new β-form being present in the larger proportion. They differ in crystalline form, melting point, water of hydration, and composition, although there is no difference in their toxic character.

α-Antiarin, $C_{27}H_{42}O_{10},4H_2O$, crystallises in glistening plates or leaflets, m. p. 220—225°

β-Antiarin, $C_{27}H_{38}O_{10},3H_2O$ or $C_{28}H_{38}O_{10},3H_2O$, crystallises in slender needles or bunches of columnar needles, m. p. 206—207°.

Emulsin is without action on either glucoside; the products of hydrolysis of β-antiarin have not been characterised. E. F. A.

Digitonin, Digitogenic Acid and their Oxidation Products. HEINRICH KILIANI (*Ber.*, 1910 **43**, 3562—3574. Compare Abstr., 1904, i, 505).—A further study of the oxidation products of digitogenin shows that digitic acid has the composition $C_{28}H_{42}O_{11}$. Molecular weight determinations are particularly difficult to carry out in the case of oxidation products of digitogenic acid. It has not been found possible so to conduct oxidation as to obtain simple products of known constitution; even with ozone, the chief product is an acid, $C_{26}H_{40}O_7$.

To prepare digitonin, German digitalis is extracted with alcohol ether, the insoluble residue is dissolved in water, the vessel placed in a bath of water at 70^c, a small quantity of amyl alcohol added, and, after inoculation, the whole is allowed to cool slowly until crystallisation is complete.

Digitic acid is tribasic, the barium salt being $(C_{28}H_{41}O_{12})_2Ba_3,18H_2O$. The normal potassium salt is hygroscopic, and the acid salt admixed with free acid; the calcium salt is amorphous, so that neither is suitable for analysis. The by-products of the oxidation consisted of acids miscible with sodium chloride solution, from which no chemical individual could be isolated, and of acids insoluble in salt solution. When further oxidised with permanganate in strongly alkaline solution, a definitely crystalline calcium salt, $C_{19}H_{26}O_7Ca,8H_2O$, was obtained (compare Kiliani and Baylen, Abstr., 1895, i, 65). The acid is indefinitely crystalline, m. p. 170° (decomp.).

Anhydrodigitic acid, when oxidised with potassium permanganate in neutral solution, forms an acid, $C_{26}H_{38}O_7$, crystallising in crusts of small pyramids, m. p. 196—200°; the magnesium salt crystallises in needles and small pyramids.

From the products of oxidation of digitogenic acid by hot permanganate in neutral solution, a new tribasic *acid*, $C_{28}H_{42}O_{11}$, has been isolated; it crystallises in leaflets, m. p. 155° (decomp.). The *barium* salt, $C_{28}H_{40}O_{11}Ba,10H_2O$, crystallises in aggregates of closely-packed needles and is strongly acid. The acid is isomeric with digitic acid.

On oxidation of digitogenic acid with ozone, more than 60% of an *acid*, $C_{26}H_{40}O_7$, is obtained; this crystallises in clusters of pyramids, m. p. 222°. A *magnesium* salt, $C_{26}H_{38}O_7Mg,11H_2O$, crystallises also in tiny pyramids. It has not been established in what form the two atoms of carbon are eliminated during the oxidation. E. F. A.

Saponification of Sinigrin. MAX GONNERMANN (*Pflüger's Archiv*, 1911, **137**, 453—469).—Sinigrin is not acted on by any enzyme with the exception of myrosin. The enzymes investigated under varying conditions of solvent, etc., were of both animal and vegetable origin; bacteria, including those in the intestine, have no effect in liberating allylthiocarbimide. This confirms Kobert's statement. Various details regarding the mode of preparation of this glucoside are given.

W. D. H.

A Saponin-Cholesterol Compound. S. Yagi (*Arch. exp. Path. Pharm.*, 1910, **64**, 141—146).—Ransom having shown that cholesterol inhibits the hæmolytic power of saponin, Windaus found that certain saponins form additive products with cholesterol; the digitonin–cholesterol compound, for instance, is crystallisable, and has the formula $C_{82}H_{140}O_{29}$, that is, a combination of one molecule of each substance ($C_{55}H_{94}O_{28} + C_{27}H_{46}O$). Other cholesterides have been separated by the same author. The present paper gives details of the preparation and properties of another crystallisable cholesteride, namely, that of dioscine, in which three molecules unite with two of cholesterol, $3C_{24}H_{38}O_6,2C_{27}H_{46}O,1$ or $2H_2O$, a microcrystalline powder, m. p. 223°; this is inactive on blood corpuscles. The feeble hæmolytics, such as Merck's saponin, sapotoxin, and dioscorea–sapotoxin, need about an equimolecular amount of cholesterol to render them inactive; half the amount leaves them still partly active; the feeble members of the group therefore do not contain active mixed with inactive molecules.

W. D. H.

Action of Nitric Acid on Aloins; Production of Tetranitroaloe-emodin and of 2 : 4 : 6-Trinitro-3-hydroxybenzoic Acid. Eugène Léger (*Compt. rend.*, 1910, **151**, 1128—1131; *Bull. Soc. chim.*, 1911, **9**, 88—97).—It has long been known that chrysammic acid and picric acid are amongst the products of the action of nitric acid on the aloins. It is now shown that the production of these compounds is preceded by the formation of two other substances, which are then converted into these acids by the further action of nitric acid.

Tetranitroaloe-emodin, $C_{15}H_6O_5(NO_2)_4$, arises from the action of nitric acid (D 1·2) on barbaloin or *iso*barbaloin at the temperature of the water-bath. It occurs in slender, golden needles, m. p. about 285° with deflagration. On long boiling with nitric acid (D 1·32), it is converted into chrysammic acid.

The mother liquor from the tetranitroaloe-emodin contains 2 : 4 : 6-trinitro-3-hydroxybenzoic acid (Griess, *Annalen*, 1861, **117**, 28); this crystallises from ether in almost colourless, efflorescent, rhombic lamellæ, m. p. 185·5—186·5° (corr.). It loses carbon dioxide when heated with nitric acid, and forms picric acid.

Tetranitrorhein, $C_{14}HO_2(NO_2)_4(OH)_2{\cdot}CO_2H$, is probably an intermediate product in the conversion of tetranitroaloe-emodin into chrysammic acid. It has been isolated as short, efflorescent prisms.

W. O. W.

Chlorophyll. X. Comparative Investigation of Chlorophyll from Different Plants. II. Richard Willstätter and Alfred Oppé (*Annalen*, 1910, **378**, 1—18. Compare Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150).—An examination of the leaves of 200 species of plants has shown that the chlorophyll present is the so-called amorphous or wax-like form which yields phytol. The phæophytin obtained from the dried leaves gives a 33% yield of phytol, provided the extraction is carried out rapidly. In many cases, for example, grass and plantains, good yields of phytol are also obtained when a slow method of extraction is used, but in others the amount of phytol isolated diminishes as length of time taken for the extraction is increased. Thus the yields of phytol from *Heracleum spondylium* are 6·0 when the extraction takes twenty-four hours, 20·2 for one hour, and 31·5% for three-quarters of an hour.

It is evident that the chlorophyll loses its phytol when its alcoholic solution is left in contact with the plant tissues, and this loss is due to enzyme action (Willstätter and Stoll, next abstract). The results account for the low percentages of phytol obtained in previous experiments (*loc. cit.*), as the slow method of extraction was used. The increase observed in the amount of phytol when the dried material is kept can be accounted for by the enzyme losing its activity with age.

Two quick methods of extraction are described. The one consists in rubbing the leaf powder with chalk and sufficient alcohol to form a thick paste (about 1 litre per kilo. of leaf powder), leaving for five minutes, filtering under pressure, and washing with small amounts of alcohol. The second method consists in making a much stiffer paste, 300 c.c. of alcohol for 1 kilo. of powder, and placing on a percolator and using low pressures. This second method is the better when comparatively concentrated solutions of chlorophyll are required.

The phæophytin was obtained by the addition of oxalic acid to the extract. When chlorophyll had not undergone decomposition, a fine compact precipitate of phæophytin mixed with oxalates was obtained, but if much phytol has been formed, the precipitate had a voluminous, coagulated appearance.

Phytochlorin-*e* and phytorhodin-*g* have been isolated from the phæophytin from 125 different plant species. The amount of phytorhodin-*g* diminishes as the boiling with the alcoholic potassium hydroxide is increased, or as the concentration of the alkali is increased. In many cases a phytochlorin somewhat more feebly-basic than phytochlorin-*e* was isolated. The usual method of hydrolysis was boiling for two to three hours with 24% methyl-alcoholic potassium hydroxide, using 5 c.c. of solution for 1 gram of phæophytin. J. J. S.

Chlorophyll. XI. Chlorophyllase. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1910, **378**, 18—72).—Willstätter and Oppe (preceding abstract) have shown that the conversion of amorphous chlorophyll into crystallised chlorophyll is accompanied by the elimination of a phytol group, and that the change occurs when the process of extraction is slow, but can be avoided by using a rapid method of extraction. It is now shown that crystallised chlorophyll contains one methoxy- and one ethoxy-group and not two methoxy-groups (Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150), and that the amorphous chlorophyll contains one methoxy- and one phytyl group; it is proved that the change of the amorphous into the crystallised chlorophyll is a process of alcoholysis, and in each stage of the change the phytol eliminated is equivalent to the ethyl alcohol entering the molecule. The reaction, which is represented by the equation:

$$CO_2H{\cdot}C_{31}H_{29}N_4Mg(CO_2Me){\cdot}CO_2{\cdot}C_{20}H_{39} + EtOH = C_{20}H_{39}{\cdot}OH + CO_2H{\cdot}C_{31}H_{29}N_4Mg(CO_2Me){\cdot}CO_2Et,$$

takes place in the presence of a specific enzyme, *chlorophyllase*, which belongs to the group of esterases. Other substances of the same group, for example, lipase from linseed or pancreas lipase, cannot bring about the same change. The enzyme reacts slowly with phæophytin, and does not react at all with waxes of an ester nature. It is highly probable that the enzyme brings about the formation of phytyl esters in the plant. Working with methyl alcohol, it has been found possible to replace the phytoxyl groups by methoxyl (methanolysis) and in the presence of moist ether to replace the phytoxyl group by hydroxyl (hydrolysis). Lipases, on the other hand, produce hydrolysis, but do not appear able to induce alcoholysis.

The following system of nomenclature is suggested for chlorophyll derivatives: the tricarboxylic acid, $C_{31}H_{29}N_4Mg(CO_2H)_3$, from which chlorophyll is derived is called *chlorophyllin*; the monomethyl ester obtained by the hydrolysis of chlorophyll is termed *chlorophyllide*; amorphous chlorophyll is *phytylchlorophyllide*; Borodin's crystallised chlorophyll is *ethylchlorophyllide*; the magnesium-free compound,

$$C_{31}H_{31}N_4(CO_2H)_3,$$

is termed *phaeophorbide*; phæophytin is thus *phytylphaeophorbide*, and the compound hitherto called phæophorbin is *ethylphaeophorbide*.

A rapid method for the extraction of chlorophyll is described which differs somewhat from those recommended by Willstätter and Oppé (preceding abstract). It consists in moistening 1 kilo. of the leaf meal for five minutes with 0·5 litre of alcohol (96%), then spreading on a thimble, and applying suction for a short time. The addition of alcohol, and suction, are used alternately until a further litre of alcohol has been added; in the course of twenty minutes, 1 litre of solution is obtained; by washing with alcohol, a further 0·9 litre of extract is obtained in thirty-five minutes more. The amount of chlorophyll in the two extracts is 80% of the total present. The solutions, although dilute, are purer than those obtained by the methods already described, and therefore yield more phæophytin.

For the estimations of phytol the method already described (Abstr., 1910, ii, 150) has been used. The amount of chlorophyll transformed into ethylchlorophyllide by means of chlorophyllase has been determined both by the estimation of the phytol liberated and by determining the amount of silver iodide obtained from the product by Zeisel's method. Details for the calculations are given. The results obtained by the two methods agree, indicating that the ethyl groups entering the molecule are equivalent to phytyl groups removed. It is highly probable that the reaction is a direct exchange of alkyl for phytyl groups, and that it does not consist in the hydrolysis of the phytyl ester to the acid and the subsequent conversion of this into the ethyl ester. The enzyme was in the form of leaf meal from which the chlorophyll had been extracted, and was used whilst moist with alcohol. The reaction was most rapid when the mixture was kept well shaken, and in each experiment the flasks were well corked in order to prevent the admission of moisture. Although the reaction mixture is non-homogeneous, it is probable that the diffusion phenomena are such that the mixture behaves as if it were a homogeneous one. The values of K, however, when calculated by means of the equation for a unimolecular reaction, are not constant, but diminish as t increases. This is shown to be due partly to the fact that the enzyme tends to become less active when kept for some time. With varying amounts of enzyme, Schütz's rule, $\mu = K\sqrt{E.t}$, holds good approximately. With chlorophyll solutions of different concentrations, the amount transformed in a given time is roughly proportional to the concentration. The addition of water to the alcoholic solutions accelerates the activity of the chlorophyllase; thus the value of $K \times 10^3$ after ten hours varies from 28 to 37 using 92% alcohol, but with 80% alcohol $K \times 10^{13}$ has the values 175, 166, and 80. Even in 80% alcohol the reaction is a true alcoholysis and not hydrolysis. The activity of the enzyme is less at 35° than at 25°; when boiled with alcohol the enzyme is gradually destroyed, and in drying leaves for the preparation of the enzyme it is necessary to avoid high temperatures. Calcium carbonate has no effect on the alcoholysis, whereas magnesium hydroxide has an appreciable retarding effect. Young leaves appear to contain a smaller amount of enzyme than older ones, and the amount tends to increase as the chlorophyll increases.

The methylchlorophyllide, obtained by using methyl in place of ethyl alcohol, is formed much less readily, and its isolation is rendered difficult by the readiness with which it is transformed into readily soluble derivatives. The reaction proceeds more readily in the presence of a small amount of water, for example, in 92% methyl alcohol, but the best results are obtained by treating fresh leaves with 50—60% methyl alcohol. The product varies with the species of plant used; that obtained from *Heracleum*, $C_{72}H_{70}O_{11}N_8Mg_2$, crystallises from ether, in which it is sparingly soluble, in steel-blue, glistening prisms. The corresponding *methylphaeophorbide*, $C_{72}H_{74}O_{11}N_8$, forms glistening, spindle-shaped crystals with a metallic lustre. The methylchlorophyllide from stinging nettles is somewhat more readily soluble in ether, and crystallises in triangular and hexagonal plates.

Chlorophyllide, $CO_2Me{\cdot}C_{31}H_{29}N_4Mg(CO_2H)_2$, may be obtained by the action of the enzyme on a moist ethereal solution of chlorophyll in the absence of alcohol. It forms green plates and is extremely unstable, and is transformed readily into the isomeric *magnesium phaeophorbide*, $CO_2Me{\cdot}C_{31}H_{31}(CO_2)_2Mg$, which forms black crystals readily decomposed by acid.

The synthesis of chlorophyll from chlorophyllide and phytol can be accomplished by means of chlorophyllase, but the yields are small. Chlorophyll always appears to be accompanied by chlorophyllase; in *Sorbus aucuparia*, *Mellitis melissoph.*, *Stachys silvitica*, *Lamium maculatum*, and *Heracleum* the amount of enzyme is comparatively large. The presence of the enzyme in stinging nettles, grass, *Sambucus*, *Aspidium*, *Equisetum*, *Taxus*, *Avena*, and *Platanus* can be demonstrated by the prolonged action of the tissue on the chlorophyll extract, when products are obtained which contain but little combined phytol.

Extracts of stinging nettles and of *Platanus* react with the enzyme from *Galeopsis* or *Heracleum* more readily than with their own enzymes, but the alcoholysis does not proceed to completion. Under conditions which result in the complete alcoholysis of the chlorophyll of *Galeopsis* or *Heracleum*, only 66% of the chlorophyll of stinging nettles is decomposed. The chlorophyll of *Heracleum* reacts only slowly with stinging-nettle meal, but the rate is greater than that between stinging-nettle meal and the chlorophyll from stinging-nettle extract. J. J. S.

Chlorophyll. XII. Phytol I. RICHARD WILLSTÄTTER, ERWIN W. MAYER, and ERNST HÜNI (*Annalen*, 1910, **378**, 73—152. Compare Willstätter and Hocheder (Abstr., 1907, i, 784).—Crude phytol and the distilled product are not identical but isomeric, and the process of distillation appears to produce a shifting of a double linking. The two are termed respectfully α- and β-phytol. An examination of the products of oxidation shows that the α-compound has the olefine linking between carbons 5 and 6, as it yields a ketone, $C_{15}H_{30}O$, whereas β-phytol yields a ketone, $C_{13}H_{26}O$, and contains an olefine linking between carbons 7 and 8. The chief oxidation products isolated are the following ketones and acids. (1) Ketone, $C_{15}H_{30}O$, obtained from α-phytol by means of chromic anhydride, or from the α-ozonide. (2) Ketone, $C_{13}H_{26}O$, from β-phytol by means of chromic anhydride, from the β-ozonide, or from the acid $C_{14}H_{28}O_2$ by means of chromic acid. (3) Ketone, $C_{11}H_{22}O$, from trihydroxyphytan and chromic acid, or by the action of ozone on the ketones 1 and 2. (4) Ketone, $C_9H_{18}O$, by the action of ozone on any of the other ketones. (5) Acid, $C_{14}H_{28}O_2$, from α-phytol and ozone, from trihydroxyphytan and chromic acid, or from the ozonide of the olefine $C_{15}H_{30}$. (6) Acid, $C_{12}H_{24}O_2$, from the ketone, $C_{15}H_{30}O$ and ozone, from the ketone $C_{13}H_{26}O$ and chromic acid, or from the acid $C_{14}H_{28}O_2$ and chromic acid. (7) Acid, $C_{10}H_{20}O_2$, from the ketone $C_{15}H_{30}O$ and ozone, and from the ozonide of the olefine $C_{15}H_{30}$.

The first two ketones are easily obtained in a state of purity, but the two lower ones are more difficult to prepare. They are all methyl ketones, although they yield only traces of bromoform with hypobromite and only small amounts of methylamine by the Beckmann transformation. The presence of the acetyl group in the ketone $C_{15}H_{30}O$ can be demonstrated by the following series of reactions: $C_{13}H_{27}\cdot CO\cdot CH_3 \longrightarrow C_{13}H_{27}\cdot CH(OH)\cdot CH_3 \longrightarrow C_{13}H_{27}\cdot CH{:}CH_2 \longrightarrow C_{13}H_{27}\cdot CH(OH)\cdot CH_2\cdot OH \longrightarrow C_{13}H_{27}\cdot CO_2H$. The four ketones resemble one another in physical properties. They are pale yellowish-green oils with relatively high b. p.'s, and it is suggested that the compounds, especially the lower members, have the tautomeric enolic structure. The acids are saturated and do not decolorise bromine, but react readily with permanganate. They do not crystallise, and resemble phytol in physical properties.

The reduction products of phytol and also numerous esters have been prepared.

α-Phytol contains the double linking in the $\beta\delta$-position with respect to the $CH_2\cdot OH$-group, as the phytenic acid obtained by oxidising with chromic acid is an $\alpha\beta$-unsaturated acid, and the following structural formula is suggested: $CHMe_2\cdot[CHMe]_5\cdot CMe{:}CMe\cdot CHMe\cdot CH_2\cdot OH$. It is possible that α-phytol is a condensation product of isoprene,

$$4C_5H_8 + H_2O + 3H_2 = C_{20}H_{40}O.$$

The formula suggested for β-phytol is

$$CHMe_2\cdot[CHMe]_4\cdot CMe{:}CMe\cdot[CHMe]_2\cdot CH_2\cdot OH.$$

α-Phytol has D_4^{20} 0·856 and n_D^{20} 1·46364, and β-phytol, D_4^{20} 0·852 and n_D^{20} 1·46380. It can be distilled in portions of 10—30 grams from Claisen flasks, and has b. p. 203—204°/9—10 mm. Both compounds give the same iodine number. A good test for the presence of phytol, for example, in phæophytin preparations, is the formation of a stable, colourless oil by heating for a short time with concentrated nitric acid. When the boiling is prolonged, a nitrogenous acid is formed, the alkaline solutions of which have an intense yellow colour. Many phytol preparations, both crude and distilled, undergo autoxidation (Engler and Weissberg, Abstr., 1899, i, 189) when kept for several months in corked vessels. A sharp, penetrating odour with an acid reaction is noticeable, and the oil becomes limpid and, at the same time, distinctly acid. The formation of a peroxide can be detected by Engler's method. The rate of autoxidation varies considerably with different samples, and it is probable that small amounts of some impurity, present in both the crude and the distilled products, act as a catalyst. The acid formed is not homogeneous and is unsaturated; the analytical numbers indicate that it may be a mixture of equal amounts of phytenic acid and a saturated acid with 10 carbon atoms.

Phytyl hydrogen phthalates, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{20}H_{39}$, are formed when the phytol and phthalic anhydride are boiled for five hours with benzene, and can be isolated by making use of the fact that their sodium salts are very sparingly soluble in water, but are soluble in ether. The α-phytyl ester is a syrup, readily soluble in most organic solvents; it yields an oily *dibromide*, which is unstable, and a *silver* salt, $C_{28}H_{43}O_4Ag$, in the form of minute, flat prisms, m. p. 119°; the isomeric *silver β-phytyl phthalate* crystallises in prisms, m. p. 116°.

Cetyl hydrogen phthalate, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{16}H_{33}$, forms indefinite crystals of a waxy consistency, and has m. p. 61—62°. The *silver* salt, $C_{24}H_{37}O_4Ag$, crystallises from benzene.

Phytyl ether, $O(C_{20}H_{39})_2$, obtained by the action of concentrated sulphuric acid on a glacial acetic acid solution of the alcohol, is a viscid oil sparingly souluble in glacial acetic acid or in methyl alcohol, and forms a dibromide.

Phytol cannot be reduced by means of sodium and ethyl or amyl alcohol, but by electrolytic reduction in cold alcoholic sulphuric acid solution, using platinised platinum electrodes with a voltage of 6 and a current density of 3 ampere per sq. m. and an earthenware diaphragm, the saturated alcohol, *phytanol* (*dihydrophytol*), $C_{20}H_{42}O$, is obtained together with the hydrocarbon phytan. Phytanol is readily prepared by reducing phytol with hydrogen in ethereal solution, using platinum-black as catalyst; a slow stream of hydrogen is passed through for about three weeks when 40 grams of phytol are used. The reduction is much quicker when the hydrogen is used under slight pressure and the apparatus is shaken continuously. It is a colourless, odourless oil, has b. p. 201·5—202°/9·5 mm., is miscible with all organic solvents, and is isomeric with arachyl alcohol (Haller, Abstr., 1907, i, 377). It forms a *sodium* derivative, $C_{20}H_{41}\cdot ONa$, in the form of a viscid oil, soluble in ether or light petroleum.

The *phenylurethane*, $NHPh\cdot CO\cdot O\cdot C_{20}H_{41}$, obtained by the combination of the alcohol with phenylcarbimide, is also a thick oil. *Phytanyl hydrogen phthalate*, $CO_2H\cdot C_6H_4\cdot CO_2\cdot C_{20}H_{41}$, is a syrup, and its *silver* salt, $C_{28}H_{45}O_4Ag$, has m. p. 106—106·5°. *Phytanyl pyruvate*,

$$CH_3\cdot CO\cdot CO_2\cdot C_{20}H_{41},$$

obtained by heating the components at 110—120°, or more readily by shaking the alcohol for a long time at the ordinary temperature with five times its weight of pyruvic acid and removing the excess of acid by means of water, has b. p. 219—220°/10 mm.; its *semicarbazone*, $C_{23}H_{47}O_3N_3$, crystallises from methyl alcohol in needles, m. p. 88—91°. *Cetyl pyruvate* has m. p. 26·5—27·5°, and its *semicarbazone*, $C_{19}H_{39}O_3N_3$. crystallises in flat prisms, m. p. 140—141°.

The esterification of β-phytol by means of glacial acetic acid at 155° has been studied; at the end of one hour, 34·5% of the acid is transformed into ester, but after one hundred and forty-four hours the yield has fallen to 6·9%, owing to decomposition of the ester into phytadiene. Geraniol and nerol react in much the same manner with glacial acetic acid at 155°. The initial rates of esterification with acetic acid at 155° of the following unsaturated alcohols have been determined: oleyl alcohol, erucyl alcohol, geraniol, nerol, cholesterol, and the values obtained are smaller than those for the corresponding saturated alcohols. *Erucyl alcohol*, $C_{22}H_{44}O$, prepared by reducing ethyl erucate with boiling amyl alcohol and sodium, has b. p. 240·5—241·5°/10 mm., and forms rhombohedral crystals, m. p. 34·5—35·5°. Its *dibromide*, $C_{22}H_{44}OBr_2$, forms glistening prisms, m. p. 45—45·5°. When reduced with hydrogen in the presence of finely-divided platinum, the unsaturated alcohol yields *docosyl alcohol*, $C_{22}H_{46}O$, which crystallises from chloroform in glistening prisms, m. p. 71—71·5°; the *phenylurethane*, $C_{29}H_{51}O_2N$, crystallises from ethyl acetate in glistening prisms, m. p. 86—86·5°. The percentages of acetic acid transformed into ester at 155° are the following: dihydrophytol, 73; arachyl alcohol, 76·2; tetrahydrogeraniol, 68·5. These values are lower than those given by normal alcohols.

Phytanic acid, $C_{20}H_{40}O_2$, is best prepared by oxidising dihydrophytol with an acetic acid solution of chromic acid in the presence of potassium hydrogen sulphate, and forms a viscid oil, b. p. 221°/7·5 mm. The *silver* salt, $C_{20}H_{39}O_2Ag$, darkens at 165° and has m. p. 177—177·5°. The *amide*, $C_{19}H_{39}\cdot CO\cdot NH_2$, crystallises when its solutions in methyl alcohol or light petroleum are well cooled, and has m. p. 53—53·5°. Δ^{β}-*Phytenic acid*, $C_{20}H_{38}O_2$, is formed together with the ketone, $C_{15}H_{30}O$, when phytol is oxidised with an acetic acid solution of chromic anhydride (5 atoms of O) in the presence of potassium hydrogen sulphate. It forms a yellow oil, b. p. 210—220°/11·5 mm., and has D_4^{20} 0·917 and n_D^{20} 0·893. The position of the ethylene linking is established by the readiness with which it yields a γ-lactone (Abstr., 1907, i, 786) when heated with sulphuric acid and water. The saturated hydrocarbon, *phytane*, $C_{20}H_{42}$, is most readily obtained by reducing phytene with hydrogen and platinum; it is a colourless, mobile oil, with b. p. 169·5°/9·5 mm. and D_4^{20} 0·803, is only sparingly soluble in cold methyl alcohol, and solidifies when cooled by liquid air. In the preparation of phytene (Abstr., 1907, i, 786) a *di-iodo-derivative*, $C_{20}H_{40}I_2$, is obtained in the form of a heavy oil, and when this is reduced with zinc dust and glacial acetic acid, or with zinc dust and hydriodic acid, it yields impure phytene, although the two iodine atoms are not attached to adjacent carbon atoms. *Phytadiene*, $C_{20}H_{38}$, is formed when β-phytol, phthalic anhydride, and benzene are heated for a day in a Babo funnel, owing to the readiness with which the phytyl hydrogen phthalate decomposes into phytadiene and phthalic acid; it has b. p. 186—187°/13 mm. and D_4^{20} 0·826, and its iodine number points to the presence of two olefine linkings.

α-Phytol ozonide, prepared by passing a current of 6% ozone into a dry chloroform solution of the alcohol and then removing the chloroform under reduced pressure at 20°, forms a pale green syrup with a pungent odour, and dissolves readily in most organic solvents. Methyl alcohol separates the crude ozonide into an insoluble "moloxide," $C_{20}H_{40}O,O_2$, and a soluble oxozonide, $C_{20}H_{40}O,O_4$. The yield of the "*moloxide*" is larger the shorter the time of ozonising, and it canbe obtained crystalline by well cooling its methyl alcoholic solution. It is an oil at the ordinary temperature, and when boiled with water yields the same products and in the same amounts as the oxozonide. This latter, when kept for some months under reduced pressure over phosphoric anhydride, yields the normal *ozonide*, $C_{20}H_{40}O,O_3$.

The best yields of the ketone, $C_{15}H_{30}O$, are obtained when α-phytol is oxidised with a glacial acetic acid solution of chromic anhydride in the presence of potassium hydrogen sulphate. With the theoretical amount of oxygen, only a small amount of the alcohol is oxidised; but with 4 to 5 atoms of oxygen to each molecule of alcohol, a 73—97% yield of ketone can be obtained. The same ketone is also formed when either of the ozonides of α-phytol is boiled with water for three hours in a reflux apparatus, using 25 grams at a time. The aqueous solution has a decided acid reaction, and gives the ordinary reactions for aldehydes. The oily product consists of the ketone together with the acid $C_{14}H_{28}O_2$ (3·5%), phytenic acid, the hydrocarbon $C_{15}H_{32}$, and a small amount of an ether. The acids can be removed by extraction with very dilute sodium hydroxide solution, and the ketone purified by distillation under reduced pressure. It forms a pale yellowish-green, limpid oil, which turns quite colourless in the course of two to three weeks. It has b. p. 173—174°/9 mm. and 291·8—292·4°/722 mm., and is optically inactive. The *oxime*, $C_{15}H_{31}ON$, is a viscid oil with b. p. 201—202°/10 mm. and D_4^0 0·885; the *semicarbazone*, $C_{16}H_{33}ON_3$, crystallises from alcohol in well-developed prisms, m. p. 64·5°, and the p-*nitrophenylhydrazone*, $C_{21}H_{35}O_2N_3$, forms a pale yellow oil. The ketone combines with bromine in chloroform solution, yielding an unstable dibromide, which is probably derived from the isomeric enolic compound. Many ketones, for example, cholestanone and methyl ethyl ketone, form colourless dibromides in solution (compare also Linnemann, *Annalen*, 1863, **125**, 307; Lippmann, *Zeitsch. Chem.*, 1869, **5**, 29). The ketone gives negative results with the following reagents for aldehydes: sodium amalgam and diazobenzenesulphonic acid, benzenesulphohydroxamic acid, pyruvic acid, and β-naphthylamine. It yields a peroxide, from which the ketones $C_{13}H_{26}O$ and $C_{11}H_{22}O$ are formed by boiling with water.

The *alcohol*, $C_{15}H_{32}O$, obtained by reducing the ketone with sodium and alcohol, is a colourless, viscid liquid, with b. p. 178—180°/12 mm. or 173—174°/8 mm., D_4^0 0·848, D_4^{20} 0·838, and n_D^{20} 1·44912. The saturated *hydrocarbon*, $C_{15}H_{32}$, occurs in the first fraction obtained by distilling the crude ketone under diminished pressure, and is deprived of the last traces of ketone by repeatedly shaking with three times its volume of glacial acetic acid, in which the ketone is readily soluble. It has b. p. 260·5—263·5°/723 mm. (corr.) or 127—130°/9·5 mm., D_4^0 0·789, D_4^{20} 0·779, and n_D^{20} 1·43322, and is also formed in small quantities when the ketone is reduced with zinc dust and glacial acetic acid. The *olefine*, $CH_2{:}CH{\cdot}CHMe{\cdot}C_{11}H_{23}$, obtained by the action of phosphoric oxide on the alcohol, $C_{15}H_{32}O$, at 60—70°, has b. p. 150—152°/11 mm. or 290°(corr.)/724 mm., D_4^0 0·803 and D_4^{20} 0·790, and combines readily with bromine. Its *ozonide*, $C_{15}H_{30}O_3$, is a viscid oil, with a pale green colour. When the alcohol $C_{15}H_{32}O$ is heated at 150° for an hour with phosphoric oxide, or when the above olefine is heated for several hours at 130° with the anhydride, a product is formed which contains a small amount of a saturated (cyclic) hydrocarbon.

The *ketone*, $C_{13}H_{26}O$, resembles its higher homologue; it has b. p. 168—170°/10 mm. or 288—289°/722 mm., D_4^0 0·865, D_4^{20} 0·848, and is optically inactive. It is not oxidised so readily as its homologue, $C_{15}H_{30}O$. The *oxime*, $C_{13}H_{27}ON$, is a viscid oil, b. p. 196—198°/11 mm. and D_4^0 0·891, and the *semicarbazone*, $C_{14}H_{29}ON_3$, forms slender needles, m. p. 62°. A 94% yield of the ketone is formed by oxidising β-phytol with a glacial acetic acid solution of chromium trioxide in the presence of potassium hydrogen sulphate, and an 82% yield by boiling β-phytol-ozonide with water. It is formed together with the acid $C_{10}H_{20}O_2$ (26—33%) by oxidising the ketone $C_{15}H_{30}O$ with a glacial acetic acid solution of chromium trioxide in the presence of concentrated sulphuric acid. A by-product formed at the same time is the *ether*, $O(C_{10}H_{21})_2$, which has b. p. 228—233°/722 mm. and D_4^0 0·836.

Trihydroxyphytane, $C_{20}H_{39}(OH)_3$, obtained by converting α-phytol dibromide into the acetate and subsequent hydrolysis, is a viscid oil, sparingly soluble in cold methyl alcohol, and when oxidised with chromium trioxide in the presence of glacial acetic and concentrated sulphuric acids yields the *ketone*, $C_{11}H_{22}O$, as a colourless, mobile oil, b. p. 168—170°/8 mm., together with the acid, $C_{14}H_{28}O_2$; its *semicarbazone*, $C_{12}H_{25}ON_3$, crystallises from alcohol in needles, m. p. 68—72°. The same ketone is formed when the product, obtained by the prolonged action of ozone on the ketone $C_{15}H_{30}O$, is boiled with water. The *ketone*, $C_9H_{18}O$, is a limpid oil, with b. p. 168°/10 mm. or 282°/720 mm., and has D_4^0 0·836. Its *semicarbazone* has m. p. 75°.

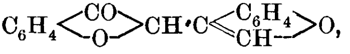
The olefine *dibromide*, $C_{15}H_{30}Br_2$, is a yellow oil, and, when shaken with silver acetate and glacial acetic acid at the ordinary temperature, yields the *bromoacetyl* derivative, $C_{15}H_{30}BrAc$, as a viscid oil, which reacts with silver acetate at 100°, yielding the *diacetate*, and this on hydrolysis with cold methyl-alcoholic potassium hydroxide yields an ether of the glycol, $(C_{15}H_{30}\cdot OH)O$, as a brown, viscid oil. The ether, when oxidised with chromium trioxide, glacial acetic and sulphuric acids, yields as intermediate product a carbonyl *compound*, $C_{15}H_{30}O_2$, and ultimately the acid $C_{14}H_{28}O_2$. The same acid is also formed when the olefine ozonide is boiled for five hours with water, but appreciable amounts of the ester, $C_9H_{17}\cdot CO_2\cdot C_{10}H_{21}$, are also formed. The *acid*, $C_{14}H_{28}O_2$, is a colourless, comparatively viscid oil, with b. p. 186—188°/8—9 mm., D_4^0 0·887 and D_4^{20} 0·870. The *silver* salt, $C_{14}H_{27}O_2Ag$, is obtained crystalline by using alcoholic solutions, and has m. p. 186—188°.

The *acid*, $C_{10}H_{20}O_2$, is a colourless, odourless, viscid oil, b. p. 155—158°/11 mm. and 261°/722 mm., D_4^0 0·956, D_4^{20} 0·936, and n_D^{20} 1·45205; it decolorises permanganate in glacial acetic acid solution after a short time. The *silver* salt, $C_{10}H_{19}O_2Ag$, forms a crystalline precipitate, and with benzene forms colloidal solutions. The *ester*, $C_9H_{17}\cdot CO_2\cdot C_{10}H_{21}$, forms a colourless, mobile oil, b. p. 175—176°/11 mm., D_4^0 0·889, and D_4^{20} 0·808. It is hydrolysed by a cold concentrated solution of potassium hydroxide in methyl alcohol. Electrical conductivity measurements of the acid $C_{10}H_{20}O_2$, phytanic acid, and Δ^β-phytenic acid were made in aqueous alcoholic solution. The unsaturated acid is a better electrolyte than the saturated acid, and the acid $C_{10}H_{20}O_2$ conducts better than acetic acid.

A distillation flask similar to that described by Michael (Abstr., 1902, i, 70) is recommended for distillations under reduced pressure. Use is made of a column of glass beads, but the capillary tube for introducing bubbles of air is passed through a side-tube fused into the body of the flask. J. J. S.

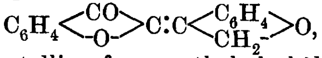
Condensation Products of 2-Coumaranone. KARL FRIES and W. PFAFFENDORF (*Ber.*, 1911, **44**, 114—124. Compare Abstr., 1910, i, 186; also Fries and Fink, Abstr., 1909, i, 42, 44).—By the condensation of 2-coumarone with sodium ethoxide solution in the absence of air, it has been found possible to obtain two isomeric compounds, $C_{16}H_{10}O_3$. The relative amounts of the two vary with the conditions, but so far it has not been found possible to ascertain the conditions which determine the proportions. Neither compound appears to have the hydroxylic structure corresponding with the acetyl derivative already described (Abstr., 1910, i, 186), as they are both very sparingly soluble in alkalis. They are represented as isomeric ketones, and both yield 2 : 1′-diketo-$\Delta^{1,2}$-1 : 2′-dicoumaran ("oxindirubin," "1 : 2-bis-coumaran-indigo"), when mixed with a small amount of bromine in glacial acetic acid solution.

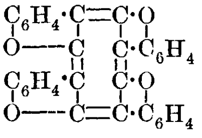
2-*Keto*-1 : 2′-*coumarancoumarone*,



$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{O}{>}CH\cdot C{<}\genfrac{}{}{0pt}{}{C_6H_4}{CH-}{>}O$,

is the chief product obtained by condensing 2-coumaranone with a hot 3% sodium ethoxide solution, and is also formed by the hydrolysis of the acetate (*loc. cit.*). It crystallises from methyl alcohol in compact, colourless needles, m. p. 116°, and its solution in concentrated sulphuric acid has a yellowish-red colour with a strong yellowish-green fluorescence. Its solutions, especially in the presence of impurities, are unstable. It yields a somewhat unstable *hydrobromide* in the form of light red needles, and with acetic anhydride and sodium acetate yields the acetate of the tautomeric hydroxy-compound.

The isomeric *2-keto-$\Delta^{1:2'}$-dicoumaran*,  $C_6H_4<^{CO}_{O}>C:C<^{C_6H_4}_{CH_2}>O$, is more readily soluble in acetone, and crystallises from methyl alcohol in brilliant coppery-red plates, m. p. 141°. It is decomposed when boiled for some time with methyl alcohol, yields a yellowish-red *hydrochloride*, and is most readily obtained by condensing 2-coumarone with glacial acetic acid saturated with hydrogen bromide.



When either of the ketones or the acetate, m. p. 106°, is heated for eight hours at 100° with a saturated solution of hydrogen chloride in glacial acetic acid, a *product*, $C_{32}H_{16}O_4$, is obtained, which crystallises from xylene in flesh-coloured needles. These are not molten at 340°, but sublime in reddish plates with a metallic lustre. The annexed formula is suggested. Nitric acid converts it into a deep black-coloured substance, the acetic acid solution of which has a reddish-violet colour.

By the condensation of 5-methylcoumaranone with sodium ethoxide, only one product is obtained, namely, *2-keto-5 : 5'-dimethyl-$\Delta^{1:2'}$-dicoumaran*, $C_{18}H_{14}O_3$. This crystallises from alcohol in yellow prisms, m.p. 156° (when quickly heated), and is readily oxidised to 5 : 5'-dimethyl-leuco-oxindirubin. It undergoes decomposition when heated alone or with glacial acetic acid. The *product*, $C_{36}H_{24}O_4$, obtained by heating the acetate, m. p. 133° (*loc. cit.*), with a saturated solution of hydrogen chloride in glacial acetic acid, crystallises from xylene in pale red needles, which melt above 340°. When rubbed with a little nitric acid it yields a blue-black compound, which dissolves in glacial acetic acid to brilliant violet-blue coloured solutions.

2 : 1'-Dihydroxy-1 : 2'-dicoumarone ("leuco-oxindirubin") yields a *phenylhydrazone*, $C_{22}H_{16}O_3N_2$, which crystallises from glacial acetic acid in pale red needles, m. p. 179°, and when hydrolysed with hydrochloric acid yields oxindirubin.

The *acetyl* derivative of 2 : 1'-dihydroxy-1 : 2'-dicoumarone, $C_{18}H_{12}O_5$, crystallises in glistening plates, m. p. 198°; when hydrolysed with alkalis it yields the *leuco*-compound, but with hydrochloric acid yields oxindirubin.

The *phenylhydrazone* of 2 : 1'-dihydroxy-5 : 5'-dimethyl-1 : 2'-dicoumarone, $C_{21}H_{20}O_3N_2$, forms red needles, m. p. 163°. The *oxime*, $C_{18}H_{15}O_4N$, crystallises from methyl alcohol in yellow needles, m. p. 194°, and the *acetyl* derivative, $C_{20}H_{16}O_5$, in yellow prisms, m. p. 200°.

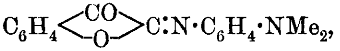
J. J. S.

Oxindigo [2 : 2-Diketo-$\Delta^{1:1'}$-dicoumaran]. KARL FRIES and A. HASSELBACH (*Ber.*, 1911, **44**, 124—128).—So far it has not been found possible to obtain "oxindigo" by the alkaline oxidation of 2-coumaranone, or from halogen derivatives of coumaranone (compare Abstr., 1897, i, 424; 1901, i, 94; 1909, i, 44, 174).

Attempts to prepare the oxygen compound of the action of ammonium sulphide on *p*-dimethylaminoanildiketocoumaran were also unsuccessful.

By the condensation of the anil derivative with 2-coumaranone in boiling xylene, a product, $C_{24}H_{20}O_4N_2$, is formed, and this, when hydrolysed by means of a mixture of glacial acetic and concentrated sulphuric acid at the ordinary temperature, yields amino-dimethylaniline and "oxindigo."

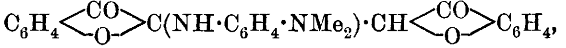
3-*Keto*-2-p-*dimethylaminoanilcoumaran*,



$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{O}C{:}N\cdot C_6H_4\cdot NMe_2,$$

prepared by the action of an alcoholic solution of 2-coumaranone on an alcoholic solution of *p*-nitrosodimethylaniline in the presence of 2*N*-sodium hydroxide solution at 3°, crystallises from benzene in large prisms with a blue-black lustre, or from alcohol in dark brown, glistening needles, m. p. 185°. It is hydrolysed by strong acids to *p*-aminodimethylaniline and *o*-hydroxyphenylglyoxylic acid.

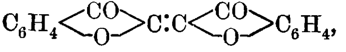
The condensation *product*, $C_{24}H_{20}O_4N_2$, probably



$$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{O}C(NH\cdot C_6H_4\cdot NMe_2)\cdot CH\genfrac{<}{>}{0pt}{}{CO}{O}C_6H_4,$$

crystallises from a mixture of benzene and light petroleum in flat prisms with a bronzy lustre, m. p. 203° (decomp.), after sintering at 190°. The yield is 30% of the theoretical, and the product dissolves in alkali hydroxides, yielding reddish-brown solutions.

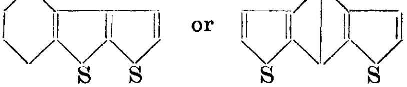
2 : 2-*Diketo*-$\Delta^{1:1'}$-*dicoumaran* ("*oxindigo*," "1 : 1-*dicoumarone-indigo*"),



$C_6H_4\genfrac{<}{>}{0pt}{}{CO}{O}C{:}C\genfrac{<}{>}{0pt}{}{CO}{O}C_6H_4$, crystallises from glacial acetic acid or from xylene in long prisms, with an intense lemon-yellow colour. It has m. p. 272° after sintering at 250°, and its solution in concentrated sulphuric acid has a yellowish-red colour.

It is decomposed by alcoholic sodium hydroxide solution, and even by sodium carbonate in the presence of alcohol. J. J. S.

A New Thiophen Compound, $C_{10}H_6S_2$, and Some of its Derivatives. M. Lanfry (*Compt. rend.*, 1911, 152, 92—94).—The tarry product obtained when a mixture of sulphur and naphthalene vapour is passed through a red-hot iron tube contains 0·2—0·4% of a compound crystallising in ruby-red leaflets or clinorhombic prisms. The substance has m. p. 118·5° (corr.), b. p. 345°, and in composition approximates to the formula $C_{10}H_6S_2$; it is supposed to be *benzdithiophen* (annexed formulæ). It gives the thiophen reaction with sulphuric acid and isatin. The *bromo*-derivative, $C_{10}S_2H_2Br_4$, crystallises in silky, orange needles, m. p. 247—248°. The *tetranitro*-derivative, $C_{10}S_2H_2(NO_2)_4$, was obtained as an orange powder, decomposing at 300°; it has well-marked acid characters, and forms highly-coloured compounds with cyclic hydrocarbons.



On treating benzdithiophen with hydrogen peroxide in acetic acid solution, it yields in the first place a *compound*, $C_{10}H_6O_2S_2$, slender rose-yellow needles, m. p. 130°, having the properties of a *p*-diphenol. On further oxidation, a second *compound*, $C_{10}H_6O_4S$, is formed; this crystallises in radiating, red needles, m. p. about 125°; it is insoluble in aqueous alkalis, and develops no coloration with sulphuric acid and isatin. W. O. W.

Silicotungstates of Coniceine, Sparteine, and Atropine.

MAURICE JAVILLIER (*Bull. Sci. Pharm.*, 1910, 315—320. Compare Abstr., 1899, ii, 456; 1909, ii, 450).—*Coniceine silicotungstate*,

$$12WO_3,SiO_2,2H_2O,4C_8H_{17}N + 3H_2O,$$

prepared by adding potassium silicotungstate to an aqueous solution of coniceine tartrate, is an amorphous substance which becomes anhydrous at 120°. It is soluble in boiling water; 100 c.c. of water at 15° dissolve about 0·02 gram of the salt.

Sparteine silicotungstate, $12WO_3,SiO_2,2H_2O,2C_{15}H_{26}N_2 + 7H_2O$, is amorphous, and loses $6H_2O$ at 120°. The precipitation of this salt is visible in aqueous solutions containing 0·0002% of sparteine, and, consequently, may be employed in estimating the alkaloid.

Atropine silicotungstate, $12WO_3,SiO_2,2H_2O,4C_{17}H_{23}O_3N + 4H_2O$, becomes anhydrous at 120°. It is less easy to obtain pure than the foregoing, owing to a tendency to undergo hydrolysis. Advantage has been taken of its sparing solubility (less than 1 in 40,000) to estimate atropine in pharmaceutical preparations. W. O. W.

Preparation of Alkyl Halides and Alkyl Nitrates of Tropeine and Scopoleine Alkaloids.

A. GERBER (D.R.-P. 228204).—*Methylatropinium methosulphite*, $C_{17}H_{23}O_3NMe{\cdot}SO_3Me$, is prepared by heating atropine with methyl sulphite and methyl alcohol in a sealed tube at 100°; the *platinichloride*, $(C_{17}H_{23}O_3NMeCl)_2PtCl_4$, forms orange-coloured leaflets. *Atropine methobromide*, m. p. 220°, and *atropine methonitrate* are formed respectively by evaporating the foregoing compound with aqueous potassium bromide, or with potassium nitrate; these compounds are soluble in water or alcohol, sparingly so in ether or acetone. F. M. G. M.

Dihydroberberine.

JOHANNES GADAMER (*Arch. Pharm.*, 1910, **248**, 670—681).—Faltis' evidence for the view that the action of potassium hydroxide on berberine results in the formation of oxyberberine and tetrahydroberberine (Abstr., 1910, i, 698) is reviewed and criticised, and further facts are brought forward in support of the author's opinion that in this reaction oxyberberine and dihydroberberine are formed (Abstr., 1902, i, 173, 555; 1905, i, 369; Freund and Beck, 1905, i, 151). Faltis' observation that by the action of zinc and acetic acid on oxyberberine, the latter is rendered colourless, could not be confirmed.

Dihydroberberine hydrochloride, prepared as already described (*loc. cit.*), crystallises with $4H_2O$, but readily loses $1H_2O$ on drying in a desiccator. Dihydroberberine is less basic than tetrahydroberberine, and is less easily removed than the latter from solution in ether by agitation with dilute hydrochloric acid. Tetrahydroberberine is resolved by crystallisation of the *d*-bromocamphorsulphonate into *d*- and *l*-canadines, but repetition of a similar fractional crystallisation of dihydroberberine *d*-bromocamphorsulphonate (Abstr., 1902, i, 173) showed that no resolution of this base took place, although tetrahydroberberine was again easily resolved, either alone or in admixture with dihydroberberine.

Dihydroberberine furnishes a *methiodide*, m. p. 205°, which dissolves in water, forming a yellow solution giving no precipitate with ammonia, but forming a white precipitate with much sodium hydroxide, the liquid at the same time developing a violet fluorescence; the precipitate is not dissolved by ether. *Tetrahydroberberine methiodide*, m. p. 245—250°, is colourless and soluble with difficulty. Oxyberberine forms an additive product with methyl sulphate.

Dihydroberberine is more poisonous to rabbits than tetrahydroberberine. T. A. H.

Corydalis Alkaloids. V. *R*-Corydaline and Phenylberberine. Johannes Gadamer (*Arch. Pharm*, 1910, **248**, 681—695).—A description of direct and indirect attempts made to resolve optically inactive corydaline, m. p. 135°, into optically active forms (Abstr., 1902, i, 306; 1905, i, 463).

[With Ernst Steinbrecher.]—Attempts to effect resolution by fractionation of the tartrate, quinate, and *d*-bromocamphorsulphonate were unsuccessful. Natural *d*-corydaline does not give a crystalline salt with the last-mentioned acid.

Attempts were then made to effect the resolution of α-methyldihydroberberine (Freund and Beck, Abstr., 1905, i, 151), and to reduce the *d*- and *l*-isomerides thus obtained, so producing active forms, which should differ from corydaline only in containing a dioxymethylene group in place of two methoxyls, and should therefore correspond with the *d*- and *l*-corydalines and to *d*- and *l*-*meso*corydaline (compare Freund and Mayer, Abstr., 1907, i, 633). The resolution of *r*-α-methyldihydroberberine could not, however, be effected, and this was also the case for phenylberberine.

Oxyberberine treated with magnesium ethyl iodide in benzene solution, with dimethylaniline as a catalyst, was recovered for the most part unchanged, but small quantities of methylnoroxyberberine (Faltis, Abstr., 1910, i, 698) and of a non-basic *substance*, m. p. 165—166°, separating from alcohol in bright yellow crystals, were obtained.

Oxyberberine reacts with magnesium phenyl bromide in ether to form (1) a tertiary *base*, which may be either a phenyltetrahydroberberine or diphenyldihydroberberine, and (2) *phenylberberine*. The latter furnishes a *hydrochloride*, m. p. 255—257° (decomp.), which separates from alcohol or water in brownish-yellow crystals. The *aurichloride*, m. p. 215—216° (decomp.), forms long, brown needles from alcohol containing hydrochloric acid. The *acid sulphate* softens at 270°, but does not melt even at 278°, and separates from dilute sulphuric acid in compact, yellow crystals. The *nitrate*, m. p. 268—270° (decomp.), is deposited from alcohol in compact, brown crystals.

On reduction with zinc and dilute sulphuric acid, phenylberberine hydrochloride yields *phenyltetrahydroberberine*, m. p. 222°, which separates from a mixture of chloroform and alcohol in compact, almost colourless crystals, and may also be obtained by reduction of phenyldihydroberberine. The latter, prepared by Freund and Beck's method (Abstr., 1905, i, 151), on oxidation with iodine in alcohol furnished iso*phenylberberine*, which gives a *hydrochloride*, m. p. 275—278° (decomp.), separating from water in silky, bright yellow crystals. The *aurichloride* forms reddish-brown, short needles, sinters at 250°, but does not melt at 280°; along with it was produced a second gold salt, m. p. 223—225°, which may be impure phenylberberine aurichloride (see above), since on decomposition with hydrogen sulphide it yielded some phenylberberine hydrochloride. This phenylberberine is probably produced in the initial oxidation along with *iso*phenylberberine. The latter, on reduction, yielded a varnish from which no crystalline derivative could be obtained. The relationship between phenylberberine and *iso*phenylberberine is uncertain, and it is regarded as improbable that the difference is due to hydrogenation of a different pyridine nucleus in each case. T. A. H.

Preparation of Curarine. RUDOLF BOEHM (*Pflüger's Archiv*, 1910, **136**, 203—207).—The action of curare is so uncertain, because commercial specimens contain other substances, in addition to its most active constituent curarine. The best kinds of curare contain only 3 to 9% of this alkaloid. Very small doses of curarine produce marked results. The methods of separating it from curare have been dealt with *in extenso* in the author's previous writings (Abstr., 1887, 1125; 1898, i, 283), and are briefly given in the present paper. W. D. H.

Preparation of Alkylhalogen Derivatives of Morphine Alkaloids. A. GERBER (D.R.-P. 228247).—The halogen double salts of the alkaloids and their quaternary compounds obtained by the action of alkyl halides and methyl sulphate have been previously described (Abstr., 1905, i, 542, 658; 1906, i, 530, 877; 1908, i, 452), and the work has now been extended to the products obtained with methyl sulphite.

Methylmorphinium methosulphite, $C_{17}H_{19}O_3NMe{\cdot}SO_3Me$, is prepared by heating morphine with methyl sulphite and methyl alcohol in a sealed tube at 100°, and subsequently evaporating in a vacuum; the amorphous, faintly coloured, hygroscopic product is rendered crystalline by dissolving in absolute alcohol and precipitating with ether; when evaporated with a saturated solution of potassium bromide, it is converted into morphine methobromide (m. p. 260°).

Methylnarcotinium methosulphite has similar properties, and is analogously prepared from narcotine; its *platinichloride*,

$$(C_{22}H_{23}O_7NMeCl)_2PtCl_4,$$

forms small, orange crystals.

*Methylcodeinium methosulphite, methyl*apo*morphinium methosulphite, methylthebanium methosulphite*, with their respective *methobromides*, were also prepared; thebaine methobromide has m. p. 185°.

F. M. G. M.

Strychnine and Brucine. II. ROBERTO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 501—505. Compare Abstr., 1910, i, 583).—When cacothelin is suspended in water acidified with hydrobromic acid and treated with bromine water until it has all dissolved, it is converted into the *hydrobromide* of an acid, $C_{19}H_{22}O_6N_2,HBr,2H_2O$, which is obtained in yellow crystals by the evaporation of the solution. The free acid, $C_{19}H_{22}O_6N_2,2H_2O$ (compare Hanssen, Abstr., 1887, 505), forms scales having a nacreous lustre. It is not toxic. The *platinichloride*, $(C_{19}H_{22}O_6N_2),H_2PtCl_6$, obtained in presence of hydrochloric acid, crystallises in small, yellow prisms. R. V. S.

Identity of Vernine and Guanosine and Notes on Vicine and Convicine. ERNST SCHULZE and G. TRIER (*Zeitsch. physiol. Chem.*, 1910, **70**, 143—151. Compare Abstr., 1910, ii, 645).—The pentose (compare Schulze and Castoro, Abstr., 1904, ii, 506) obtained by the hydrolysis of vernine yields *l*-arabinose-*p*-bromophenylosazone (Levene and Jacobs, Abstr., 1909, i, 858), and is presumably *d*-ribose. A detailed comparison of vernine with Levene and Jacobs' guanosine (Abstr., 1910, i, 620) has proved that the two are identical.

The following formulæ are suggested for vicine and convicine, namely, $C_{20}H_{36}O_{15}N_8$ and $C_{20}H_{28}O_{16}N_6,2H_2O$.

The hydrolysis of vicine is represented by the equations:

$$(1)\ C_{20}H_{36}O_{15}N_8 + H_2O = \underset{\text{Divicin.}}{C_8H_{14}O_4N_8} + \underset{\text{Hexoses.}}{2C_6H_{12}O_6}$$

$$(2)\ C_8H_{14}O_4N_8 + 4H_2O = C_8H_{10}O_8N_4 + 4NH_3,$$

and that of convicine by the equation:

$$C_{20}H_{28}O_{16}N_6,2H_2O + 4H_2O = \underset{\text{Alloxanthin.}}{C_8H_6O_8N_4,2H_2O} + 2C_6H_{12}O_6 + 2NH_3$$

(compare Ritthausen, Abstr., 1881, 1158; 1899, i, 715).

The two compounds are thus glucosides formed by the condensation of hexoses with pyrimidine derivatives. J. J. S.

Indole in Coal Tar. RUDOLF WEISSGERBER (*Ber.*, 1910, **43**, 3520—3528).—The *sodium* derivative of indole, $C_6H_4{<}\begin{matrix}CH\\NNa\end{matrix}{>}CH$, is obtained in the form of a brown, amorphous mass, m. p. 140°, by heating indole with sodamide at 150—160°, or with sodium at 170—180°; it reacts with methyl iodide, yielding 1-methylindole, together with small quantities of 2-methylindole and 3-methylindole.

On warming with benzoyl chloride in benzene solution, it yields *benzoylindole*, $C_6H_4{<}\begin{matrix}CH\\NBz\end{matrix}{>}CH$; the latter crystallises from alcohol in compact, rhombic plates, m. p. 67—68°, b. p. 213°/16 mm., and is readily hydrolysed by aqueous sodium hydroxide.

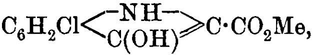
The *potassium* derivative of indole is obtained as a light-coloured mass by heating indole with potassium hydroxide.

The formation of the potassium compound furnishes a ready means of separating indole from coal tar. The fraction, b. p. 240—260°, freed from phenols and bases by shaking with alkali hydroxide and dilute sulphuric acid is heated with potassium hydroxide at 190—200°, the unattacked oil removed by washing with benzene, and the potassium indole decomposed by water; the separation may also be effected by means of sodium or sodamide.

The crude indole may be purified by converting it into the bisulphite compound (Hesse, Abstr., 1900, i, 48), or into the sodium salt of indolecarboxylic acid (compare Zatti and Ferratini, Abstr., 1890, i, 292), by heating with sodium at 190—200° in a stream of carbon dioxide. The free acid obtained from the sodium salt by acidification loses carbon dioxide when heated in a vacuum at 230—250° and yields indole. F. B.

Preparation of Halogenindoxylic Acids and their Esters.

Badische Anilin- & Soda-Fabrik (D.R.-P. 226689).—The conversion by alkalis of phenylglycine-*o*-carboxylic acids into derivatives of indoxyl has been described (compare Abstr., 1908, i, 974, 1019), and it is now found that the reaction can be applied successfully to halogenated derivatives of the acid.

Methyl 5 : 7-*dichloroindoxylcarboxylate*,  $C_6H_2Cl\Big<\begin{matrix}NH\\C(OH)\end{matrix}\Big>C\cdot CO_2Me$, colourless needles, m. p. 195°, is prepared by boiling *dimethyl* 4 : 6-*dichlorophenylglycine-2-carboxylate*, m. p. 77—78°, in toluene solution with sodium or sodium methoxide; the toluene can be replaced by other indifferent solvents.

Dimethyl 6-*chloro*-4-*bromophenylglycine*-2-*carboxylate*, m. p. 81—83° (obtained from 6-chloro-4-bromophenylglycine-2-carboxylic acid, m. p. 238°, in the usual manner), yielded on similar treatment *methyl* 7-*chloro*-5-*bromoindoxylcarboxylate*, $C_6H_2ClBr\Big<\begin{matrix}NH\\C(OH)\end{matrix}\Big>C\cdot CO_2Me$, long needles, m. p. 203—205°.

Methyl 4 : 6-*dichlorophenylglycine*-2-*carboxylate*, colourless needles, m. p. 133—134°, on treatment with sodium ethoxide yielded *sodium* 5 : 7-*dichloroindoxylcarboxylate*, a yellow powder which is readily converted into 5 : 7 : 5′ : 7′-tetrachloroindigotin by the action of air and water. F. M. G. M.

Betaine Formation and Steric Hindrance.

Alfred Kirpal (*Monatsh.*, 1910, 31, 969—979. Compare Abstr., 1908, i, 679).—Nicotinic, *iso*nicotinic, and cinchomeronic acids interact with chloroacetic acid in neutral solution, giving almost theoretical yields of the corresponding betaines; picolinic and quinolinic acids, under the same conditions, react incompletely, whilst dipicolinic acid remains unchanged. The author suggests that these results may be explained on the assumption that the carboxyl group in the α-position exerts a negative influence on the nitrogen atom, which therefore shows less tendency to assume the quinquevalent condition. This explanation is, however, not applicable to quinaldine and 2 : 6-dimethylpyridine, both of which, on treatment with chloroacetic acid, do not yield betaine, but are converted into their hydrochlorides; the non-formation of betaines in these cases is referred to steric influences.

iso*Nicotinic acid betaine*, $C_8H_7O_4N$, prepared by heating *iso*nicotinic acid and chloroacetic acid in faintly alkaline, aqueous solution, crystallises in needles, m. p. 262° (decomp.).

Nicotinic acid betaine forms monoclinic prisms or octahedral crystals, and has m. p. 190° (decomp.).

Picolinic acid betaine crystallises in short, pointed prisms, m. p. 165° (decomp.); the *hydrochloride* has m. p. 181°.

Cinchomeronic acid betaine, $C_9H_7O_6N$, forms rhombic plates, m. p. 180° (decomp.).

Quinolinic acid betaine, $C_9H_7O_6N,H_2O$, crystallises in colourless prisms, which, when heated at 100°, lose their water of crystallisation and carbon dioxide, yielding nicotinic acid betaine; the same decomposition also takes place on boiling its aqueous solution; the *hydrochloride* is readily hydrolysed, aqueous solutions rapidly depositing the free betaine.

a-Picolinebetaine, $C_8H_9O_2N$, prepared by heating *a*-picoline with chloroacetic acid on the water-bath and isolated by means of its platinichloride, crystallises in colourless, hygroscopic needles, which turn brown at 100° and decompose at 162°; the *platinichloride* forms yellow prisms, m. p. 212° (decomp.); the *hydrochloride* has m. p. 188° (decomp.). F. B.

Derivatives of 2-Phenylquinoline. II. ERNST MURMANN (*Monatsh.*, 1910, 31, 1303—1306. Compare Abstr., 1892, 1003).—

Disulphonic acids can be obtained by heating 1-phenylquinoline with four times its weight of commercial fuming sulphuric acid on the water-bath until a test drop gives no crystals (monosulphonic acid) when heated with five drops of water and no turbidity on addition of aqueous ammonia.

The mass is diluted with five times its weight of water, and a small amount of monosulphonic acid separates during the course of a day. After further dilution, boiling with animal charcoal, and neutralising with barium carbonate, crystals of a *barium* salt,

$$C_{15}H_9O_6NS_2Ba,6H_2O,$$

in the form of long, colourless needles, are obtained. The *calcium* salt, $C_{15}H_9O_6NS_2Ca,6H_2O$, forms slender, yellow needles, sparingly soluble in water, and the *zinc* salt crystallises with $5H_2O$ in large, felted needles.

The filtrate from the barium salt contains an isomeric salt, which is sparingly soluble in alcohol, and crystallises with $12H_2O$. The first barium salt, when fused with potassium hydroxide, yields a red *phenol*, m. p. 140—141°. J. J. S.

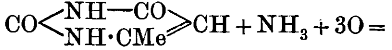
Formation of Acyl Derivatives of Phenylhydrazine in Aqueous Solution. STEPHAN JAROSCHY (*Monatsh.*, 1910, 31, 951—967).—

The phenylhydrazides of formic, acetic, propionic, butyric, and *iso*butyric acids are readily formed by heating the acids with phenylhydrazine in aqueous solution. The relative velocities of formation of these hydrazides under various conditions at 100° have been investigated by estimating the amount of unchanged acid by titration with barium hydroxide. With the same concentration of acid and of base, it is found that the rates of formation stand in the same order as the magnitude of the dissociation constants of the acids.

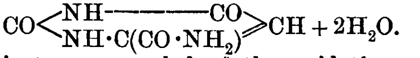
The effect of temperature was studied in the case of the formyl derivative. Increase of temperature is accompanied by an increase in the relative velocity, and the same effect is produced by increasing the concentration of the acid.

The addition of a small quantity of hydrochloric acid was found to diminish the rate of formation of the acetyl derivative. The author suggests that this is to be referred to the diminution in the ionisation of the acetic acid; on this assumption, the acylation is due to the anions. F. B.

Oxidation of Methyluracil. ROBERT BEHREND and KARL STRUVE (*Annalen*, 1910, **378**, 153—169. Compare Behrend and Dietrich, Abstr., 1900, i, 120; Behrend and Grünewald, Abstr., 1902, i, 834; Behrend and Fricke, Abstr., 1903, i, 739; Behrend and Osten, Abstr., 1906, i, 309; Behrend and Hufschmidt, Abstr., 1906, i, 310; Hobel, Abstr., 1907, i, 557; Offe, *ibid.*, 645).—When oxidised with potassium ferricyanide in ammoniacal solution, methyluracil yields the amide of uracilcarboxylic acid:

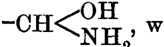


$\mathrm{CO}<\begin{matrix}\mathrm{NH{-}CO}\\ \mathrm{NH\cdot CMe}\end{matrix}>\mathrm{CH} + NH_3 + 3O =$

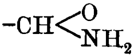


$\mathrm{CO}<\begin{matrix}\mathrm{NH{-}{-}{-}{-}CO}\\ \mathrm{NH\cdot C(CO\cdot NH_2)}\end{matrix}>\mathrm{CH} + 2H_2O.$

This appears to be the first instance recorded of the oxidation of a $-CH_3$ to a $-CO\cdot NH_2$ group. The reaction does not consist in the oxidation of the methyl to a carboxylic group and the conversion of the latter into the $-CO\cdot NH_2$ group by means of ammonia, as it is shown that a temperature of 240° is required for the latter reaction. It is possible that an aldehyde group is first formed, and that this yields an aldehyde-ammonia,

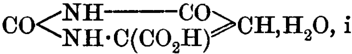


$-\mathrm{CH}<\begin{matrix}\mathrm{OH}\\ \mathrm{NH_2}\end{matrix}$, which is then oxidised to the



$-\mathrm{CH}<\begin{matrix}\mathrm{O}\\ \mathrm{NH_2}\end{matrix}$ group. When the oxidation takes place in the presence of potassium hydroxide the product is uracilcarboxylic acid.

In the preparation of the amide, the mixture is heated at 50—60° for five to six hours and allowed to cool, when potassium ferrocyanide separates; this is removed, and the filtrate heated until all the ammonia is driven off and an odour of hydrogen cyanide is noticed. The solution is filtered hot and kept for one to two days at the ordinary temperature, when methyluracil separates as octahedra or needles, and in the course of a week or so the amide separates in a crystalline form. It is most readily freed from uracil by conversion into its sparingly soluble *potassium* derivative, $C_5H_4O_3N_3K,2H_2O$, which crystallises from hot water in well-developed prisms. Its solution has an alkaline reaction. The *amide*, $C_5H_5O_3N_3,H_2O$, crystallises in small, lancet-shaped plates, dissolves in 110 parts of boiling water, and in 2000 parts of water at 20°. When boiled with alkalis, it yields *uracilcarboxylic acid*,

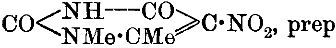


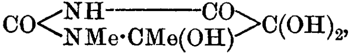
$\mathrm{CO}<\begin{matrix}\mathrm{NH{-}{-}{-}CO}\\ \mathrm{NH\cdot C(CO_2H)}\end{matrix}>\mathrm{CH},H_2O$, in the form of rhombic plates, which lose their water of hydration at 120°. The anhydrous compound decomposes above 300° without melting. The hydrated compound dissolves in 70 parts of water at 100° and in 500 parts at 18°, The addition of acetic acid to a solution of the carboxylic acid in potassium hydroxide solution precipitates *potassium uracilcarboxylate*, $C_5H_3O_4N_2K$. The *ammonium* salt, $C_5H_7O_4N_3,H_2O$, crystallises in small, six-sided plates. The acid is identical with the product obtained by hydrolysing the ester described by Müller (Abstr., 1897, i, 549).

When methyluracil is oxidised with potassium ferricyanide in the presence of potassium hydroxide solution, it is best to leave the mixture for twenty days at the ordinary temperature and then to acidify with acetic acid, when potassium uracilcarboxylate is precipitated.

It has not been found possible to oxidise the carboxylic acid with potassium ferricyanide, but with permanganate (3O) at 15° the acid yields oxaluric and oxalic acids. J. J. S.

Oxidation of α- and β-Dimethyluracils. Paul Henkel (*Annalen*, 1910, **378**, 170—187. Compare Behrend and Grünewald, Abstr., 1902, i, 834).—The oxidation of α- and β-dimethyluracils is analogous to that of methyluracil (compare table given by Osten, *Annalen,* 1905, **343**, 151). Methylparabanic acid can be isolated from the oxidation products of both compounds, under conditions such that its formation from methyloxaluric acid is excluded. The two dimethyluracils have been transformed into corresponding α- and β-trihydroxydimethyldihydrouracils by Osten's method (Abstr., 1906, i, 309). These hydroxy-derivatives exist in only one form, whereas the corresponding trihydroxymethyldihydrouracil exists in two forms (Abstr., 1908, i, 840). Although it has not been found possible to isolate an acetylmethylallanturic acid by the action of alkali on the trihydroxy-derivatives, it is shown that a conversion of the six-membered ring into a five-membered ring must take place under the influence of alkalis, since, when oxidised with permanganate in the presence of excess of potassium hydrogen carbonate, the α-trihydroxy-derivative yields methylparabanic acid together with methyloxaluric acid, but no trace of acetylmethylcarbamide. Trihydroxy-β-dimethyldihydrouracil is oxidised much less readily, and under similar conditions yields *s*-acetylmethylcarbamide together with methyloxaluric acid and methylparabanic acid; but when the solution of the hydroxy-compound is left in contact with the potassium hydrogen carbonate for twenty-four hours before the addition of the permanganate, the products obtained are methylparabanic acid and methyloxaluric acid. Acetylmethyloxaluric acid is not formed during the oxidation in the presence of the carbonate.

Nitro-α-dimethyluracil (*5-nitro-2:6-dioxy-3:4-dimethyldihydropyrimidine*),  $CO<\begin{matrix}NH{-}{-}{-}CO\\NMe\cdot CMe\end{matrix}>C\cdot NO_2$, prepared by Osten's method (*loc. cit.*), crystallises from water in yellow plates, m. p. 249—250°, and when reduced by Behrend and Grünewald's method (*loc. cit.*) yields the corresponding *amino*-derivative, $C_6H_9O_2N_3$, in the form of yellow crystals, m. p. 281—282°.

Trihydroxy-α-dimethyldihydrouracil (*4:5:5-trihydroxy-2:6-dioxy-3:4-dimethyldihydropyrimidine*),  $CO<\begin{matrix}NH{-}{-}{-}{-}{-}{-}CO\\NMe\cdot CMe(OH)\end{matrix}>C(OH)_2$, obtained by oxidising the amino-α-dimethyluracil with bromine water at low temperatures, crystallises when its aqueous solution is concentrated at the ordinary temperature under 4 mm. pressure, and decomposes at 120°. When heated at 70—80° for fifteen minutes with ethyl alcohol, it yields the 5 : 5-*diethoxy*-derivative, $CO<\begin{matrix}NH\text{———}CO\\NMe\cdot CMe(OH)\end{matrix}>C(OEt)_2$, which crystallises from alcohol, and has m. p. 114—116°.

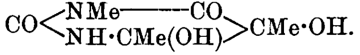
Nitro-β-dimethyluracil (*5-nitro-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*), $CO<\begin{matrix}NMe—CO\\NH\cdot CMe\end{matrix}>C\cdot NO_2$, crystallises from water in pale yellow prisms, m. p. 229—230° (decomp.); the corresponding *amino*-derivative has m. p. 256—257° (decomp.), and *trihydroxy-β-dimethyldihydrouracil* (*4 : 5 : 5-trihydroxy-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*), $CO<\begin{matrix}NMe\text{———}CO\\NH\cdot CMe(OH)\end{matrix}>C(OH)_2$, crystallises from dilute acetic acid, and decomposes at 133°.

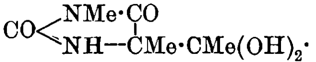
Bromo-β-dimethyluracil, $CO<\begin{matrix}NMe\cdot CO\\NH\cdot CMe\end{matrix}>CBr$, is sometimes formed as a by-product; it has m. p. 243°. *4-Hydroxy-5 : 5-diethoxy-2 : 6-dioxy-1 : 4-dimethyldihydropyrimidine*, $C_{10}H_{18}O_5N_2$, crystallises from alcohol, has m. p. 124—126° (decomp.), and dissolves in 20 parts of cold absolute alcohol.

Methylparabanic acid is readily transformed into methyloxaluric acid when its alcoholic solution is made alkaline with *N*/5-alcoholic potash and kept for an hour.

It has not been found possible to obtain either of the above-mentioned nitro-derivatives by the action of methyl iodide and alkali on nitromethyluracil. J. J. S.

Action of Potassium Permanganate and of Bromine on 1 : 4 : 5-Trimethyluracil. KARL BREMER (*Annalen*, 1910, **378**, 188—209).—By analogy with methyluracil (Abstr., 1906, i, 310) it was thought probable that by the oxidation of 1 : 4 : 5-trimethyluracil with cold permanganate, methylacetylcarbamide and pyruvic acid would be formed, and that with warm permanganate, acetyldimethylhydantoin or its oxidation products would be obtained. Actual experiment has shown that the products are the same at both temperatures, using 2 atoms of oxygen; in both cases only acetylmethylcarbamide and a syrup are formed. No trace of pyruvic acid can be detected in the syrup, and the only product so far isolated from the syrup is oxalic acid. Dihydroxytrimethyldihydrouracil has been prepared by Behrend, Osten, and Beer's method (Abstr., 1906, i, 309), but it has not been settled definitely whether the compound has the constitution of the uracil (1) or whether it is the isomeric acetyldimethyl hydantoin (2).

(1) 
$$CO<\begin{matrix}NMe\text{———}CO\\NH\cdot CMe(OH)\end{matrix}>CMe\cdot OH.$$

(2) 
$$CO<\begin{matrix}NMe\cdot CO\\NH—CMe\cdot CMe(OH)_2\end{matrix}.$$

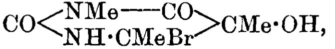
In favour of the latter formula are the facts that it is not readily oxidised, and does not appear to be affected by alkalis.

Attempts to oxidise 1-phenyl-4 : 5-dimethyluracil were unsuccessful, owing to the slight solubility of the compound in water.

Behrend and Hennicke's method (Abstr., 1906, i, 314) for the preparation of thiontrimethyluracil gives a 25% and not an 80% yield. A 45—50% yield is obtained when a mixture of equivalent quantities of methyl thiocarbimide and ethyl β-amino-α-methyl crotonate is heated to 55—60° and then kept for twenty-four hours in an ice chest; after removing the crystals, the filtrate is heated to 70°, and on cooling gives a further crop of crystals. The desulphurisation is accomplished most readily by heating the compound in a reflux apparatus with 65% sulphuric acid for about forty-five minutes at 150—160° and subsequent dilution with three times the volume of water. The yield of trimethyluracil is 80%; it crystallises from hot water, and has m. p. 222—223°.

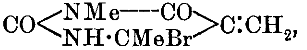
1-Phenyl-4 : 5-dimethyluracil, $C_{12}H_{12}O_2N_2$, is formed when ethyl phenylcarbamidomethylcrotonate (Abstr., 1901, i, 136), prepared from ethyl β-amino-α-methylcrotonate and phenylcarbimide, is hydrolysed with 5% potassium hydroxide solution and the solution acidified with hydrochloric acid; it has m. p. 235°.

4-*Bromo*-5-*hydroxy*-1 : 4 : 5-*trimethyldihydrouracil*,

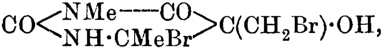
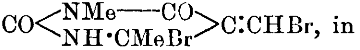
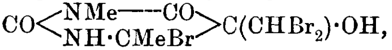


$$\mathrm{CO}{<}\begin{matrix}\mathrm{NMe}\text{---}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}{>}\mathrm{CMe\cdot OH},$$

obtained by the action of water and an excess of bromine on trimethyluracil at the temperature of the water-bath, crystallises from hot water in needles, m. p. 127° after sintering at 120°. When heated with alcohol, or by itself at 95°, and then at 115°, it loses water and yields 4-*bromo*-1 : 4-*dimethyl*-5-*methylenedihydrouracil*,



$$\mathrm{CO}{<}\begin{matrix}\mathrm{NMe}\text{---}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}{>}\mathrm{C{:}CH_2},$$

which crystallises from benzene or dilute alcohol, and has m. p. 195° after sintering at 170°. This unsaturated compound reacts with bromine water, yielding 4-*bromo*-5-*hydroxy*-1 : 4-*dimethyl*-5-*bromomethyldihydrouracil*,  $\mathrm{CO}{<}\begin{matrix}\mathrm{NMe}\text{---}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}{>}\mathrm{C(CH_2Br)\cdot OH}$, m. p. 150—151° after sintering at 145°, and this, when heated at 90—100° for three hours, yields 4-*bromo*-1 : 4-*dimethyl*-5-*bromomethylenedihydrouracil*,  $\mathrm{CO}{<}\begin{matrix}\mathrm{NMe}\text{---}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}{>}\mathrm{C{:}CHBr}$, in the form of well-developed needles, m. p. 175—178°, which again react with bromine water, yielding 4-*bromo*-5-*hydroxy*-1 : 4-*dimethyl*-5-*dibromomethyldihydrouracil*,  $\mathrm{CO}{<}\begin{matrix}\mathrm{NMe}\text{---}\mathrm{CO}\\ \mathrm{NH\cdot CMeBr}\end{matrix}{>}\mathrm{C(CHBr_2)\cdot OH}$, as colourless crystals.

Dibromohydroxymethyldihydrouracil does not yield an unsaturated compound when heated at 150°.

Chlorohydroxytrimethyldihydrouracil, $C_7H_{11}O_3N_2Cl$, obtained by the action of chlorine water on trimethyluracil, crystallises from hot water, and has m. p. 154—155°.

4-*Bromo*-5-*hydroxy*-1-*phenyl*-4 : 5-*dimethyldihydrouracil*, $C_{12}H_{13}O_3N_2Br$, has m. p. 195°.

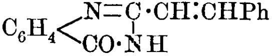
4 : 5-*Dihydroxy*-1 : 4 : 5-*trimethyldihydrouracil*, $C_7H_{12}O_4N_2$, prepared from the bromohydroxy-compound by Behrend and Grünewald's method, crystallises from water in large prisms, m. p. 165°. It reacts with boiling acetic anhydride, yielding an *acetyl* derivative, $C_9H_{14}O_5N_2$, m. p. 135—150°, and with phenyldydrazine yields a *phenylhydrazide*, $C_{13}H_{18}O_3N_4$, in the form of needles, m. p. 155—158° after sintering at 145°.

J. J. S.

Quinazolines. XXVI. Synthesis of Some Stilbazoles, Hydrazones, and Schiff Bases in the 4-Quinazolone Group.

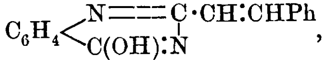
Marston T. Bogert, George Denton Bell, and Carl Gustave Amend (*J. Amer. Chem. Soc.*, 1910, **32**, 1654—1664).—It has been shown in earlier papers (Bogert and Gortner, Abstr., 1909, i, 679; Bogert, Amend, and Chambers, Abstr., 1910, i, 893) that derivatives of 4-quinazolone can be easily prepared which contain a 2-methyl group and amino-groups attached to either or both the benzene and metadiazine portions of the nucleus. A study has been made of the behaviour of these different groups towards aldehydes, and the results show that with reference to their reactivity with benzaldehyde they may be arranged in the following order: (1) the 3-amino-group (in the metadiazine nucleus); (2) the 2-methyl group; and (3) the 7-amino-group (in the benzene nucleus).

When 2-methyl-4-quinazolone is boiled for ten minutes with benzaldehyde, it is converted into the stilbazole, namely, 2-*styryl*-4-*quinazolone* (2-*styryl*-4-*hydroxyquinazoline*),



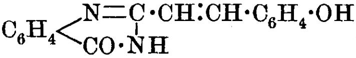
$C_6H_4<\begin{array}{l}N{=}C\cdot CH{:}CHPh\\ CO\cdot NH\end{array}$

or



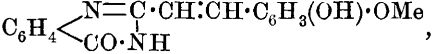
$C_6H_4<\begin{array}{l}N{=}C\cdot CH{:}CHPh\\ C(OH){:}N\end{array}$

, m. p. 252—253° (corr.), which forms colourless, silky needles, and yields a *bromo*-derivative. 2-o-*Hydroxystyryl*-4-*quinazolone*,



$C_6H_4<\begin{array}{l}N{=}C\cdot CH{:}CH\cdot C_6H_4\cdot OH\\ CO\cdot NH\end{array}$

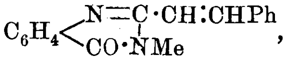
, m. p. 307° (decomp.), obtained by the action of salicylaldehyde on 2-methyl-4-quinazolone, crystallises in minute, pale yellow needles, and yields bright yellow *salts* with hydrochloric acid and potassium hydroxide. 2-p-*Hydroxy*-m-*methoxystyryl*-4-*quinazolone*,



$C_6H_4<\begin{array}{l}N{=}C\cdot CH{:}CH\cdot C_6H_3(OH)\cdot OMe\\ CO\cdot NH\end{array}$

, m. p. 280° (corr.), forms minute, pale yellow needles and gives dark yellow alkali salts.

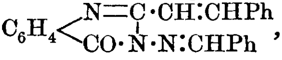
When 2 : 3-dimethyl-4-quinazolone is boiled with benzaldehyde, 2-*styryl*-3-*methyl*-4-*quinazolone*,



$C_6H_4<\begin{array}{l}N{=}C\cdot CH{:}CHPh\\ CO\cdot NMe\end{array}$

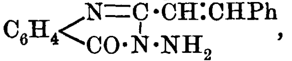
, m. p. 170° (corr.), is produced, which forms light yellow, slender needles.

3-Amino-2-methyl-4-quinazolone was prepared by the action of hydrazine hydrate on acetylanthranil (Bogert and Gortner, *loc. cit.*). In one experiment, a compound, m. p. 193° (corr.), was isolated, which crystallises in prisms, and is probably *acetylanthranylacetylhydrazide*, $NHAc\cdot C_6H_4\cdot CO\cdot NH\cdot NHAc$. The hydrazone, 3-benzylideneamino-2-methyl-4-quinazolone, obtained by boiling 3-amino-2-methyl-4-quinazolone (1 mol.) with benzaldehyde (1 mol.), has m. p. 187° (corr.), and not 183° as stated by Bogert and Gortner (*loc. cit.*); its *hydrochloride* softens at 220°, and decomposes without melting at about 300°. When 3-amino-2-methyl-4-quinazolone (1 mol.) is boiled with benzaldehyde (2 mols.), 3-*benzylideneamino*-2-*styryl*-4-*quinazolone*,



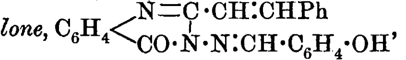
$C_6H_4<\begin{array}{l}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot N{:}CHPh\end{array}$

, m. p. 155° (corr.), is obtained, which forms minute, nearly colourless, stellate groups of crystals; its *hydrochloride* does not melt below 300°. When this substance is treated with boiling dilute hydrochloric acid and the product distilled with steam, benzaldehyde passes over with the distillate, and 3-*amino*-2-*styryl*-4-*quinazolone*,



$$C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot NH_2\end{matrix},$$

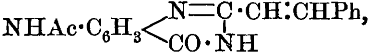
m. p. 164° (corr.), is obtained, which crystallises in plates or broad needles, and when heated with benzaldehyde is reconverted into its benzylidene derivative; the *benzoyl* derivative has m. p. 195° (corr.). When 3-amino-2-methyl-4-quinazolone is heated with cinnamaldehyde, salicylaldehyde, or vanillaldehyde, the methyl group is not affected, but condensation takes place only with the amino-group. 3-*Cinnamylideneamino*-2-*methyl*-4-*quinazolone*, m. p. 148—149° (corr.), forms bright yellow needles. The corresponding *salicylidene* derivative, m. p. 171° (corr.), crystallises in short, pale yellow needles, yields a bright yellow *potassium* salt and a *hydrochloride*, m. p. 250° (decomp.), and is hydrolysed by hydrochloric acid or potassium hydroxide with formation of salicylaldehyde. Although the salicylidene compound refuses to condense with a second mol. of salicylaldehyde, it condenses readily with benzaldehyde with formation of 3-*salicylideneamino*-2-*styryl*-4-*quinazolone*,



$$C_6H_4<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot N{:}CH\cdot C_6H_4\cdot OH\end{matrix},$$

m. p. 232—233° (corr.), which crystallises in yellow needles. 3-*Vanillylideneamino*-2-*methyl*-4-*quinazolone*, m. p. 215—216° (corr.), forms small, yellow prisms or needles, and gives deep, yellow salts with hydrochloric acid and potassium hydroxide.

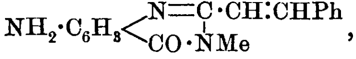
In the case of 7-amino-2-methyl-4-quinazolone, as in that of the 3-amino-derivative, condensation is possible with either the methyl or amino-group or with both. The amino-group, however, is differently situated, being in the benzene instead of the metadiazine nucleus and attached to a carbon instead of a nitrogen atom. Aldehydes condensing with the 7-amino-group should therefore yield true Schiff bases instead of hydrazones. In one experiment, a *benzylidene* derivative, m. p. 324° (corr.), was obtained, which seemed to be the Schiff base, since it was hydrolysed by potassium hydroxide with formation of benzaldehyde and the quinazolone, but this compound could not be obtained subsequently; its *acetyl* derivative has m. p. 274—276° (corr.). 7-*Acetylamino*-2-*styryl*-4-*quinazolone*,



$$NHAc\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot NH\end{matrix},$$

m. p. 323—324° (corr.), obtained by boiling 7-acetylamino-2-methyl-4-quinazolone with benzaldehyde, forms short, colourless needles.

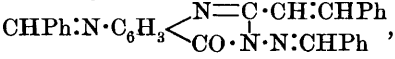
7-Amino-2 : 3-dimethyl-4-quinazolone condenses with benzaldehyde to form 7-*amino*-2-*styryl*-3-*methyl*-4-*quinazolone*,



$$NH_2\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot NMe\end{matrix},$$

m. p. 229·5—230° (corr.), which crystallises in yellow prisms; its *acetyl* derivative has m. p. 272° (corr.).

When 3 : 7-diamino-2-methyl-4-quinazolone is boiled with an excess of benzaldehyde, 3 : 7-*dibenzylideneamino*-2-*styryl*-4-*quinazolone*,



$$CHPh{:}N\cdot C_6H_3<\begin{matrix}N{=}C\cdot CH{:}CHPh\\ CO\cdot N\cdot N{:}CHPh\end{matrix},$$

m. p. 238° (corr.), is produced, together with small quantities of two other *substances*, m. p. 196° (corr.) and 172° (corr.), which seem to be isomeric dibenzylidene derivatives. 7-*Acetylamino-3-benzylideneamino-2-styryl-4-quinazolone*, m. p. 261° (corr.), obtained by boiling 3-amino-7-acetylamino-2-methyl-4-quinazolone with excess of benzaldehyde, forms yellow needles; its solution in alcohol has a green fluorescence. 3 : 7-Diacetylamino-2-methyl-4-quinazolone condenses with benzaldehyde with formation of 3 : 7-*diacetylamino-2-styryl-4-quinazolone*, m. p. 283—284° (corr.).

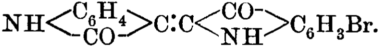
3-Amino-6-acetylamino-2-methyl-4-quinazolone condenses similarly with benzaldehyde with production of 6-*acetylamino-3-benzylideneamino-2-styryl-4-quinazolone*, m. p. 238—239° (corr.), which forms short, silky, yellow needles. E. G.

Constitution of Indirubin. I. and II. André Wahl and P. Bagard (*Bull. Soc. chim.*, 1910, [iv], 7, 1090—1101; 1911, 9, 56—83. Compare Abstr., 1909, i, 330, 735).—I. Maillard's objection (Abstr., 1910, i, 138) to the view that the authors' new synthesis of indirubin (Abstr., 1909, i, 330) supports von Baeyer's formula for this substance is based on two main contentions: (*a*) that proof of the formation of indirubin was insufficient; (*b*) that molecular transformation may have occurred in the reaction.

In regard to (*a*) it is now shown that the synthetic indirubin, like commercial indirubin, yields Schunk and Marchlewski's colourless, crystalline compound, m. p. 204°, when reduced with zinc and acetic anhydride in presence of anhydrous sodium acetate (Abstr., 1895, i, 288). Contention (*b*) implies that both oxindole and indoxyl should condense with isatin chloride to give indirubin, but actual trial shows that when the reaction is conducted in presence of pyridine to remove the hydrogen chloride formed, indoxyl gives indigotin and no indirubin, whereas oxindole gives indirubin as chief product.

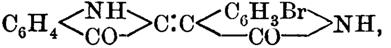
II. *m*-Bromoisatin chloride condenses with oxindole to furnish a bromoindirubin, which is isomeric with, but different from, that obtained by condensing *m*-bromoisatin with indoxylic acid. The production of isomerides in these two reactions can be explained easily from von Baeyer's, but only with difficulty from Maillard's, formula.

m-Bromoisatin chloride condenses with oxindole in benzene solution to form a *bromoindirubin*, having the formula



$$NH<\begin{matrix}C_6H_4\\CO\end{matrix}>C:C<\begin{matrix}CO\\NH\end{matrix}>C_6H_3Br.$$

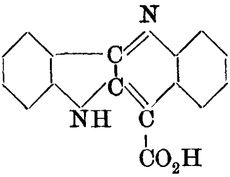
It forms dichroic, triclinic crystals, showing oblique extinction and angle $ph' = 126°$. Its solubility is 0·192—0·199 gram in 100 grams of acetic acid at 25°. The bromoindirubin obtained by condensing *m*-bromoisatin with indoxylic acid has the formula



$$C_6H_4<\begin{matrix}NH\\CO\end{matrix}>C:C<\begin{matrix}C_6H_3Br\\CO\end{matrix}>NH,$$

and has been prepared already by von Baeyer (Abstr., 1882, 198). It forms dichroic crystals which belong to the monoclinic system, and show right extinction and angle $ph' = 101°$. Its solubility is 0·042—0·052 gram in 100 grams of acetic acid at 25°. T. A. H.

Quindoline and "Thioquindoline." Emilio Noelting and O. R. Steuer (*Ber.*, 1910, **43**, 3512—3517).—Indoxylic acid condenses with *o*-aminobenzaldehyde in hydrochloric acid solution, yielding quindoline (compare Fichter and Böhringer, Abstr., 1907, i, 92; Fichter and Rohner, this vol., i, 85). This is identical with indoline described by Schützenberger (this Journ., 1877, ii, 898).

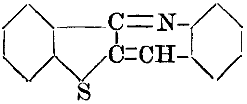


By heating indigotin with an alkaline solution of sodium thiosulphate, Geraud (Abstr., 1879, 936; 1881, 51) obtained a substance to which he assigned the formula $C_{32}H_{24}O_3N_4$. Since the same compound is also produced by the condensation of indoxyl and isatin in alkaline solution, it must be a *quindolinecarboxylic acid* of the annexed structure.

2-o-*Nitrobenzylidene-indoxyl*, $C_6H_4{<}^{CO-}_{NH}{>}C{:}CH{\cdot}C_6H_4{\cdot}NO_2$, prepared by the condensation of *o*-nitrobenzaldehyde and indoxylic acid in aqueous acetic acid solution, crystallises in red needles, m. p. 217°; on reduction with zinc dust and acetic acid it yields quindoline.

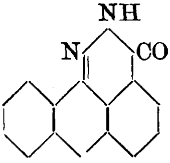
By condensing indoxylic acid with *o*-aminobenzaldehyde in the presence of a little hydrochloric acid, 2-o-*aminobenzylidene-indoxyl*, $C_6H_4{<}^{CO-}_{NH}{>}C{:}CH{\cdot}C_6H_4{\cdot}NH_2$, is produced; if the condensation is carried out in more acid solution, quindoline hydrochloride is obtained.

3-*Keto*-2-o-*nitrobenzylidene-thionaphthen*, $C_6H_4{<}^{CO}_{-S-}{>}C{:}CH{\cdot}C_6H_4{\cdot}NO_2$, prepared from *o*-nitrobenzaldehyde and 3-hydroxythionaphthen-2-carboxylic acid in acetic acid solution, crystallises from alcohol in orange-yellow needles, m. p. 171°; on reduction it yields "*thioquindoline*" (annexed formula). The latter crystallises in almost colourless needles, m. p. 169°, and with concentrated acids forms yellow salts, which are decomposed by water; the *hydrochloride* and *picrate* are described.

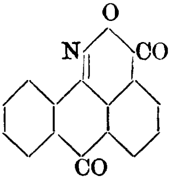


Quindoline and "thioquindoline" dye tannin-mordanted wool, silk, and cotton pale yellow; with quindolinecarboxylic acid the shade is somewhat deeper. F. B.

Anthraquinone-1-carboxylic Acid. Fritz Ullmann and Willem van der Schalk (*Ber.*, 1911, **44**, 128—129).—*Anhydro-anthraquinone-9-hydrazone-1-carboxylic acid* (*pyridazonanthrone*) (I), obtained by the action of hydrazine hydrate on the chloride of anthraquinone-1-carboxylic acid, crystallises in needles which are sparingly soluble in the usual solvents, but dissolve in sodium hydroxide to orange-yellow solutions. Phenylhydrazine gives the corresponding *N*-phenylpyridazonanthrone. Anthraquinone-1-carb-



(I.)



(II.)

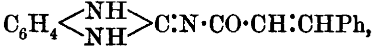
oxylic acid reacts readily with hydroxylamine in the presence of sodium acetate solution, yielding *oxazonanthrone* (II) in the form of pale yellow needles, m. p. 247°. J. J. S.

Method for Preparing Aromatic Acylguanidines. Paul Pierron (*Compt. rend.*, 1910, **151**, 1364—1366. Compare Wheeler and Johnson, Abstr., 1902, i, 27).—Aromatic acylguanidines are best prepared by boiling the aromatic acylcyanamides with the hydrochloride of an aromatic amine in alcoholic solution; thus benzoylcyanamide and aniline hydrochloride yield benzoylphenylguanidine, the *hydrochloride* of which has m. p. 159°. *Benzoyl*-m-*tolylguanidine*, $C_7H_8\cdot NH\cdot C(NHBz){:}NH$, crystallises in needles or leaflets, m. p. 71°; the *hydrochloride* has m. p. 170°. *Cinnamoylphenylguanidine*,

$$\mathrm{CHPh{:}CH\cdot CO\cdot NH\cdot C(NHPh){:}NH},$$

forms prismatic needles, m. p. 140°; *benzoyl-ψ-cumidylguanidine*, $C_{17}H_{19}ON_3$, occurs in prismatic needles, m. p. 140—141°.

On boiling acylcyanamides with *o*-phenylenediamine in alcoholic solution, an acylaminobenziminazole is produced. The arylcyanamides do not readily undergo this condensation. *Cinnamoyl*-o-*phenyleneguanidine* [*2-cinnamoyliminobenziminazole*],



$$C_6H_4{<}{\overset{NH}{\underset{NH}{}}}{>}C{:}N\cdot CO\cdot CH{:}CHPh,$$

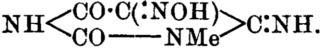
crystallises in needles, m. p. 262°. W. O. W.

Pechmann's Isomeric Hydrazidines. Henry L. Wheeler and Treat B. Johnson (*Ber.*, 1911, **44**, 151).—The authors have already shown (Abstr., 1904, i, 628) that the formulæ suggested by Busch and Ruppenthal (this vol., i, 86) for Pechmann's hydrazidines (Abstr., 1896, i, 31), namely, $NH_2\cdot NPh\cdot CPh{:}NPh$ and $NHPh\cdot NH\cdot CPh{:}NPh$, are correct. J. J. S.

Preparation of 4-*iso*Valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone and of 4-α-Bromo*iso*valerylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. Knoll & Co. (D.R.-P. 227013).—Compounds possessing valuable therapeutic properties are obtained by introducing *iso*valeryl or substituted *iso*valeryl residues into 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone.

4-iso*Valerylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone*, m. p. 203°, odourless and with a bitter taste, is prepared by heating 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone with *iso*valeric acid and phosphorus trichloride at 125° during half an hour, treating with sodium carbonate, and crystallising the dried product from benzene; its aqueous solutions give a blood-red coloration with ferric chloride.

4-*α-Bromo*iso*valerylamino*-1-*phenyl*-2 : 3-*dimethyl*-5-*pyrazolone* is obtained when α-bromo*iso*valeryl bromide is substituted for the *iso*valeric acid and phosphorus trichloride in the foregoing preparation; it forms glistening, colourless needles, m. p. 206° (decomp.), is odourless, but has a bitter taste, and forms crystalline *salts* with acids and a yellow coloration with ferric chloride. F. M. G. M.

Preparation of 4-Imino-5-oximino-2 : 6-diketopyrimidine and its 3-Alkyl Derivative. Emanuel Merck (D.R.-P. 227390).—The action of nitrous acid on a hot dilute acetic acid solution of cyano-acetylmethylcarbamide, $NHMe\cdot CO\cdot NH\cdot CO\cdot CH_2\cdot CN$, yields *oximinocyanoacetylmethylcarbamide*, $NHMe\cdot CO\cdot NH\cdot CO\cdot C(:NOH)\cdot CN$, colourless crystals, m. p. 218° (decomp.). When this substance is warmed with 30% sodium hydroxide (4 parts), an orange-yellow precipitate slowly separates, which on the addition of acetic acid is converted into the characteristic red crystals of 4-imino-5-oximino-2 : 6-diketo-3-methylpyrimidine,  $NH<\begin{matrix}CO\cdot C(:NOH)\\ CO\text{——}NMe\end{matrix}>C:NH$. Analogous results are obtained when cyanoacetylcarbamide is employed in the foregoing reaction; a yellow, crystalline *sodium* derivative separates on treatment with sodium nitrite, yielding on acidification *oximinocyanoacetylcarbamide*, glistening, colourless crystals, m. p. 220°, which are readily converted into the corresponding 4-imino-5-oximino-2 : 6-diketopyrimidine. The sodium hydroxide can in this reaction be replaced by sodamide, sodium ethoxide, or an alkylcarbamide. F. M. G. M.

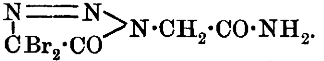
Preparation of Anthrapyrimidines and Anthrapyrimidones.

FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 225982).—The reaction between aminoanthraquinones and acid amides has been previously described (Abstr., 1910, i, 445); the same result is now obtained with acylaminoanthraquinones and ammonia, 1-anthrapyrimidone (*loc. cit.*) having been prepared by heating aminoanthraquinoneurethane with ammonium hydroxide at 150°; likewise, 1 : 4-diaminoanthraquinonemonourethane yields 4-*amino*-1-*anthrapyrimidone*, brown crystals, and 2-*bromo*-4-*amino*-1-μ-*methylanthrapyrimidine*, a brown powder, is obtained from 2 : 4-dibromo-1-acetylaminoanthraquinone.

A tabulated description of the following compounds, with the colours of their solutions in various solvents, is given in the original: 1-*aminoanthraquinoneurethane*, greenish-yellow crystals; 1-*aminoanthraquinonecarbamide chloride*, orange crystals; 1 : 4-*diaminoanthraquinonemonourethane*, garnet-red crystals; 4-*chloro*-1-*aminoanthraquinoneurethane*, golden-yellow crystals; 2 : 4-*dibromo*-1-*acetylaminoanthraquinone*, brownish-yellow crystals; 4-*amino*-1-*anthrapyrimidone*, dark brown crystals. F. M. G. M.

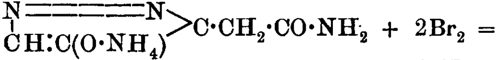
4-Dibromo-1 : 2 : 3-triazol-5-one-1-acetamide.

THEODOR CURTIUS and ERNST WELDE (*Ber.*, 1910, 43, 857—862).—The dibromo-derivative mentioned previously (Abstr., 1907, i, 450) is shown to be 4-*dibromo*-1 : 2 : 3-*triazole*-5-*one*-1-*acetamide*,



$$\begin{matrix}N{=\!=}N\\ |\\ CBr_2\cdot CO\end{matrix}>N\cdot CH_2\cdot CO\cdot NH_2.$$

Its formation from the ammonium salt of 5-hydroxy-1 : 2 : 3-triazole-1-acetamide is represented by means of the equation:



$$\begin{matrix}N{=\!=\!=\!=}N\\ |\\ CH:C(O\cdot NH_4)\end{matrix}>C\cdot CH_2\cdot CO\cdot NH_2 + 2Br_2 =$$

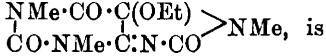
$$C_4H_4O_2N_4Br_2 + HBr + NH_4Br,$$

and its formation from the nitroso-derivative by the equation:

$$C_4H_8O_3N_5 + 2Br_2 = C_4H_4O_2N_4Br_2 + NOBr + NH_4Br,$$

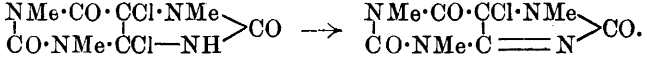
the nitrosyl bromide formed immediately yielding nitrous and hydrobromic acids.

The dibromo-derivative crystallises from hot alcohol in colourless, glistening needles, m. p. 151° (decomp.), after turning brown at 120°. It changes colour when exposed to the air for several hours, and then has an odour of bromine. When boiled with dilute sulphuric acid, it is hydrolysed to nitrogen, ammonia, glycine, and dibromoglycollic acid, the last of which is further hydrolysed to hydrobromic and oxalic acids. The same decomposition occurs, only more slowly, when the bromo-derivative is boiled with water. J. J. S.

Derivatives of *iso*Uric Acid. Heinrich Biltz (*Ber.*, 1910, **43**, 3553—3562).—It has been shown (Abstr., 1909, i, 740) that diethoxy-4 : 5-diphenyldihydroglyoxalone is converted on heating at the m. p. into 5-ethoxy-4 : 5-diphenyl*iso*glyoxalone. Diethoxy-1 : 3 : 7-trimethyluric acid might be expected to behave similarly, but it does not change at the m. p. However, on boiling it in glacial acetic acid solution, *5-ethoxy-trimethyl*iso*uric acid*,  $\begin{array}{l}\text{NMe·CO·C(OEt)}\\ \text{CO·NMe·C:N·CO}\end{array}\!\!>\text{NMe}$, is formed. This can be crystallised from cold alcohol without change, but on boiling with alcohol containing a little acid, the diethoxy-derivative is regenerated. On reduction with zinc and acetic acid, hydrogen is added at positions 4 and 9, that in 4 is immediately eliminated with the ethoxyl group in position 5, and trimethyluric acid is obtained.

5-Ethoxytrimethyl*iso*uric acid is completely analogous to 5-ethoxydiphenyl*iso*glyoxalone, and the conclusion is drawn that the ethoxyl group in position 4 and the imino-hydrogen in position 9 are on opposite sides of the plane of the glyoxalone ring.

By the action of chlorine on trimethyluric acid in chloroform solution, a dichloride is first formed soluble in chloroform, chlorine being added in positions 4 and 5. This is unstable, hydrogen chloride being eliminated between positions 4 and 9, and a chlorine derivative of *iso*uric acid is obtained,



$$\begin{array}{l}\text{NMe·CO·CCl·NMe}\\ \text{CO·NMe·CCl—NH}\end{array}\!\!>\text{CO} \longrightarrow \begin{array}{l}\text{NMe·CO·CCl·NMe}\\ \text{CO·NMe·C}=\!=\!=\text{N}\end{array}\!\!>\text{CO}.$$

Alcohol converts this chloride into 5-ethoxy-1 : 3 : 7-trimethyl*iso*uric acid; water readily converts it into *apo*caffeine.

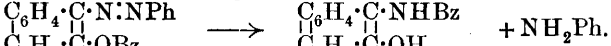
*5-Ethoxy-1 : 3 : 7-trimethyl*iso*uric acid* forms long, thin, colourless needles, m. p. 174—176°.

*5-Methoxy-1 : 3 : 7-trimethyl*iso*uric acid* crystallises in obliquely cut, six-sided, columnar forms, m. p. 205°.

*5-Chloro-1 : 3 : 7-trimethyl*iso*uric acid* separates in colourless, flat needles or prisms with oblique end faces and a rectangular cross section, m. p. 158° (decomp.). The corresponding 5-bromo-compound could not be obtained. E. F. A.

Hydroxyazo-compounds and Ketohydrazones. I.—III. Karl Auwers [and, in part, Hugo Dannehl and A. Boennecke] (*Annalen*, 1910, **378**, 210—260. Compare Auwers, Abstr., 1908, i, 477).—The results of previous investigations indicate that when possible the phenylhydrazones of benzoquinones and naphthaquinones undergo molecular rearrangement into azo-compounds, whereas with mixed azo-derivatives the reverse process takes place.

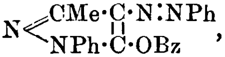
Phenanthraquinonephenylhydrazone (Zincke, Abstr., 1883, 1135; Werner, *Annalen*, 1902, **321**, 304), when benzoylated in the presence of pyridine, yields a benzoyl derivative which is identical with the product obtained by condensing phenanthraquinone with *as*-benzoylphenylhydrazine in the presence of mineral acids. From the readiness with which it is hydrolysed and from the fact that when reduced with zinc dust and cold acetic acid the chief products are aniline and 9-benzoylamino-10-hydroxyphenanthrene (87% yield), the conclusion is drawn that the benzoyl compound is an *O*-derivative:

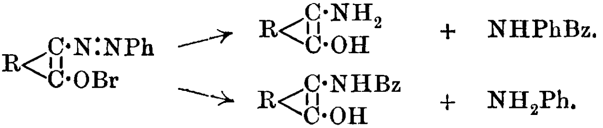


$$\begin{array}{l} C_6H_4\cdot C\cdot N{:}NPh \\ C_6H_4\cdot C\cdot OBz \end{array} \longrightarrow \begin{array}{l} C_6H_4\cdot C\cdot NHBz \\ C_6H_4\cdot C\cdot OH \end{array} + NH_2Ph.$$

In the condensation of phenanthraquinone with benzoylphenylhydrazine, a wandering of the benzoyl group from nitrogen to oxygen occurs, a wandering analogous to that observed in the condensation of β-naphthaquinone with benzoylphenylhydrazine. The same *O*-acetyl derivative is obtained by acetylating phenanthraquinonephenylhydrazone and by condensing phenanthraquinone with *as*-acetylphenylhydrazine. This acetyl derivative is so readily hydrolysed that it is difficult to purify. The general conclusion drawn is that phenanthraquinonephenylhydrazone is 9-benzeneazo-10-phenanthrol.

9-*Benzeneazo*-10-*phenanthryl benzoate*, $C_{27}H_{18}O_2N_2$, crystallises from glacial acetic acid in glistening, red plates, m. p. 193—194°. 9-*Benzoylamino*-10-*phenanthrol*, $C_{21}H_{15}O_2N$, crystallises from glacial acetic acid in glistening, flat needles, m. p. 248—249°. 9-*Benzeneazo*-10-*phenanthryl acetate*, $C_{22}H_{16}O_2N_2$, crystallises from light petroleum in brilliant red plates, m. p. 139—140°, and is hydrolysed when warmed with alcohol or acetic acid.

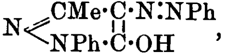
The question as to the constitution of Knorr's 4-benzeneazo-5-keto-1-phenyl-3-methylpyrazolone has been investigated (Knorr, Abstr., 1887, 678; 1888, 724; Japp and Klingemann, Trans., 1888, **53**, 519; Wedekind, *Annalen*, 1897, **295**, 330; Bülow, Abstr., 1899, i, 355; Eibner, Abstr., 1903, i, 871). The same benzoyl derivative is obtained by: (1) the action of benzoyl chloride on the sodium derivative suspended in dry ether; (2) the action of benzoyl chloride and sodium hydroxide solution on an aqueous acetone solution of the pyrazolone; (3) the condensation of ketophenylmethylpyrazolone with *as*-phenylbenzoylhydrazine hydrochloride in dilute alcohol. It is regarded as the *O*-benzoyl derivative,  $N{<}\begin{smallmatrix} CMe\cdot C\cdot N{:}NPh \\ NPh\cdot C\cdot OBz \end{smallmatrix}$, since when reduced with zinc dust and cold acetic acid it yields appreciable amounts of aniline, together with benzanilide and rubazonic acid.



$$R{<}\begin{smallmatrix} C\cdot N{:}NPh \\ C\cdot OBr \end{smallmatrix} \begin{array}{l} \longrightarrow R{<}\begin{smallmatrix} C\cdot NH_2 \\ C\cdot OH \end{smallmatrix} + NHPhBz. \\ \longrightarrow R{<}\begin{smallmatrix} C\cdot NHBz \\ C\cdot OH \end{smallmatrix} + NH_2Ph. \end{array}$$

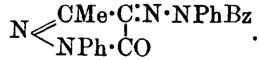
It has not been found possible to isolate the *N*-benzoyl derivative of the aminohydroxyphenylmethylpyrazole.

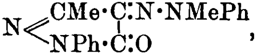
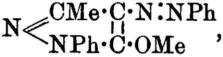
Knorr's compound is thus a true azo-derivative, and as it dissolves readily in alkalis, it is represented by the enolic formula



$$\mathrm{N}\left<\begin{array}{l}\mathrm{CMe{\cdot}C{\cdot}N{:}NPh}\\ \quad\;\;\Vert\\ \mathrm{NPh{\cdot}C{\cdot}OH}\end{array}\right.,$$

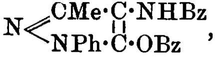
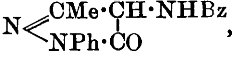
and is 4-benzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole.

When the β-phenylhydrazone of $\alpha\beta$-diketobutyric acid is condensed with benzoylphenylhydrazine, water is eliminated, and Knorr's azo-compound and ethyl benzoate are obtained, instead of the expected *N*-benzoyl derivative,  $\mathrm{N}\left<\begin{array}{l}\mathrm{CMe{\cdot}C{:}N{\cdot}NPhBz}\\ \quad\;\;|\\ \mathrm{NPh{\cdot}CO}\end{array}\right.$. The free hydroxypyrazole is also formed (1) when the benzoylated osazone of the diketobutyric acid is warmed with benzene and phosphoric oxide; (2) when the β-phenylhydrazone of ethyl $\alpha\beta$-diketobutyrate is condensed with *as*-benzoylphenylhydrazine hydrochloride in alcoholic solution, both with and without the addition of sodium acetate, and (3) when the dibenzoyl derivative of the osazone of the ethyl diketobutyrate is warmed with alcoholic potassium hydroxide.

The methyl derivative obtained by condensing ketophenylmethylpyrazolone with *as*-phenylmethylhydrazine must be the *N*-methyl ether,  $\mathrm{N}\left<\begin{array}{l}\mathrm{CMe{\cdot}C{:}N{\cdot}NMePh}\\ \quad\;\;|\\ \mathrm{NPh{\cdot}C{:}O}\end{array}\right.$, as alkyl groups do not wander under these conditions. This constitution is confirmed by the fact that when reduced with zinc and acetic acid, methylaniline is obtained, but no trace of aniline. The same methyl ether, together with a small amount of the isomeric *O*-methyl ether,  $\mathrm{N}\left<\begin{array}{l}\mathrm{CMe{\cdot}C{\cdot}N{:}NPh}\\ \quad\;\;\Vert\\ \mathrm{NPh{\cdot}C{\cdot}OMe}\end{array}\right.$, is formed when Knorr's azo-compound is methylated by means of methyl iodide or sulphate and alkali. When reduced, the *O*-methyl ether yields appreciable amounts of aniline.

The *N*-methyl ether is readily hydrolysed to the monomethyl derivative of ethyl diketobutyrate osazone, whereas the *O*-ether is not acted upon when boiled with alcoholic potassium hydroxide.

The *benzoyl* derivative of 4-benzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole, $C_{23}H_{18}O_2N_4$, crystallises from alcohol in long, yellow, glistening needles, or from light petroleum in quadratic plates, m. p. 137°, which are readily hydrolysed when boiled with 50% acetic acid.

The *dibenzoyl* derivative of 4-*amino*-5-*hydroxy*-1-*phenyl*-3-*methylpyrazole*,  $\mathrm{N}\left<\begin{array}{l}\mathrm{CMe{\cdot}C{\cdot}NHBz}\\ \quad\;\;\Vert\\ \mathrm{NPh{\cdot}C{\cdot}OBz}\end{array}\right.$, prepared by benzoylating the corresponding amine, crystallises from dilute alcohol in colourless, glistening needles, m. p. 196°, and on hydrolysis yields a colourless compound, m. p. 110—115°, probably the acid $\mathrm{NHPh{\cdot}N{:}CMe{\cdot}CH(NHBz){\cdot}CO_2H}$, which, when heated, yields the N-*benzoyl* derivative,  $\mathrm{N}\left<\begin{array}{l}\mathrm{CMe{\cdot}CH{\cdot}NHBz}\\ \quad\;\;|\\ \mathrm{NPh{\cdot}CO}\end{array}\right.$, m. p. 183°. Keto-1-phenyl-3-methylpyrazolone, prepared by Sachs and Barschall's method (Abstr., 1902, i, 504), has m. p. 121°. The *monobenzoylosazone* of $\alpha\beta$-diketobutyric acid,

$$\mathrm{NHPh{\cdot}N{:}CMe{\cdot}C(CO_2H){:}N{\cdot}NBzPh},$$

crystallises from light petroleum in slender, pale yellow needles, m. p.

110—111°, and dissolves in cold sodium hydroxide solution without undergoing hydrolysis. Ethyl αβ-diketobutyrate and benzoylphenylhydrazine yield the *dibenzoylated osazone*, $C_{32}H_{28}O_4N_4$, even in the presence of an excess of ester. It crystallises from dilute methyl alcohol in long, colourless prisms, m. p. 190°. Ethyl αβ-diketobutyrate and phenylmethylhydrazine yield the *dimethylosazone*,

$NMePh\cdot N:CMe\cdot C(CO_2Et):N\cdot NMePh$,

which crystallises from alcohol in pale yellow, glistening prisms, m. p. 103—104°. The *phenylmethylhydrazone* of 4-keto-1-phenyl-3-methyl-5-pyrazolone, $C_{17}H_{16}ON_4$, crystallises from dilute alcohol in glistening, orange-yellow, felted needles, m. p. 144°, and is insoluble in alkalis; the isomeric *O-methyl ether* forms compact, yellow prisms, m. p. 78°.

It has not been found possible to acetylate or benzoylate Graebe and Gfeller's acenaphthenequinonephenylhydrazone (Abstr., 1893, i, 657), but the *benzoyl* derivative, $C_{25}H_{16}O_2N_2$, can be prepared by condensing the quinone with benzoylphenylhydrazine hydrochloride and alcohol. It crystallises in glistening, orange-red needles, m. p. 170°, and is readily hydrolysed by cold alcoholic sodium hydroxide. When reduced with zinc and acetic acid, it yields no trace of aniline, and is therefore a *N*-benzoyl derivative, and the phenylhydrazone probably has the hydrazone and not the azo-structure.

Acenaphthenequinonephenylmethylhydrazone, $C_{19}H_{14}ON_2$, crystallises from acetone in dark red needles, m. p. 114°, and, when reduced, yields methylaniline and no trace of aniline.

Camphorquinonephenylhydrazone cannot be directly acylated, but the *benzoyl* derivative, $C_{23}H_{24}O_2N_2$, can be obtained, by condensing the quinone with benzoylphenylhydrazine, in the form of colourless, felted needles, m. p. 153°. This is also a *N*-benzoyl derivative, and the parent substance a hydrazone, which exists in one form only (compare Lapworth and Hann, Trans., 1902, **81**, 1514).

The two *N*-benzoyl derivatives, unlike most other *N*-benzoylated compounds, are readily hydrolysed. The following new *N*-benzoyl derivatives, prepared by condensing the ketones with benzoylphenylhydrazine, are not readily hydrolysed by alkalis: *Ethyl acetoacetate benzoylphenylhydrazone*, $C_{19}H_{20}O_3N_2$, forms compact, colourless, quadratic crystals, m. p. 144—145°, and with alcoholic potash yields the *benzoylphenylhydrazone* of acetoacetic acid, $C_{17}H_{16}O_3N_2$, in the form of small, colourless prisms, m. p. 203°.

Diacetyldibenzoylosazone, $C_{30}H_{26}O_2N_4$, crystallises from boiling glacial acetic acid in slender needles, m. p. 249°, and is formed even at $-15°$ in the presence of an excess of the ketone. *Benzil-benzoylphenylhydrazone*, $C_{27}H_{20}O_2N_2$, crystallises from light petroleum in slender, prismatic needles, m. p. 176°.

Baeyer and Claisen's phenylazoacetylacetone (Abstr., 1888, 828) is best prepared by the gradual addition of a solution of phenyldiazonium chloride exactly neutralised with sodium carbonate to a cold solution of acetylacetone (1 mol.) in sodium carbonate (0·5 mol.). The benzoyl derivative (Pechmann, Abstr., 1893, i, 84) is most readily prepared by the Schotten-Baumann method; it has m. p. 160—161°, is readily hydrolysed by alkalis, and is sometimes accompanied by an *isomeride*, m. p. 134°. When reduced, the benzoyl derivative yields benzanilide, but no trace of aniline. The compound is thus a *N*-benzoyl derivative, and the parent substance a γ-phenylhydrazone of βγδ-triketopentane and not an azo-derivative.

Benzoylacetylacetone, in the form of its sodium derivative, reacts with a neutralised solution of phenyldiazonium chloride, yielding O-*benzeneazodiacetylbenzoylmethane*, NPh:N·O·CMe:CBzAc, which crystallises from methyl alcohol in golden-yellow, prismatic needles, m. p. 77—78°. The compound is not affected when boiled with alcohol; with cold alkalis, or with an ethereal solution of hydrogen chloride, it yields the phenylhydrazone of phenyl methyl triketone, and when boiled with glacial acetic acid yields benzoylacetone. The reaction with hydrogen chloride is similar to that described by Dimroth and Hartmann as characteristic of *O*-azo-compounds (Abstr., 1909, i, 66). The azo-compound (m. p. 77—78°) reacts with an alcoholic solution of β-naphthol, yielding benzeneazo-β-naphthol and benzoylacetylacetone. When reduced with zinc dust and acetic acid, the azo-compound yields appreciable amounts of aniline. The isomeric *acetylphenylhydrazone* of phenyl methyl triketone,

CAcBz:N·NAcPh,

is formed when the *O*-azo-compound is boiled for four hours with toluene; it separates from alcohol in colourless crystals, m. p. 158°, and when reduced yields acetanilide, but no trace of aniline. The compound is isomeric with the benzoyl derivative of phenylazoacetylacetone, m. p. 160°.

These results agree with Pechmann's view that the compounds derived from diazo-compounds and aliphatic ketones with the reactive ·CO·CH_2· group are not azo-compounds, but hydrazones.

Generalisations based on the constitution of *N*-benzoyl derivatives and the readiness with which they are hydrolysed cannot be drawn.

J. J. S.

Method for Determining the Individuality or Plurality of Diastases in a Liquid.

PIERRE ACHALME and BRESSON (*Compt. rend.*, 1910, **151**, 1369—1372).—In order to ascertain whether a particular liquid contains one or more enzymes, the authors suggest that it should be allowed to act, under identical conditions, on solutions of two different substances capable of being hydrolysed by it, and on a solution containing a mixture of the same two substances. If two diastases are present, the action on the mixture should be the sum of the action on the two substances taken individually, whilst if only one enzyme is present, the action on the mixture should not exceed that on either substance alone. The results of illustrative experiments are given in tabular form. It is found that the time taken to effect hydrolysis in the three solutions is the same if two diastases are present, but that when only one enzyme is acting, a longer period is required to hydrolyse the mixture. W. O. W.

Chlorophyll. XI. Chlorophyllase.

RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1910, **378**, 18—72).—See this vol., i, 141.

Organic Chemistry.

Synthesis of *as*-Heptachloropropane from Tetrachloroethylene and Chloroform with the Co-operation of Aluminium Chloride. JACOB BÖESEKEN and H. J. PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 685—687).—It has previously been shown (Abstr., 1910, i, 152) that when dichloroacetyl chloride is decomposed by aluminium chloride, one of the products is a crystalline substance, m. p. 32°, to which the composition C_5Cl_{10} was assigned. A larger quantity of this substance has now been prepared, and it is found to be identical with the *as*-heptachloropropane obtained by Fritsch from pentachloroacetone and phosphorus pentachloride (Abstr., 1898, i, 63). The heptachloropropane may also be prepared by the direct addition of chloroform to tetrachloroethylene under the influence of aluminium chloride.

This synthesis gives another proof that the theory of the formation of intermediate products as an explanation of Friedel and Crafts' reaction must be abandoned, as there are no indications of the formation of such products. It may be assumed that aluminium chloride renders the chloroform active, so that the molecular parts $CHCl_2$ and Cl attach themselves to the double linking of the ethylene perchloride, also rendered active.

It is also shown that pentachloroethane yields *as*-heptachloropropane with chloroform and aluminium chloride. N. C.

Preparation of Bromides from Primary and Secondary Saturated Alcohols. FELIX TABOURY (*Bull. Soc. chim.*, 1911, [iv], 9, 124—125).—Fournier (Abstr., 1906, i, 787) has shown that hydrogen bromide reacts with primary and secondary saturated alcohols at the ordinary pressure, giving good yields of alkyl bromides. The author states that it is unnecessary to prepare the hydrogen bromide separately, and gives details for carrying out the reaction in one large flask. Yields varying from 75 to 85% of methyl, ethyl, propyl, and *iso*propyl bromides were obtained in this way. In the case of *iso*butyl bromide the yield fell to 50%, owing to a secondary action of the bromine on the bromide produced. It was found in this case that on raising the temperature at the end of the experiment, a liquid was obtained, b. p. 149—150°; this is dibromo*iso*butane, $CH_2Br{\cdot}CMe_2Br$. N. C.

Acetylenic Pinacone [$\beta\epsilon$-Dimethyl-Δ^γ-hexinene-$\beta\epsilon$-diol]. GEORGES DUPONT (*Compt. rend.*, 1911, **152**, 197—199).—$\beta\epsilon$-Dimethyl-Δ^γ-hexinene-$\beta\epsilon$-diol, $OH{\cdot}CMe_2{\cdot}C{\vdots}C{\cdot}CMe_2{\cdot}OH$ (Jotsitch, *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 1545) is a colourless substance, m. p. 95°, which, unlike corresponding saturated compounds, does not form a hydrate. It resembles these subtances, however, in its behaviour towards the halogen acids, but approaches more closely to $\beta\delta$-dimethylpentaneβδ-diol (Franke, Abstr., 1905, i, 111; 1907, i, 816) in its reactions with dehydrating agents.

The corresponding *dibromide*, $CMe_2Br\cdot C\vdots C\cdot CMe_2Br$, m. p. 39°, b. p. 219°, is an exceedingly stable substance. In its formation by the action of hydrogen bromide, an unstable intermediate compound was noticed, m. p. about 50°. The corresponding *dichloride* has m. p. 29°, b. p. 62—63°/15 mm.

By the action of dilute sulphuric acid on the diol, the two following substances are obtained in proportions varying with the concentration and duration of heating. (1) *β-Methyl-ε-methylene-Δγ-hexinene-β-ol*, $CH_2\colon CMe\cdot C\vdots C\cdot CMe_2\cdot OH$, a pale yellow liquid with an agreeable odour, m. p. −2°, b. p. 159—160°, D^{15} 0·8772, n_D 1·4687. When treated with hydrogen in presence of spongy platinum it yields dimethyl*iso*amylcarbinol (Konowaloff, Abstr., 1902, i, 336). (2) *βε-Dimethylene-Δγ-hexinene*, $CH_2\colon CMe\cdot C\vdots C\cdot CMe\colon CH_2$, is a colourless, mobile liquid, b. p. 123—124°, D^{15} 0·7898, n_D 1·4859, which rapidly becomes resinous on exposure to air. It is best prepared by the action of potassium hydroxide on the foregoing dibromide. On reduction it yields βε-dimethylhexane. W. O. W.

Existence of Chlorosulphinic Esters. ARTHUR STÄHLER and ERIK SCHIRM (*Ber.*, 1911, 44, 319—323).—Well-cooled ethyl alcohol is treated slowly with thionyl chloride, and the mixture is distilled under 19 mm. pressure after being kept overnight. The resulting ethyl chlorosulphinate, $Cl\cdot SO_2Et$, b. p. 29°/13 mm., is a faintly yellow liquid, which decomposes at its b. p., 122°, under ordinary pressure into sulphur dioxide and ethyl chloride, as found by previous investigators. The methyl ester, b. p. 19°/13 mm. or 102°/755 mm. (decomp.), is obtained, and behaves in a similar manner. Neither of the esters, however, can be separated completely from the excess of the thionyl chloride on account of proximity of b. p. The *propyl* ester, however, has been obtained in a pure state as a colourless liquid, b. p. 78°/75 mm. The iso*butyl* ester has b. p. 48·5°/9 mm.

The chlorosulphinic esters are very unstable substances, which are vigorously decomposed by water into sulphur dioxide, hydrogen chloride, and an alcohol. C. S.

Delepine's Phosphorescent Esters. JAIME FERRER HERNÁNDEZ and ANGEL DEL CAMPO Y CERDAN (*Anal. Fis. Quim.*, 1911, 9, 17—26. Compare Delepine, Abstr., 1910, i, 295, 545).—The authors have repeated Delepine's observations on the phosphorescence of dimethyl dithiocarbonate, $OMe\cdot CS\cdot SMe$, and find that ionisation of the air is produced during the phenomenon, whilst the compound appears to possess feeble radioactivity. The potassium methyl salt, $OMe\cdot CS\cdot SK$ yields methyl tetrathionate when oxidised by potassium permanganate or sodium perborate in dilute acid solution. G. D. L.

Separation of the Liquid Fatty Acids (Unsaturated) from the Solid Fatty Acids (Saturated) in Natural Mixtures of Fatty Acids, and the Ammonium Salts of Some Fatty Acids. II. PIETRO FALCIOLA (*Gazzetta*, 1910, 40, ii, 425—435. Compare this vol., i, 5).—When applied to mixtures of natural origin the method previously described does not effect a rigorously quantitative separation, but nevertheless it may be employed with more or less success, and yields more satisfactory results in the case of mixtures containing a preponderance of the solid acids. The ammonium salts of the solid fatty acids (such as the palmitate and stearate) are more soluble in ammoniacal alcohol containing ammonium salts of liquid fatty acids (for example, the oleate) than in that solvent alone. Moreover, the solid fatty acids separated by the method always contain appreciable quantities of the liquid fatty acids.

Ammonium linoleate, $C_{17}H_{31}\cdot CO_2\cdot NH_4$, is prepared by passing dry ammonia into a cold ethereal salution of the acid in an atmosphere of hydrogen. In presence of ammonia and lime, the pasty mass obtained becomes solid. It begins to melt at 57—58°, and is completely melted at 75°, forming a red liquid. *Ammonium erucate*,

$$C_{22}H_{41}O_2\cdot NH_4,$$

is similarly prepared, and has m. p. 70—77°. *Ammonium laurate*, $C_{11}H_{23}\cdot CO_2\cdot NH_4$, is a white substance, m. p. about 75°. *Ammonium myristate*, $C_{13}H_{27}\cdot CO_2\cdot NH_4$, has m. p. about 75—90°. *Ammonium octoate*, $C_8H_{15}O_2\cdot NH_4$, has m. p. 70—85°. Ammonium hexoate may be prepared in the same way. *Ammonium crotonate*, $C_3H_4\cdot CO_2\cdot NH_4$, forms colourless crystals, m. p. 105—115°. *Ammonium butyrate*, $C_3H_7\cdot CO_2\cdot NH_4$, has m. p. 70—85°. R. V. S.

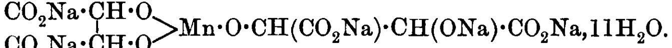
Linolenic Acid and Linseed Oil. ADOLF ROLLETT (*Zeitsch. physiol. Chem.*, 1911, **70**, 404—407).—Polemical (compare Erdmann and Bedford, Abstr., 1910, i, 810; Rollet, Abstr., 1909, i, 760). Pure linolenic acid has the iodine value 273·7. E. F. A.

Action of the Chlorides of α-Alkyloxy-acids on Organometallic Derivatives of Zinc. EDMOND É. BLAISE and L. PICARD (*Compt. rend.*, 1911, **152**, 268—269).—The chlorides of α-alkyloxy-acids are acted on abnormally by organozinc iodides, giving rise under some conditions to an ether, in addition to the usual alkyloxy-ketone. This arises from the elimination of carbon monoxide from the acid chloride, probably through catalytic influence of the zinc compound. The action is represented as: $R\cdot O\cdot CH_2\cdot COCl = R\cdot O\cdot CH_2Cl + CO$; $R\cdot O\cdot CH_2Cl + ZnR'I = ZnClI + R\cdot O\cdot CH_2R'$. The yield of ether increases and that of ketone diminishes as the temperature of reaction rises. The proportion of ether increases also with the molecular weight of the zinc salt; thus, from zinc *n*-heptyl iodide only ethyl octyl ether was obtained. When R or R′ are cyclic, only the ketone is formed; thus ethoxyacetyl chloride and zinc *p*-tolyl bromide gave p-*tolyl ethoxymethyl ketone*, $OEt\cdot CH_2\cdot CO\cdot C_7H_7$, b. p. 135°/9·5 mm.; the *oxime* has m. p. 57°, and the p-*nitrophenylhydrazone*, m. p. 80°. The yield of ketone increases also with the weight of R. *iso*Butoxyacetyl chloride and zinc ethyl iodide gave *n*-propyl *iso*butyl ether (10%) and *ethyl* iso*butoxymethyl ketone* (50%), b. p. 68—69°/13 mm.; *oxime*, b. p. 116—117°/14 mm.; *semicarbazone*, m. p. 72°. Phenoxyacetyl chloride gave only *phenoxymethyl ethyl ketone*, b. p. 129°/14 mm.; *semicarbazone*, m. p. 102°; p-*nitrophenylhydrazone*, prisms, m. p. 153°.

W. O. W.

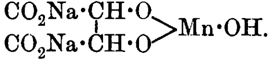
The Preparation of β-Alkyloxy-compounds. M. H. PALOMAA and SULO KILPI (*Chem. Zentr.*, 1910, ii, 1453; from *Ann. Finn. Akad. Wiss.*, *A* 2, No. 3).—The preparation of the esters of hydracrylic acid by the action of sodium alkyloxides on ethyl β-chloropropionate gave unsatisfactory results; the action was better in the case of the β-iodopropionate. *Methyl β-methoxypropionate*, $OMe\cdot CH_2\cdot CH_2\cdot CO_2Me$, is a colourless liquid, b. p. 143·4—143·6°/750 mm., D^{15}_{15} 1·0148. *Ethyl β-ethoxypropionate* has b. p. 49·5—49·8°/7 mm., D^{15}_{15} 0·9536. *Propyl β-propoxypropionate* is a colourless, agreeably smelling liquid, b. p. 74·5—75·5°/7 mm., D^{15}_{15} 0·9386 N. C.

A Green, Crystalline Manganitartrate. ANDRÉ JOB and P. GOISSEDET (*Compt. rend.*, 1911, **152**, 265—268. Compare Abstr., 1907, ii, 553; Durrant, Trans., 1905, **87**, 1781).—Eighteen grams of manganous sulphate dissolved in water (20 c.c.) are added to a solution of sodium tartrate (450 grams) in a litre of water. The solution is shaken in an atmosphere of oxygen, and 100 grams of sodium hydroxide in 250 c.c. of water added slowly. The red liquid gradually deposits green crystals of *sodium manganitartrate*,



$$\begin{array}{l} CO_2Na\cdot CH\cdot O \\ CO_2Na\cdot CH\cdot O \end{array}\!\!>Mn\cdot O\cdot CH(CO_2Na)\cdot CH(ONa)\cdot CO_2Na,11H_2O.$$

This salt dissolves in water, forming an alkaline solution, which deposits manganic hydroxide and probably, through hydrolysis having occurred, contains the salt,



$$\begin{array}{l} CO_2Na\cdot CH\cdot O \\ CO_2Na\cdot CH\cdot O \end{array}\!\!>Mn\cdot OH.$$

On the addition of sodium tartrate the liquid becomes green and remains stable. The green solutions are unable to afford green crystals, although these appear on the addition of an alkali carbonate, when the liquid becomes red. An explanation of this fact is suggested.

W. O. W.

Basic Citrates and Tartrates of Barium. ANTONIO QUARTAROLI (*Chem. Zentr.*, 1910, ii, 1131—1132; from *Staz. sperim. agrar. ital.*, 1910, **43**, 396—408).—The author states than when excess of barium hydroxide is added to a solution of citric acid at a temperature of at least 18°, a tetrabasic citrate is formed; at lower temperatures (+5—10°) a less basic citrate is formed, which is more soluble. The citrate formed above 18° dissolves to the extent of 10—13% in water. With tartaric acid, in the same way, a tribasic tartrate is obtained; the same modification is formed at 18° and at 5—10°, but at 100° a crystalline form is obtained. N. C.

Preparation of Formaldehyde from Methyl Alcohol by the Contact Process. MAX LE BLANC and E. PLASCHKE (*Zeitsch. Elektrochem.*, 1911, **17**, 45—57).—A constant, measured current of air is passed through methyl alcohol, kept at a constant temperature. The mixture of air and alcohol vapour, then passes over a spiral of silver, silver-plated copper, or copper gauze, and the products (consisting of formaldehyde, unchanged methyl alcohol, carbon monoxide and dioxide, hydrogen and nitrogen) are collected and analysed.

The maximum yield of formaldehyde is always obtained at about the same temperature. Measured near the end of the silver gauze spiral at which the gases entered it, the best temperature is 450°, but this is not the maximum temperature of the spiral, which often reaches a bright red heat in the middle. When the temperature of the contact is kept constant and the ratio of air to alcohol in the mixture is gradually increased, the yield of aldehyde increases to a maximum and then diminishes again. The maximum yield is obtained with about 0·46 gram of oxygen to 1 gram of alcohol. The loss of alcohol (the part not accounted for by aldehyde or unchanged alcohol in the products) increases rapidly and continuously as the oxygen is increased. The length of the contact layer also affects the results; in the 30 mm. tube used by the authors, the most favourable length was 70 mm., which gave the highest yield of formaldehyde observed, namely, 58% of the theoretical quantity.

The results with copper were very similar to those obtained with silver, the best length of layer being 80—90 mm., and the best mixture containing 0·39 gram of oxygen per gram of methyl alcohol.

A consideration of the composition of the gaseous products (which always contain more hydrogen than the sum of the carbon monoxide and dioxide) leads to the conclusion that the formation of formaldehyde is due, not to oxidation of methyl alcohol, but rather to its decomposition, thus: $CH_3{\cdot}OH = CH_2O + H_2$. The main source of loss is the decomposition of formaldehyde by heat: $CH_2O = CO + H_2$. To test this, methyl alcohol vapour was passed over freshly reduced copper at 700°. The yield of formaldehyde is fairly good at first, but falls off rapidly. (In six experiments with the same spiral, it fell from 28% in the first to 4% in the sixth.) The activity of the copper is restored by oxidising it and reducing it again. It appears, therefore, that the function of the air in the usual contact process is to keep the copper constantly in its most active form by continually oxidising it, the reduction being brought about by the hydrogen and carbon monoxide present. T. E.

Electrosyntheses. VI. Sima M. Losanitsch (*Ber.*, 1911, **44**, 312—315. Compare Abstr., 1910, i, 542).—It has been shown previously (Abstr., 1897, i, 179) that under the action of the silent discharge a mixture of carbon monoxide and hydrogen gives formaldehyde, which immediately condenses to yellow aldehydic products. Further investigation shows that these products consist of a liquid portion, soluble in water, alcohol and ether, and a solid portion, which is only soluble in water. The liquid portion is viscous, has the odour of paraldehyde, and contains formic acid. The yellow, solid portion has a composition corresponding with $C_{12}H_{18}O_{11}$. It is probably the first anhydride of $C_6H_{12}O_6$, since cryoscopic experiments show that the freshly made aqueous solution contains molecules corresponding with $C_{12}H_{18}O_{11}$, and these, on keeping, split up into $C_6H_{12}O_6$ molecules. Evaporation of the aqueous solution on the water-bath leaves a dark residue with the composition $C_6H_8O_5$; if the evaporation is carried out in a vacuum, the yellow compound, $C_{12}H_{18}O_{11}$, is left.

The aqueous solution of the yellow solid readily gives glyoxal phenylosazone with phenylhydrazine, and glyoxime with hydroxylamine, from which it is probable that the yellow solid is a readily decomposable condensation product of glyoxal.

The formaldehyde produced from the carbon monoxide and hydrogen by the silent discharge probably condenses to the two following aldehydes: $2CH_2O = OH{\cdot}CH_2{\cdot}CHO$ and $2CH_2O = CHO{\cdot}CHO + H_2$, and these then form the compound $CHO{\cdot}CHO,2OH{\cdot}CH_2{\cdot}CHO$, which is the yellow solid.

The condensation product obtained from carbon monoxide and methane (Abstr., 1908, i, 866) also contains a part soluble and a part insoluble in water. The former is identical with the above yellow solid, $C_{12}H_{18}O_{11}$.

A mixture of carbon dioxide and hydrogen behaves similarly to a mixture of carbon monoxide and hydrogen towards the silent discharge, since the carbon dioxide is first reduced to the monoxide.

T. S. P.

α-Bromocrotonaldehyde. Paul L. Viguier (*Compt. rend.*, 1911, **152**, 269—271. Compare Abstr., 1909, i, 691; 1910, i, 461).—α-Bromocrotonaldehyde forms an *oxime*, m. p. 110—111°, which becomes pasty on keeping. The *semicarbazone* has m. p. 228—230°. 5-Methylpyrazole is produced when the aldehyde is added to an alcoholic solution of hydrazine hydrate. The *phenylhydrazone*, lamellæ, m. p. 124—125°, is unstable; when treated with alcoholic potassium hydroxide, it forms 1-phenyl-5-methylpyrazole; on heating with excess of phenylhydrazine, it furnishes a *compound*, $C_{16}H_{18}N_4$, m. p. 117—119°.

When α-bromocrotonaldehyde or its acetal is allowed to act on urethane in aqueous solution in presence of a little hydrochloric acid, a *compound*, $C_{13}H_{24}O_6N_3Br$, is obtained. This crystallises in colourless, slender needles, m. p. 124—125°, and is useful for characterising the aldehyde. W. O. W.

Photochemical Synthesis of Carbohydrates from Carbon Dioxide and Hydrogen in the Absence of Chlorophyll. Julius Stoklasa and Wenzel Zdobnický (*Biochem. Zeitsch.*, 1911, **30**, 433—456; *Monatsh.*, 1911, **32**, 53—75).—A figure is given of the apparatus employed for carrying out experiments in the presence of ultra-violet light, the chief feature of which is the form of the basin in which the reactions were investigated, which was suspended from a mercury-quartz lamp which served as the source of light. It was found that water does not act on carbon dioxide in ultra-violet light in the absence of potassium hydroxide, neither formaldehyde nor carbohydrate being formed in this case. If potassium hydroxide is added, however, formaldehyde, but no carbohydrate, is formed. The hydrogen must be in the nascent state for the reaction to take place, and ultra-violet light must be present. In the absence of the latter, formic acid is formed. A sugar is also formed when nascent hydrogen reacts with carbon dioxide in the presence of ultra-violet rays. The nature of the carbohydrate has not yet been definitely established. The osazone melts at 196—200°, and is not, therefore, either formose, β-formose, or β-acrose. S. B. S.

Nomenclature of the Sugars. EMIL VOTOČEK (*Ber.*, 1911, **44**, 360—361).—The prefix *epi* is used to denote the new carbohydrate formed by the interchange of the H and OH groups on the α-carbon atom; thus mannose becomes *epi*glucose, ribose becomes *epi*arabinose, talose becomes *epi*galactose, etc. The isomeric pair are spoken of as *epimerides*, and the change as *epimerism*. The nomenclature is extended to the alcohols and acids of the carbohydrates. E. F. A.

***epi*Rhodeose.** EMIL VOTOČEK and CYRILL KRAUZ (*Ber.*, 1911, **44**, 362—365. See preceding abstract).—Rhodeonic acid, prepared by oxidation of rhodeose with bromine, is partly converted on heating with pyridine at 150—160° into epi*rhodeonic acid*. The *barium* salt forms colourless, matted crystals, which are optically inactive. The crystalline *lactone* is reduced by sodium amalgam in the usual manner to epi*rhodeose*; this is a syrup, yielding the same phenylosazone as rhodeose, but the *methylphenylhydrazone* has m. p. 175°. On oxidation with nitric acid, the trihydroxyglutaric acid obtained has m. p. 184—185°, $[\alpha]_D$ +12°, falling to +2·5° on boiling, and differs slightly from the inactive lactone described by Fischer and Piloty (m. p. 170—171°; compare Abstr., 1892, 440). It is pointed out that ribohydroxyglutaric acid, although itself completely symmetric, forms a lactone, which is not symmetric. Fischer's lactone is an equimolecular mixture of *d*- and *l*-lactones, but that from *epi*rhodeose is possibly completely derived from *d*-lactone or from a mixture of *d*- and *l*-lactones in unequal proportions. E. F. A.

Solubility of Lime in Aqueous Solutions of Sucrose and of Glycerol. FRANK K. CAMERON and HARRISON E. PATTEN (*J. Physical Chem.*, 1911, **15**, 67—72).—When lime in excess is added to sucrose solution, a soluble compound of lime and sugar is formed, but some of the sucrose passes into the solid phase. The relation between the amount of lime dissolved and the amount of sucrose in solution is not a linear one, since the liquid is in equilibrium with a series of solid solutions of the lime-sucrose compound in lime. The solid phase, consisting of fine globular granules, was separated by a centrifuge, and contained upwards of 10·8% of sucrose.

Solutions containing more than 20% of sucrose could not be investigated owing to their high viscosity. The 20% solution dissolves about 6% of lime at 25°.

The presence of glycerol increases the solubility of lime to 1·34% in a 55% solution of glycerol. The ratio of lime to glycerol is a strictly linear one, and no glycerol passes into the solid phase. R. J. C.

Cellobiose and the Acetolysis of Cellulose. WILHELM SCHLIEMANN (*Annalen*, 1911, **378**, 366—381).—The treatment of cellulose (filter-paper or cotton wool) with a mixture of acetic anhydride and concentrated sulphuric acid at low temperatures yields products quite different from those obtained at higher temperatures, because the acetolysis (that is, the acetylation and hydrolysis of the cellulose molecule) is less quickened by the sulphoacetic acid produced in the acetylating mixture at high temperatures (Stillich, Abstr., 1905, i, 318; 1906, i, 552, 626) than by the acetylsulphuric acid formed at low temperatures.

The product obtained by acetylating cellulose by Skraup and König's method (Abstr., 1902, i, 135) or by Maquenne and Goodwin's process (Abstr., 1904, i, 799), after hydrolysis by alcoholic potassium hydroxide, yields cellobiose, which, after being completely dried at 100°, has the formula $C_{12}H_{22}O_{11}$, and $[\alpha]_D^{20}$ 34·6° in 2—17% aqueous solutions. It can be estimated by Fehling's solution by Wein's method, and forms a *phenylosazone*, m. p. 208—210°, $[\alpha]_D$ $-17·5°$ in alcoholic solution.

By treatment with acetic anhydride and sulphuric acid (or a little zinc chloride) it yields the same octa-acetylcellobiose, m. p. 221·5—222°, $[\alpha]_D^{20}$ 41·5° in chloroform, as is produced by the action of this acetylating mixture on cellulose (Maquenne and Goodwin, *loc. cit.*). The isomeric octa-acetylcellobiose, m. p. 191·5—192°, obtained by boiling cellobiose with acetic anhydride and sodium acetate, has $[\alpha]_D^{20}$ $-7·8°$ in chloroform and $-24·9°$ in benzene. Both octa-acetylcellobioses can be converted into the acetochloro-compound, m. p. 186—187° (Geinsperger, Abstr., 1906, i, 57; Hardt-Stremayr, Abstr., 1907, i, 389), from which, according to the author, silver acetate produces the octa-acetylcellobiose, m. p. 191°, $[\alpha]_D^{20}$ $-7·5°$ in chloroform, whilst Geinsperger obtained an acetate, $[\alpha]_D$ $-30·05°$ in chloroform, and Hardt-Stremayr an acetate, $[\alpha]_D$ 30·51°; the discrepancy is inexplicable.

In view of Jungius' experiments on the equilibrium of the penta-acetyldextroses (Abstr., 1905, i, 573), cellobiose and its two octa-acetyl derivatives have been treated with acetic anhydride and sulphuric acid, acetic anhydride and zinc chloride, and acetic anhydride and sodium acetate. The last-mentioned reagent does not change either of the octa-acetylcellobioses once it has been formed; with the other two reagents, mixtures of the two acetates are obtained, containing respectively 84% and 77% of the octa-acetyl compound, which has $[\alpha]_D^{20}$ 41·5° in chloroform. The two acetates in the mixture can be separated by cold benzene, in which the acetate, m. p. 191°, $[\alpha]_D^{20}$ $-7·7°$ in chloroform, is the more soluble. Evidence is stated which indicates that the octa-acetylcellobiose, m. p. 191°, belongs to the β-series.

The amorphous by-products, obtained in addition to octa-acetylcellobiose by the acetolysis of cellulose, have been examined in regard to the content of acetic acid liberated by hydrolysis; the author is of opinion that the products containing 66·3—67·3% of acetic acid are the immediate precursors of the octa-acetylcellobiose. C. S.

Action of Water and of Alkali on Cotton Wool Cellulose. CARL G. SCHWALBE and MICHAEL ROBINOFF (*Zeitsch. angew. Chem.*, 1911, **24**, 256—258. Compare Tauss Dingler's *Polyt. Jour.*, 1889, **273**, 276; 1890, **276**, 411).—It is shown that the formation of hydrocelluloses, that is, compounds with strongly reducing properties, under the influence of water occurs only when the cellulose is partly altered; for example, filter-paper or strongly-bleached cellulose. With pure cellulose the formation of hydrocellulose is extremely small, even under a pressure of 20 atmospheres. When a temperature of 150° is reached, marked decomposition of the cellulose occurs.

The action of dilute sodium hydroxide solutions on cellulose has been studied; the maximum effect at the ordinary temperature is obtained with a 4% alkali solution, as shown by the fact that the product after such treatment gives the highest copper values (corrected). At temperatures of 100° and above, the solubility increases, but diminishes as the concentration of the alkali is increased; at 150° the solubility is appreciable. The "gum value" has been obtained for a number of samples; by gum value is understood the weight of amorphous precipitate obtained by neutralising the alkaline extract. Pure cellulose has a "gum value" of practically nil, whereas impure forms have higher values. At 150°, however, the differences are small, and here it is also noticeable that the 4% alkali has the maximum effect. In treatment of cellulose, temperatures above 150°, and an alkali concentration of 4% are to be avoided. The acid used after bleaching should not be stronger than 0·1%; with still more dilute acid, a purer white is obtained, but the amount of oxycellulose is increased. J. J. S.

Action of Hydracids on Starch. II. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1910, 848—849. Compare Abstr., 1910, i, 655).—Starch (1·7 grams), water (50 grams), and hydrochloric acid (2 c.c.) after being left for seven minutes at 18·5° and then heated for four minutes gave a reddish-orange precipitate with Fehling's solution. Hydrobromic acid (1·5 c.c.) behaved similarly; hydriodic acid (1 c.c.) produced only a slight, although distinct, precipitate. After four hours at 17°, each acid had acted on starch sufficiently to cause slight reduction of Fehling's solution. E. F. A.

Dextrin. WILLIAM OECHSNER DE CONINCK and A. REYNAUD (*Bull. Acad. roy. Belg.*, 1910, 846—847).—A mixture of 0·8 gram of dextrin, 40 grams of water, and twenty drops of concentrated hydrochloric acid gave a yellow precipitate with Fehling's solution (Cu_2O,H_2O) after twenty-four hours at 22°. With hydrobromic acid (twelve drops) the reduction (Cu_2O) was marked in five hours; with five drops of hydriodic acid, cuprous oxide (Cu_2O) was precipitated after five minutes' or five hours' action. With five drops of hydrochloric acid the precipitate with Fehling's solution was cuprous oxide; with ten drops, it consisted of a mixture of cuprous oxide and its hydrate, and with fifteen drops, it was entirely the hydrated oxide, Cu_2O,H_2O. E. F. A.

Formation of Crystalline Polysaccharides (Dextrins) from Starch Paste by Microbes. FRANZ SCHARDINGER (*Centr. Bakt. Par.*, 1911, ii, 29, 188—197).—Certain micro-organisms convert starch paste into substances soluble in water closely resembling dextrins. *Bacillus macerans* renders potato-starch completely soluble, arrowroot-starch nearly completely so, but has far less effect on rice and wheat starch. Part of the dextrin formed, about 25—30% of the starch taken, is crystalline, the rest being amorphous and gum-like. Two different crystalline dextrins distinguished as α and β have been obtained from all four varieties of starch, the α-isomeride predominating. It crystallises in colourless, hexagonal plates or lancet-shaped needles, and is doubly refractive, $[\alpha]_D +128°$; the coloration of the crystalline precipitate with iodine is blue in thin layers when wet, greyish-green when dry. The β-isomeride crystallises in reniform aggregates of rhombic crystals, $[\alpha]_D +136°$; the crystalline precipitate with iodine is a reddish-brown both wet and dry; it sinters and decomposes at 260°.

Both dextrins are precipitated from aqueous solution by alcohol, ether, chloroform, and iodine solution; they do not reduce Fehling's solution, and are not fermented by yeast. E. F. A.

Tellurium. ALEXANDER GUTBIER and FERDINAND FLURY (*J. pr. Chem.*, 1911, [ii], 83, 145—163. Compare Abstr., 1907, ii, 255).—The majority of the results recorded by previous investigators on the tellurichlorides and the telluribromides of the alkali metals and of aliphatic ammonium compounds have been confirmed; the existence of Rammelsberg's compounds, $8KCl,3TeCl_4$ and $8NH_4Cl,3TeCl_4$, and of the hydrated potassium tellurichloride described by von Hauer and by Wheeler (Abstr., 1893, ii, 457) is denied.

The salts described below are prepared by mixing an excess, generally one half to three-quarters, of a solution of carefully purified tellurium dioxide in the halogen acid with a solution of the alkali or substituted ammonium halide; with suitably selected concentrations, the desired salt crystallises more or less rapidly and is recrystallised from the dilute halogen acid. The tellurium is estimated by Lenher and Homberger's process (Abstr., 1908, ii, 426). The salts are characterised by their splendid colour and crystallise well, generally in the regular system. They dissolve without decomposition in a small quantity of water at the ordinary temperature or by gentle warming, but are extensively decomposed by even a small excess of water with the separation of tellurous acid. The telluribromides are stable in the air.

[With H. MICHELER.]—The following salts have been obtained: Ammonium tellurichloride is prepared best from dilute solutions and by spontaneous evaporation; it crystallises in sulphur-yellow octahedra. *Trimethylammonium tellurichloride*, $2NMe_3,H_2TeCl_6$, pale yellow needles; *diethylammonium*, $2NHEt_2,H_2TeCl_6$, sulphur-yellow, monoclinic crystals; *triethylammonium*, $2NEt_3,H_2TeCl_6$, yellow needles; *propylammonium*, $2NH_2Pr^{\alpha},H_2TeCl_6$, yellow, rhombic plates; iso*propylammonium*, $2NH_2Pr^{\beta},H_2TeCl_6$, greenish-yellow, monoclinic plates; *dipropylammonium*, $2NHPr^{\alpha}_2,H_2TeCl_6$, yellow, rhombic (or tetragonal) crystals; *butylammonium*, $2C_4H_9\cdot NH_2,H_2TeCl_6$, long, pale yellow needles; iso*butylammonium*, $2C_4H_9\cdot NH_2,H_2TeCl_6$, like the preceding salt. *Diethylammonium telluribromide*, $2NHEt_2,H_2TeBr_6$, orange-red needles; *triethylammonium*, $2NEt_3\cdot H_2TeBr_6$, orange-red, monoclinic crystals; *propylammonium*, $2NH_2Pr^{\alpha},H_2TeBr_6$, orange-red plates; iso*propylammonium*, $2NH_2Pr^{\beta},H_2TeBr_6$, orange-red, tetragonal needles; *dipropylammonium*, $2NHPr_{\alpha 2},H_2TeBr_6$, orange-red, monoclinic plates; *butylammonium*, $2C_4H_9\cdot NH_2,H_2TeBr_6$, orange-red needles; iso*butylammonium*, $2C_4H_9\cdot NH_2,H_2TeBr_6$, orange-red plates. C. S.

Salts of Pertitanic Acid with Organic Bases. EDUARD KUROWSKI and L. NISSENMANN (*Ber.*, 1911, **44**, 224—229).—The authors describe the preparation and properties of a number of salts of pertitanic acid with primary and secondary aliphatic amines. The method of preparation adopted consists in the gradual addition of a mixture of the amine and 30% hydrogen peroxide to titanium trioxide and subsequent precipitation of the salt by the addition of a mixture of alcohol and ether, the temperature being maintained at $-10°$ to $-15°$.

The salts are all unstable, dissolve in water with a green colour, and decompose rapidly at the ordinary temperature. They dissolve in dilute sulphuric acid with the formation of hydrogen peroxide.

The *methylamine* salt, $(NH_3Me{\cdot}O)_2TiO_4,3H_2O$, has a yellowish-green colour; when exposed to the air it forms oily drops, and then decomposes with the liberation of carbon.

The *ethylamine* salt, $NH_3Et{\cdot}O{\cdot}TiO_4H,1\frac{1}{2}H_2O$, is a yellow powder.

The *propylamine* salt, $2NH_3Pr^{\alpha}{\cdot}O{\cdot}TiO_4H,H_2O_2,2H_2O$, has a yellowish-green colour; a second less stable salt has also been obtained.

Of the salts with secondary aliphatic amines, only the *diethylamine* salt, $2NH_2Et_2{\cdot}O{\cdot}TiO_4H,H_2O_2,14H_2O$, was obtained in a pure condition; it is a yellow powder.

The *dimethylamine* and *dipropylamine* salts so readily decompose that their composition has not been determined.

Attempts to prepare salts of pertitanic acid with tertiary amines and also with aniline were unsuccessful. F. B.

Ruthenihalides. ALEXANDER GUTBIER [with G. A. LEUCHS] (*Ber.*, 1911, **44**, 306—308).—The following compounds were prepared according to a method previously described (Abstr., 1907, i, 289):

Triethylammonium ruthenichloride, $(NHEt_3)_2RuCl_6$, forms large, broad, blackish-red plates. *Triethylammonium ruthenibromide*, $(NHEt_3)_2RuBr_6$, crystallises in large, black plates. iso*Propylammonium ruthenichloride*, $(NH_3Pr^{\beta})_2RuCl_6$, forms glistening, dark greenish-brown or black needles. iso*Propylammonium ruthenibromide*, $(NH_3Pr^{\beta})_2RuBr_6$, is obtained in dark bluish-black needles. n-*Butylammonium ruthenichloride*, $(C_4H_9{\cdot}NH_3)_2RuCl_6$, forms dark, greenish-brown, glistening needles. n-*Butylammonium ruthenibromide*, $(C_4H_9{\cdot}NH_3)_2RuBr_6$, forms deep bluish-black needles. *Benzylammonium ruthenichloride*, $(C_7H_7{\cdot}NH_3)_2RuCl_6$, crystallises in greenish-brown, slender needles. *Benzylammonium ruthenibromide*, $(C_7H_7{\cdot}NH_3)_2RuBr_6$, forms black, felted needles. *Pyridinium ruthenichloride*, $(C_5H_6N)_2RuCl_6$, forms brown needles *Pyridinium ruthenibromide*, $(C_5H_6N)_2RuBr_6$, crystallises in light bluish-black needles. α-*Picolinium ruthenichloride*, $(C_5NH_5Me)_2RuCl_6$, is obtained in small, bronze-coloured leaflets. α-*Picolinium ruthenibromide*, $(C_5NH_5Me)_2RuBr_6$, forms shining, bluish-black needles.

T. S. P.

Labile Hydrated Forms Fixed by means of an Organic Base. GIUSEPPE A. BARBIERI and F. CALZOLARI (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 584—590).—The authors have acted on various metallic salts in aqueous solution with hexamethylenetetramine, and on the hypothesis that this substance combines with hydrates already existing in the solution, the composition of the solid substances which separate yields information as to the nature of the hydrates in question (compare Kurnakoff, Abstr., 1898, ii, 475). The following facts accord with the supposition that the hexamethylenetetramine is not united with the metallic atom, but is added to the molecule of the hydrated salt present in the solution: (1) anhydrous cobalt chloride forms with hexamethylenetetramine a compound in which the base is attached to the metal, and this compound is blue; (2) a compound, $(AcONa,3H_2O)_2C_6H_{12}N_4$, exists, and it is not probable that the base could be attached to sodium; (3) with salts which usually are anhydrous, or give hydrates containing little water, hexamethylenetetramine compounds are obtained which contain little or no water. The compounds described are, therefore, to be regarded as amines of hydrated salts.

The following compounds are prepared by acting on concentrated (20%) aqueous solutions of the chlorides, bromides, and iodides of magnesium, manganese, cobalt, and nickel with concentrated aqueous solutions of hexamethylenetetramine (2—4 mols.). They form large, measurable crystals, which are not deliquescent. The tendency to effloresce in contact with dehydrating agents is greatest in the case of the chlorides, least with the iodides, which are stable to air and light. In solution, the manganese derivatives gradually deposit manganous hydroxide. The *compound*, $MgCl_2,10H_2O,2C_6H_{12}N_4$, forms colourless, transparent, tabular crystals belonging to the triclinic system (holosymmetric):

$[a:b:c=0{\cdot}8321:1:0{\cdot}8573;\ \alpha=125°43', \beta=50°21', \gamma=123°56']$.

The *compound*, $MnCl_2,10H_2O,2C_6H_{12}N_4$, forms minute crystals of a pale flesh colour. The *compound*, $CoCl_2,10H_2O,2C_6H_{12}N_4$, crystallises in reddish-violet laminæ, which in contact with phosphoric oxide lose all their water and become intensely blue. The *compound*,

$NiCl_2,10H_2O,2C_6H_{12}N_4$,

crystallises in green laminæ, which on dehydration in an oven become first yellow, then violet. The *compound*,

$MgBr_2,10H_2O,2C_6H_{12}N_4$,

forms plates which are almost square; they belong to the monoclinic system (holosymmetric): $[a:b:c=0{\cdot}9022:1:0{\cdot}5111;\ \beta=90°40']$. The *compound*, $MnBr_2,10H_2O,2C_6H_{12}N_4$, forms almost colourless crystals. The *compound*, $CoBr_2,10H_2O,2C_6H_{12}N_4$, forms reddish-violet crystals. The *compound*, $NiBr_2,10H_2O,2C_6H_{12}N_4$, crystallises in green laminæ. The *compound*, $MgI_2,10H_2O,2C_6H_{12}N_4$, forms long, colourless, transparent crystals, which belong to the monoclinic system (holosymmetric): $[a:b:c=0{\cdot}8802:1:0{\cdot}495;\ \beta=90°1']$. The *compound*,

$MnI_2,10H_2O,2C_6H_{12}N_4$,

is a white powder. The *compound*, $CoI_2,10H_2O,2C_6H_{12}N_4$, forms rose-coloured, tabular crystals. The *compound*,

$NiI_2,10H_2O,2C_6H_{12}N_4$,

forms emerald-green crystals. In some cases where the analytical results do not permit of the exact determination of the amount of contained water, the question can be settled from relations of isomorphism and power to form mixed crystals which exist between many of the substances. The crystallographic measurements were executed by E. Billows. R. V. S.

Alkylation of Acid Amides. Motooki Matsui (*Mem. Coll. Sci. Eng. Kyoto*, 1910, **2**, 397—400).—In the alkylation of amides, silver oxide may be replaced by cuprous oxide, lead oxide, or anhydrous potassium carbonate.

When a mixture of acetamide and ethyl iodide is heated for three to four hours on the water-bath with one of these substances, ethyl iminoacetate is produced. Benzamide, under the same conditions, yields ethyl iminobenzoate.

It is therefore highly probable that in alkylating with silver oxide and an alkyl iodide, the silver oxide accelerates the reaction merely by the removal of the hydriodic acid produced, and not by the intermediate formation of a silver derivative (compare Lander, Trans., 1900, **77**, 729).

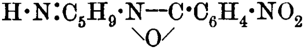
The author considers it probable that the formation of imino-esters by the action of methyl sulphate on amides is due to the direct alkylation of the enolic form: $NH:CR\cdot OH$, and not to the addition of methyl sulphate to the ketonic form, as suggested by Bühner (Abstr., 1904, i, 882). F. B.

Formation and Decomposition of Calcium Cyanamide. Max Le Blanc and M. Eschmann (*Zeitsch. Elektrochem.*, 1911, **17**, 20—34).—It is shown that the reaction $CaC_2 + N_2 \rightleftarrows CaCN_2 + C$ is reversible. The equilibrium pressure of nitrogen, however, is dependent on the quantity of nitrogen which has been taken up by the carbide. Measurements of the pressures are made at 1200° and 1300°. After almost saturating a quantity of carbide with nitrogen, successive quantities of nitrogen are removed from it by diminishing the pressure, and the corresponding equilibrium pressures are measured; the quantity of combined nitrogen is then increased by adding fresh nitrogen, and the pressures again measured. The two curves do not agree with each other, the pressure corresponding with a given percentage of combined nitrogen constantly decreases with the duration of the experiments; apparently the cyanamide becomes more stable. A careful chemical examination of the reaction shows that the reversible formation of calcium cyanamide is really the reaction being observed, but the calcium cyanamide gradually volatilises out of the mixture and condenses in the cooler parts of the apparatus, where it can no longer decompose, partly owing to the lower temperature and partly owing to the absence of carbon. T. E.

Some Solid Ammoniates. Carlo Gastaldi (*Gazzetta*, 1910, **40**, ii, 475—481).—When a concentrated aqueous solution of potassium ferricyanide is added to an ammoniacal solution of silver nitrate, a fine-grained, deep red, crystalline precipitate is deposited, which has the composition $2[Ag_3Fe(CN)_6],5NH_3$. By varying the conditions, the substance can be obtained as an amorphous, flocculent precipitate, or, by dissolving freshly precipitated silver ferricyanide in ammonia and evaporating the solution at the ordinary temperature, in large crystals. In all cases the composition is the same. When the ammonia is replaced by methylamine or ethylamine, *methyl-* and *ethyl-ammoniates* of similar composition are obtained.

The qualitative test for the ferricyanic radicle may be masked by the presence of simple cyanides in a solution under investigation. If aluminium and hydrochloric acid are added to the liquid, however, the production of a coloration with an iron salt will indicate the presence of a ferricyanide, for in these circumstances the formation of the complex from a cyanide and the iron salt cannot occur. R. V. S.

Action of Hydroxylamine on Nitrosochlorides and Nitrosates. III. αβ-Amylenehydroxylamineoxime and Derivatives.

GUIDO CUSMANO (*Gazzetta*, 1910, **40**, i, 525—536. Compare Abstr., 1910, i, 863).—*β-Hydroxylamino-β-methylbutan-γ-oneoxime* (*amylenehydroxylamineoxime*), $OH\cdot NH\cdot CMe_2\cdot CMe{:}N\cdot OH$, is prepared by suspending amylene nitrosate in a mixture of methyl alcohol and ether containing hydroxylamine (2 mols.). The reaction commences on warming, and then proceeds spontaneously. After removal of the solvent, the residue is dissolved in a little water and treated with sodium carbonate to dissolve the hydroxylamine nitrate present, and from the solution β-hydroxylamino-β-methylbutan-γ-oneoxime crystallises out on cooling. It forms rhombohedra, or laminar, hexagonal prisms, m. p. about 112° (previously softening), and reduces Fehling's solution readily in the cold. The *hydrochloride*, $C_5H_{12}O_2N_2,HCl$, forms clusters of crystalline leaflets, m. p. 125—130°, and are very deliquescent. The *nitroso-oxime* is obtained as an oil of a blue tinge by oxidising the hydroxylamino-oxime with the calculated quantity of permanganate. The p-*nitrobenzylidene* derivative,  $OH\cdot N{:}C_5H_9\cdot\underset{\diagdown O\diagup}{N-C}\cdot C_6H_4\cdot NO_2$ (from *p*-nitrobenzaldehyde), forms pale yellow, hexagonal laminæ, m. p. about 187°. It dissolves in alkalis, producing a red coloration.

β-Hydroxylamino-β-methylbutan-γ-oneoxime reacts readily with nitrous acid, yielding *β-nitrosohydroxylamino-β-methylbutan-γ-oneoxime*, $OH\cdot N(NO)\cdot CMe_2\cdot CMe{:}N\cdot OH$, which is a very stable substance, crystallising in long, colourless needles, m. p. 81—82°. It does not reduce Fehling's solution, but yields a bluish-green coloration with a solution of phenol in sulphuric acid. It can be boiled with water without suffering decomposition, but it is readily decomposed by dilute acids even in the cold. It dissolves in sodium carbonate with effervescence, and the solution on concentration yields the *sodium* salt of the *iso*nitroamine. The *iso*nitroamine can displace nitrous acid, so that this sodium salt can be prepared by mixing concentrated solutions of hydroxylamino-oxime and sodium nitrite in the presence of a little sulphuric acid. It crystallises with $3H_2O$, which it loses at 116°. The *anhydrous* salt, $C_5H_{10}O_3N_3Na$, has m. p. 130° (decomp.).

β-Hydroxylamino-β-methylbutan-γ-oneoxime, when kept in an alcoholic ethereal solution saturated with hydrogen chloride, eventually deposits a *hydrochloride*, $C_5H_{11}O_2N,HCl$, in tufts of long, acicular crystals, m. p. 145° (decomp.), which are not deliquescent. On treatment with sodium carbonate, a base is obtained, crystallising in long, colourless prisms, m. p. 96—98°. This base readily reduces Fehling's solution in the cold. To it is ascribed the constitution of *β-hydroxylamino-β-methylbutan-γ-one*, $OH\cdot NH\cdot CMe_2\cdot COMe$, and this is confirmed by the existence of a *p*-nitrobenzylidene derivative, $C_{12}H_{14}O_4N_2$, which crystallises in yellow, rectangular tablets, decomposing at 176°.

If hydroxylaminomethylbutanoneoxime is dissolved in concentrated alkali, and the solution after some days is treated with carbon dioxide, a precipitate is obtained, from which two substances can be isolated. One crystallises in small, colourless prisms, m. p. 96—100°, and from its composition and properties is *β-hydroxy-β-methylbutan-γ-oneoxime*, $OH\cdot CMe_2\cdot CMe\colon NOH$. The other *compound* forms long, colourless prisms, m. p. 184° (decomp.).

To explain the differences between the hydroxylamino-oximes of pinene and amylene and that of limonene, it is suggested that the two first, being saturated compounds, exist solely, or chiefly, as *trans*-forms, whilst the unsaturated limonene compound can also assume the labile *cis*-form. R. V. S.

Unsaturated Lead Alkyls. JULIUS TAFEL (*Ber.*, 1911, **44**, 323—337).—In his electrolytic experiments on organic substances with mercury or lead cathodes, the author has frequently observed the formation of small quantities of oily products; with lead cathodes the oil is red. At his suggestion, Renger (following abstract) has studied the formation of these oily products, and has obtained the red oil in larger quantities from acetone; he considers that it consists essentially of lead tetra-*iso*propyl, since lead di-*iso*propyl dibromide is produced from it by the action of bromine. Since the lead tetra-alkyl compounds are colourless and the formation of a di-alkyl compound from a tetra-alkyl has hitherto been unknown, the author has extended the investigation of these oils.

The apparatus consists of a glass cathodic vessel shaped like a separating funnel and provided with a closely fitting lead cover, through apertures in which are fitted a thermometer, an inlet-tube for the delivery of carbon dioxide into the cathodic compartment, and the porcelain anodic cell. The cathode consists of six strips of lead, and the anode of a lead cylinder. The anodic liquor is 20% sulphuric acid; the cathodic solution is a mixture of 20% sulphuric acid and acetone (in the case of higher ketones a little alcohol must also be added). The temperature is kept at 45—50°, and the cathodic current density at about 0·5 amp./sq. cm. During the experiment the cathodic solution is well agitated by a current of carbon dioxide, and the red oil collects together with a white precipitate at the bottom of the vessel. It is run out into an apparatus (figured and described), in which it can be washed with dilute potassium hydroxide and with water, dried over sodium sulphate, and filtered, all of the operations being performed with the exclusion of air. The purified product is a viscous oil with the colour of bromine and an unpleasant odour. It loses its red colour rapidly in the light, leaving a golden-yellow oil consisting chiefly of lead tetra-*iso*propyl. When rapidly heated, the red oil decomposes at 150° with separation of finely divided lead; it decomposes at 85° in a vacuum. In contact with oxygen, the oil becomes coated with a yellowish-brown, strongly alkaline skin. When a solution of the red oil in an indifferent solvent is treated with oxygen, it acquires a pale yellow colour, and after filtration contains lead tetra-*iso*propyl and lead di-*iso*propyl oxide; the latter is extracted with dilute acetic acid, and is isolated in the form of *lead di-*iso*propyl dibromide*, $PbPr^{\beta}Br_2$. This salt, which crystallises in felted needles and decomposes when kept, even in darkness, is also obtained by carefully treating the red oil in well-cooled ether or ethyl acetate with bromine until the latter only slowly disappears. The corresponding *dichloride*, *dinitrate*, and *chromate* are described. When the oxidised filtered solution of the red oil is distilled at 40° in a vacuum, and the yellowish residue, which exhibits the properties of lead tetra-*iso*propyl, is triturated with concentrated hydrochloric acid, *lead tri-*iso*propyl chloride*, $PbPr^{\beta}Cl$, is obtained. It has a very unpleasant odour, is more volatile with steam, and is less stable than the dichloride. The corresponding *iodide* is described. The author is of opinion that the red oil consists essentially of lead tetra-*iso*propyl together with about 20% of lead di-*iso*propyl, to which the colour is due.

Pure lead tetra-*iso*propyl has not been obtained on account of its great instability, but the behaviour of lead tetra-ethyl is quite analogous to that of the red oil mentioned above; thus with bromine (1 mol.) in well-cooled ether or ethyl acetate it yields *lead triethyl bromide*, $PbEt_3Br$, which crystallises in large, colourless needles, and has an unpleasant odour; with 2 mols. of the halogen, lead tetra-ethyl yields *lead diethyl dibromide*, $PbEt_2Br_2$, the properties of which are quite analogous to those of the di-*iso*propyl dibromide.

C. S.

Lead Alkyl Compounds from Methyl Ethyl Ketone and Diethyl Ketone. GEORG RENGER (*Ber.*, 1911, **44**, 337—338. Compare preceding abstract).—The electrolytic reduction of methyl ethyl ketone and of diethyl ketone (in the presence of alcohol) at lead cathodes proceeds in a manner quite analogous to that of acetone. The resulting red oils have been characterised by chlorination and bromination in chloroform or ether, whereby the following salts, which are even more unstable than the *iso*propyl compounds, have been obtained. *Lead tri-*sec.*-butyl chloride*, $Pb(C_4H_9)_3Cl$, forms pale yellow needles, has an unpleasant odour, and melts and suddenly explodes at about 130° when heated rapidly. *Lead di-*sec.*-butyl bromide*,

$$Pb(C_4H_9)_2Br_2,$$

crystallises in yellow needles. *Lead di-γ-amyl dibromide*, $Pb(C_5H_{11})_2Br_2$, obtained from the oil from diethyl ketone, forms extremely unstable, brownish-yellow crystals.

C. S.

Constitution of Copper Acetylide. II. JOHANNES SCHEIBER and HANS RECKLEBEN [and, in part, K. STRAUSS] (*Ber.*, 1911, **44**, 210—223. Compare Scheiber, Abstr., 1908, i, 933).—Further experiments have confirmed the existence of copper acetylide in the hydrated form C_2Cu_2,H_2O, and in the anhydrous form C_2Cu_2.

The fact that when the acetylide is decomposed by mild chemical reagents, for example, hydrogen sulphide and potassium cyanide, quantitative yields of acetylene are obtained, points to the conclusion that its constitution must be closely related to that of acetylene. No indication of the conversion of the hydrate into an aldehyde derivative has been observed, either by leaving in contact with water or ammonia, by drying, or under the influence of substances which may be present during its formation.

The structural formulæ of the compounds depend on that of acetylene. According to Nef's scheme, the anhydrous compound would be $Cu_2C\colon C\colon$, and the hydrate, $Cu_2C\colon C\cdots OH_2$.

The black carbonaceous material usually obtained when copper acetylide is decomposed is shown to be due to oxidation; if oxygen or oxidising substances are excluded during the preparation and decomposition of the acetylide, no carbonaceous residue is obtained. If, on the other hand, the water used contains dissolved air, or if the pure carbide is heated in an atmosphere of carbon dioxide at 100°, or if oxidising agents, such as cupric or ferric salts, are used for washing the acetylide, appreciable amounts of black residue are obtained (compare Söderbaum, Abstr., 1897, i, 309). Analyses of the carbonaceous compound agree with the formulæ $(C_{11}H_6O_3)_x$ for the product when dilute hydrochloric acid is used, and $(C_{11}H_5O_3)_2$ for the product when concentrated acid is used.

The detection by means of acetylene of copper in solutions of ammoniacal cupric salts reduced by means of hydroxylamine can be carried out at a dilution of 1 in 1,100,000, or in the presence of large quantities of ammonium acetate or tartrate, of 1 in 200,000.

J. J. S.

Sulphonation of Benzene. ROBERT BEHREND and MARTIN MERTELSMANN (*Annalen*, 1911, **378**, 352—365).—The sulphonation of benzene by pure, concentrated sulphuric acid at 240—250° results almost exclusively in the formation of the *m*-disulphonic acid, less than 1% of the para-isomeride being produced after one and a-half-hours' heating. The addition of a little mercury causes the formation of the *m*- and the *p*-disulphonic acids in the proportion 2 : 1; ferrous sulphate acts similarly, about 10% of benzene *p*-disulphonic acid being produced. The two acids are readily separated in the form of their sodium salts, since sodium benzene-*p*-disulphonate is practically insoluble in a concentrated solution of sodium benzene-*m*-disulphonate.

The two acids are interconvertible by heating with concentrated sulphuric acid and a little mercury at 240—250°, an equilibrium mixture of about 2 parts of the *m*-disulphonic acid and 1 part of the para-isomeride being formed; the same result is attained, but extremely slowly, in the absence of the mercury.

The sodium salts of both acids, by treatment with pure concentrated sulphuric acid at 240—250°, are converted into benzene-1 : 3 : 5-trisulphonic acid, which is also formed to some extent by heating benzene with concentrated sulphuric acid and potassium pyrosulphate at 240—250°. C. S.

Action of Strong Tertiary Bases on Sulphonyl Chlorides. EDGAR WEDEKIND and D. SCHENK (*Ber.*, 1911, **44**, 198—202).—Triethylamine reacts with sulphonyl chlorides when dissolved in indifferent solvents, for example, benzene, provided a hydrogen atom is attached to the α-carbon atom with respect to the sulphonyl group. Hydrogen chloride is eliminated as in the case of the chlorides of carboxylic acids (Abstr., 1906, i, 437; 1909, i, 459), but the phenylsulphens, for example, $CHPh\colon SO_2$, cannot be isolated. With benzylsulphonyl chloride, stilbene is obtained by the elimination of sulphur dioxide and the union of the two CHPh: groups.

The chlorides of aromatic sulphonic acids do not react with tertiary bases.

Diphenylmethanesulphonic acid, $CHPh_2\cdot SO_3H,1\cdot 5H_2O$, crystallises from benzene in hygroscopic needles, m. p. 94—96°; when fused with potassium hydroxide, it yields *p*-hydroxydiphenylmethane (Trans., 1882, **41**, 34), and when heated with water at 240° for eight hours, it yields diphenylmethane. The acid chloride has not been prepared. Sodium sulphite solution and ω-chlorodiphenylmethane at 120—125° yield *benzhydrol ether*, $C_{26}H_{22}O$, m. p. 109°. J. J. S.

Phenanthrene-2-sulphonic Acid and Some of its Derivatives. HÅKAN SANDQVIST (*Annalen*, 1911, **379**, 79—90).—The phenanthrene-2-sulphonic acid used in the experiments is obtained in the form of the potassium salt from the by-products of the sulphonation of phenanthrene by Kunz's process. The acid is prepared from the acid chloride and water at 130—135°, from the barium salt and sulphuric acid, or from the lead salt and hydrogen sulphide. The acid contains H_2O, has m. p. about 150°, and is freed from its solvents only with difficulty; its electrical conductivity does not differ much from that of the 3-sulphonic acid (Abstr., 1909, i, 779). The following salts are described, the solubilities being expressed as before (*loc. cit.*): potassium ($\frac{1}{2}H_2O$), sol. 0·273; ammonium, sol. 0·37; *sodium* ($\frac{1}{2}H_2O$), white leaflets or needles, sol. 0·42; *calcium*, sol. 0·024; barium ($\frac{1}{2}H_2O$), sol. 0·016; *magnesium* ($6H_2O$), elongated leaflets, sol. 0·051; *zinc* ($6H_2O$), sol. 0·083; ferrous ($5H_2O$), sol. 0·044; lead (H_2O), sol. 0·014; *copper* (H_2O), bluish-green crystals, sol. 0·25; *silver*, sol. 0·099. *Phenanthrene-2-sulphonyl chloride*, obtained from the potassium salt and phosphorus pentachloride, has m. p. 156°, is oxidised by acetic and chromic acids to *phenanthraquinone-2-sulphonyl chloride*, yellow leaflets or needles, m. p. 245—246° (decomp.), and forms a *sulphonamide*, m. p. 253—254°, and *sulphonanilide*, $C_{14}H_9\cdot SO_2\cdot NHPh$, m. p. 157—158°, by the usual methods.

Methyl phenanthrene-2-sulphonate is dimorphous, the stable modification forming rhombic plates, the labile modification leaflets. The fact that many derivatives of phenanthrene have two m. p.'s may be due to dimorphism; the preceding ester, crystallised from methyl alcohol, has m. p. 92·5—93° and 101·5°, whilst in a capillary tube the m. p. is either 85°, 98°, or 101·5°. By oxidation with chromic and acetic acids the ester yields *methyl phenanthraquinone-2-sulphonate*, yellow leaflets, m. p. 196—197°, or elongated leaflets, m. p. 192—192·5°. *Ethyl phenanthrene-2-sulphonate* has m. p. 88·5°.

C. S.

An Organo-metallic Compound of the Aniline Series. E. RATTENBURY HODGES (*Chem. News*, 1910, **103**, 52).—By slow addition of zinc chloride solution to a saturated aqueous solution of aniline, slender, colourless, highly refractive crystals of a compound of zinc chloride with aniline chloride were obtained. N. C.

Osmichlorides. ALEXANDER GUTBIER [with P. WALBINGER] (*Ber.*, 1911, **44**, 308—312).—The following osmichlorides were prepared by interaction of sodium osmichloride (Abstr., 1910, ii, 45) and aryl substituted ammonium chlorides. They were purified by recrystallisation from dilute hydrochloric acid; the aqueous sulutions undergo decomposition. The salts are all anhydrous and stable in the air.

Phenylammonium osmichloride, $(NH_3Ph)_2OsCl_6$, forms brownish-red, rhombic leaflets. *Phenylmethylammonium osmichloride*,

$$(NH_3MePh)_2OsCl_6,$$

forms brownish-red, monoclinic crystals, showing pleochroism. o-*Tolylammonium osmichloride*, $(C_6H_4Me{\cdot}NH_3)_2OsCl_6$, is obtained in yellow or brownish-red, rhombic needles, which are pleochroic. m-*Tolylammonium osmichloride* forms slender, pleochroic, brownish-red, rhombic needles. p-*Tolylammonium osmichloride* crystallises in yellowish-red, rhombic, pleochroic leaflets. o-4-*Xylylammonium osmichloride*,

$$(C_6H_3Me_2NH_3)_2OsCl_6,$$

forms shining red, monoclinic needles. m-4-*Xylylammonium osmichloride* forms strong, pleochroic, ruby-red, rhombic crystals. p-5-*Xylylammonium osmichloride* is obtained in red, rhombic, pleochroic needles. *Pyridinium osmichloride*, $(C_5H_6N)_2OsCl_6$, forms red, rhombic plates. *a-Picolinium osmichloride*, $(C_5NH_5Me)_2OsCl_6$, forms yellowish-red, rhombic leaflets. *Quinolinium osmichloride*, $(C_9NH_8)_2OsCl_6$, is obtained in yellowish-red, feebly pleochroic, monoclinic needles. *Benzylammonium osmichloride*, $(C_7H_7{\cdot}NH_3)_2OsCl_6$, forms brownish-red, monoclinic plates. *a-Naphthylammonium osmichloride*, $(C_{10}H_7{\cdot}NH_3)_2OsCl_6$, crystallises in brownish-red, pleochroic, rhombic needles. *β-Naphthylammonium osmichloride* forms brownish-red, pleochroic, rhombic leaflets. T. S. P.

Lactyl Compounds of Primary Aromatic Amines. KARL ELBS (*J. pr. Chem.*, 1911, [ii], **83**, 1—21) [with K. SINNER.]—The lactylation of several primary aromatic amines has been studied quantitatively at about 100° by heating mixtures of the amine and lactic acid, with or without water, in a water-bath and titrating the unchanged acid after definite intervals of time, phenolphthalein being used as indicator. In the experiments without water, the lactate of the amine is used. The results, which are expressed graphically, show that the formation of the lactyl compound is retarded by the presence of water, but is facilitated, contrary to Menschutkin's experience in the case of acetanilide, by using an excess of the amine (*p*-toluidine).

The lactylation of different amines under the same conditions, namely, 1 mol. of base, 1 mol. of acid, and 1·66 mols. of water at 100°, shows that the reactivity of the amino-group in aniline is affected slightly by the presence of a methyl group in the para-position, considerably and unfavourably by methyl in the ortho-position, and favourably by the ethoxy-group in the para- and still more so in the ortho-position.

[With FR. METTE.]—Lactophenin in glacial acetic acid at 0° is converted by nitric acid, D 1·40, into *2-nitro-4-ethoxylactanilide* (*2-nitrolactophenin*), $OEt\cdot C_6H_3(NO_2)\cdot NH\cdot CO\cdot CHMe\cdot OH$, yellow needles or leaflets, m. p. 112°, the position of the nitro-group being determined by the fact that the substance and nitrophenacetin give the same nitrophenetidine by hydrolysis. Nitric acid, D 1·40, converts powdered lactophenin into 2 : 6-*dinitroethoxylactanilide*, yellow needles or leaflets, m. p. 135°, which yields the known dinitrophenacetin by hydrolysis and treatment of the product with acetic anhydride. Concentrated sulphuric and nitric acids at 0° convert dinitrolactophenin into the *nitrate*, $OEt\cdot C_6H_2(NO_2)_2\cdot NH\cdot CO\cdot CHMe\cdot ONO_2$, yellow leaflets, m. p. 192° (decomp.), which yields dinitrophenetidine, amongst other products, by hydrolysis with dilute alcoholic potassium hydroxide.

[With A. SCHUSTER.]—3-*Nitrolacto*-p-*toluidide*,

$$NO_2\cdot C_6H_3Me\cdot NH\cdot CO\cdot CHMe\cdot OH,$$

yellow needles, m. p. 86—87°, obtained from an acetic acid solution of lacto-*p*-toluidide and nitric acid, D 1·48, at 0°, yields 3-nitro-*p*-toluidine by hydrolysis. 3 : 5-*Dinitrolacto*-p-*toluidide*, yellow needles, m. p. 139—140°, obtained from the preceding compound and concentrated nitric and sulphuric acids at 0°, yields 3 : 5-dinitro-*p*-toluidine by hydrolysis. The *nitrate*, $C_6H_2Me(NO_2)_2\cdot NH\cdot CO\cdot CHMe\cdot ONO_2$, white needles, decomp. 160°, obtained from lacto-*p*-toluidide and concentrated sulphuric acid and nitric acid, D 1·48, at 0°, also yields 3 : 5-dinitro-*p*-toluidine by hydrolysis.

Owing to the ease with which lactotoluidides are hydrolysed even by dilute alkali, the electrolytic reduction of 3-nitrolacto-*p*-toluidide must be effected in an approximately neutral solution which is slightly alkaline in the immediate neighbourhood of the cathode. Even then the reduction does not proceed smoothly, for with an anodic liquid consisting of cold saturated sodium carbonate and a cathodic solution of acetic acid and sodium acetate, and a cathodic current density of 3—3·5 amperes per sq. dcm., the nitrolactotoluidide yields a number of products, from which 3 : 3′-*azoxylacto*-p-*toluidide*,

$$ON_2(C_6H_3Me\cdot NH\cdot CO\cdot CHMe\cdot OH)_2,$$

yellow needles or leaflets, m. p. 234° (decomp.), is isolated. By hydrolysis by dilute alcoholic potassium hydroxide, it yields 3 : 3′-*azoxy*-p-*toluidine*, red needles, m. p. 188°, which is converted by electrolytic reduction in sulphuric acid into the sparingly soluble sulphate of 3 : 4-tolylenediamine. The electrolytic reduction of 3-nitrolacto-*p*-toluidide in acid solution by Boehringer's process yields, amongst other products, acetaldehyde and 40—60% of 5-*methylbenziminazolone*,

$$C_6H_3Me{<}{\substack{NH\\NH}}{>}CO,$$

white crystals, m. p. 292—295° (*acetyl* derivative, m. p. 176°), the constitution of which is proved by the formation of the same substance from 3 : 4-tolylenediamine and carbamide.

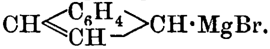
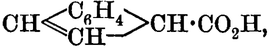
[With Fr. Mette and A. Schuster.]—The electrolytic reduction of 2-nitroethoxylactanilide in approximately neutral (cathodic) solution at the b. p. yields 2 : 2′-*azoethoxylactanilide*,

$$N_2[C_6H_3(OEt)\cdot NH\cdot CO\cdot CHMe\cdot OH]_2,$$

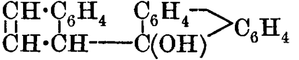
yellowish-red needles, m. p. 269°, in 15—20% yield. By hydrolysis the azo-compound yields *azo*-p-*phenetidine*, m. p. 143°, which forms an acetyl derivative, m. p. 306°, identical with the azophenacetin obtained by the electrolytic reduction of nitrophenacetin.

The electrolytic reduction of 2-nitroethoxylactanilide in acid solution yields acetaldehyde, several unidentified products, one of which has m. p. 161°, and ethoxybenziminazolone (Cohn, Abstr., 1899, i, 944), the *diacetyl* derivative of which has m. p. 163°. C. S.

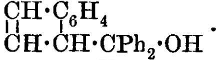
The Solubility of Sodium Picrate in Solutions of Sodium Salts. Woldemar Fischer and P. Miloszewski (*Chem. Zentr.*, 1910, ii, 1048; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 538—542).—The solubility of sodium picrate in aqueous solutions of sodium, carbonate, chloride, sulphate, phosphate, nitrate, bromide, and hydroxide of various strengths at 25° was determined. The measurements have proved that, contrary to the statement of Reinhard (*Zeitsch. anal. Chem.*, 1910, **49**, 269), the solubility of sodium picrate is lowered by the presence of the sodium ions in accordance with the law of mass action. N. C.

New Derivatives of Indene. Victor Grignard and Charles Courtot (*Compt. rend.*, 1911, **152**, 272—274).—Organo-magnesium bromides act on indene, giving rise to a sparingly soluble *magnesium indenyl bromide*,  $CH{<}{\overset{C_6H_4}{\underset{CH}{}}}{>}CH\cdot MgBr$. When treated in the usual way, this yields the two following compounds: 1-*Indenol*, C_9H_8O, yellow prisms, m. p. 57—58°, b. p. 140°/10 mm., with partial dehydration. *Indene-1-carboxylic acid*,  $CH{<}{\overset{C_6H_4}{\underset{CH}{}}}{>}CH\cdot CO_2H$, chamois-coloured, prismatic needles, m. p. 161°.

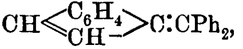
Magnesium indenyl bromide reacts with fluorenone at 120° to give a theoretical yield of tert.-1-*indenylfluorenol* (I):



(I.)



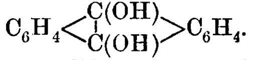
(II.)

This compound crystallises in colourless needles, m. p. 151—152°. In the same way, benzophenone gives 1-*indenyldiphenylcarbinol* (II), a substance occurring in pale yellow tablets, m. p. 131—132°. A portion of the carbinol undergoes dehydration during the preparation, forming *diphenylbenzfulvene*,  $CH{<}{\overset{C_6H_4}{\underset{CH}{}}}{>}C{:}CPh_2$, orange-yellow spangles, m. p. 111—112°. W. O. W.

Anthracene. I. Anthranol and Anthraquinol. Kurt H. Meyer (*Annalen*, 1911, **379**, 37—73).—Dimroth's dianthrone and

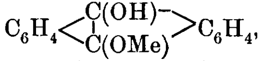
Meyer's dianthranol (Abstr., 1909, i, 168), which are stable separately, not only in the solid state, but also in solution, and are mutually interconvertible only by energetic chemical means, are distinct isomerides, not tautomerides of the enol-keto-type, claimed by Thiele and by Baly for phenols of the benzene series. In the present paper the author shows that the monohydric and dihydric meso-phenols of the anthracene series, anthranol and anthraquinol, can each exist in two stable desmotropic forms.

The substance, long known as anthranol, reacts sometimes as a phenol, sometimes as a ketone; it is colourless, completely insoluble in cold aqueous alkalis, and its solutions generally are non-fluorescent. When its 5—10% solution in boiling sodium hydroxide is cooled rapidly to $-5°$ and treated with cold 5% sulphuric acid, a new *substance*, $C_{14}H_{10}O$, is obtained, which crystallises in brownish-yellow leaflets, is easily soluble in cold aqueous alkalis, and forms solutions with an intense blue fluorescence; it sinters at 120° and melts completely at about 152°, but when placed in a bath previously heated to 120°, it melts at once. This substance is called anthranol, the name anthrone being reserved for the older substance. Anthranol changes into anthrone by keeping in a desiccator. The two substances attain a state of equilibrium when fused or dissolved, the change being easily followed by the formation or the disappearance of the blue fluorescence. Since both substances separately are stable for a long time in alcohol, it is possible to answer the question whether the activity of phenols is due to the enolic or to the keto-modification. In cold alcohol anthrone is not attacked by iodine, bromine, ferric chloride, or amyl nitrite; on boiling, however, particularly in solvents which cause a rapid transformation of anthrone into anthranol, reactions occur. In cold alcohol anthranol is attacked at once by bromine or iodine, and is oxidised to dianthrone by ferric chloride; also amyl nitrite in benzene at the ordinary temperature oxidises anthranol to dianthrone; dianthranol is never produced, not even when anthranol is oxidised by alkaline potassium ferricyanide. An alcoholic solution of anthranol at 25° couples readily with *p*-nitro*anti*diazobenzene hydrate to form Kaufler and Suchannek's anthraquinone-*p*-nitrophenylhydrazone; under similar conditions anthrone does not couple; also nitrosodimethylaniline condenses with anthranol, but not with anthrone, in alcoholic solution. Thus the reactivity of the hydroxylic modification supports Dimroth's results in connexion with the reactivity of enol-keto-tautomerides in the aliphatic series (Abstr., 1907, i, 662).

As is well known, anthraquinol (oxanthranol), obtained by reducing anthraquinone with zinc dust and alkali, forms brown leaflets, dissolves in cold aqueous sodium hydroxide to form a red disodium salt, yields solutions with an intense green fluorescence, and is rapidly oxidised to anthraquinone by iodine, bromine, or oxygen; its *dibenzoate* has m. p. 292°, and is non-fluorescent. Consequently oxanthranol is the true anthraquinol,  $C_6H_4{<}\begin{matrix}C(OH)\\ |\\ C(OH)\end{matrix}{>}C_6H_4$. It cannot be readily transformed into the keto-modification, *oxanthrone*,

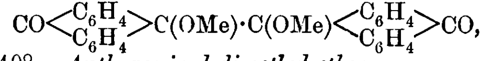
$C_6H_4{<}\substack{\text{—CO—}\\ CH(OH)}{>}C_6H_4$, which is readily obtained, however, by hydrolysing bromoanthrone (Goldmann's bromoanthranol) by boiling 50% aqueous acetone (see also following abstract). Oxanthrone, m. p. 167°, forms yellow, almost colourless needles, gives colourless solutions which are non-fluorescent and are not attacked by oxygen, iodine, or bromine in the cold, is easily reduced to anthranol by zinc dust and acetic acid (anthraquinol is not reduced), and is unchanged by cold aqueous alkalis. Boiling alkalis convert oxanthrone into anthraquinol. The two substances can be fused without changing the one into the other. Also, in boiling solvents they are for the most part unchanged; the addition of a catalyst, however, such as hydrogen chloride or sodium acetate, to the alcoholic solutions causes an almost complete change of the oxanthrone into anthraquinol. *Oxanthrone acetate*, $C_6H_4{<}\substack{\text{—CO—}\\ CH(OAc)}{>}C_6H_4$, m. p. 108°, is obtained from bromoanthrone and potassium acetate in hot glacial acetic acid; the action of acetyl chloride on oxanthrone in pyridine yields Liebermann's anthraquinyl diacetate.

Meisenheimer's methoxyanthrone, $C_6H_4{<}\substack{\text{—CO—}\\ CH(OMe)}{>}C_6H_4$, obtained by boiling bromoanthrone with methyl alcohol, is partly converted by boiling alcohol and hydrochloric acid or by luke-warm dilute sodium hydroxide into *anthraquinyl methyl ether*,



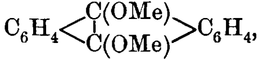
$$C_6H_4{<}\substack{C(OH)-\\ |\\ C(OMe)}{>}C_6H_4,$$

m. p. 164°, which is also obtained by shaking an alkaline solution of anthraquinol with methyl sulphate, filtering in hydrogen, and extracting the filtrate with ether in an atmosphere of carbon dioxide. The ether forms an *acetate*, m. p. 174°, and a *benzoate*, m. p. 224°, separates in stout, brown crystals, yields solutions with a bluish-green fluorescence, and dissolves in cold alkalis, forming reddish-yellow solutions which are easily oxidised by iodine, bromine, or oxygen to anthraquinone and 9 : 9′-*dimethoxydianthrone*,



$$CO{<}\substack{C_6H_4\\ C_6H_4}{>}C(OMe)\cdot C(OMe){<}\substack{C_6H_4\\ C_6H_4}{>}CO,$$

m. p. 239—240°. *Anthraquinyl dimethyl ether*,



$$C_6H_4{<}\substack{C(OMe)\\ |\\ C(OMe)}{>}C_6H_4,$$

m. p. 202°, obtained as a by-product in the reaction between anthraquinol and methyl sulphate, forms colourless plates with a blue fluorescence; its solutions also are fluorescent, and are not attacked by iodine or bromine in the cold. *Anthraquinyl diethyl ether*, m. p. 148°, obtained from anthraquinol and ethyl sulphate and purified by means of 80% alcohol, forms colourless needles with a blue fluorescence; its solution in chloroform or carbon disulphide is decolorised by bromine, anthraquinone being formed. The alcoholic mother-liquor contains Liebermann's ethyloxanthrone, m. p. 107°.

By a consideration of the distribution of the residual affinity, Meisenheimer has shown that addition takes place at the *meso*-carbon atoms in derivatives of anthracene, and at the oxygen atom in those of anthrone and anthraquinone. The author shows that this theory is applicable, not only to explain, but also to predict, the preceding results. C. S.

Anthracene. II. Oxidation of Anthracene. KURT H. MEYER (*Annalen*, 1911, **379**, 73—78. Compare preceding abstract).—Most oxidising agents which attack anthracene convert it into anthraquinone. By using lead dioxide and glacial acetic acid, Schulze obtained a substance which was supposed to be different from anthraquinol (oxanthranol), and was called β-oxanthranol. It is, however, anthraquinol itself, produced, as the sequel shows, from the initially-formed oxanthrone acetate by the boiling alkali used by Schulze in the process of purification.

By oxidising anthracene in glacial acetic acid at 50° by lead dioxide (1 mol.), the author obtains 40—50% of anthranyl acetate, together with a little oxanthrone acetate and anthraquinone. When the oxidation is effected at 70° by 2 mols. of lead dioxide, the main product is oxanthrone acetate.

The oxidation of anthracene by manganese dioxide, cerium acetate, or vanadic acid proceeds in a similar manner, provided that glacial acetic acid is used as the solvent; a solution of anthracene in alcohol and toluene is oxidised by manganese dioxide and a drop of sulphuric acid to viscous products, amongst which occurs dianthrone.

Anthracene is oxidised very smoothly to oxanthrone by bromine in aqueous acetone, only a trace of anthraquinone being formed; the action of chlorine on an aqueous suspension of anthracene is similar, but less satisfactory, as regards purity of product. By allowing solutions of anthracene in glacial acetic acid and of bromine in methyl alcohol to flow simultaneously into a large volume of methyl alcohol, methoxyanthrone together with a little anthraquinone and unchanged anthracene are produced. C. S.

***p*-Xylyl Sulphide and its Derivatives.** Z. MARTYNOWICZ (*Chem. Zentr.*, 1910, ii, 1048; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 594—596).—p-*Xylyl sulphide*, $S(CH_2{\cdot}C_6H_4Me)_2$, obtained by the action of an alcoholic solution of potassium sulphide on *p*-xylyl bromide, forms colourless needles, m. p. 76°. By oxidation with nitric acid, it forms p-*xylylsulphoxide*, $SO(CH_2{\cdot}C_6H_4Me)_2$, which crystallises in silky needles, m. p. 117°. Both these substances form on oxidation with potassium permanganate, p-*xylylsulphone*, $SO_2(CH_2{\cdot}C_6H_4Me)_2$, which forms shining plates, m. p. 197°. N. C.

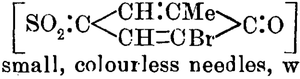
The Action of Ammonia on Aromatic Thiocyanates. MARYA STRZELECKA (*Chem. Zentr.*, 1910, ii, 1135; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 585—589).—When aromatic thiocyanates are boiled for a long time with alcoholic ammonia, ammonium cyanide is split off with the formation of disulphides. In this way the following disulphides were prepared: benzyl disulphide, $(CH_2Ph)_2$, white crystals, m. p. 71—72°; p-*xylyl disulphide*, white radiating tufts of needles, m. p. 43°; o-*xylyl disulphide*, white plates, m. p. 83—85°. The *meta*-compound could not be obtained in this way. N. C.

Phenyl Thiocarbonate. ANGELO CASOLARI (*Gazzetta*, 1910, **40**, ii, 389—402).—Potassium trithiocarbonate reacts with diazobenzene chloride in aqueous solution with formation of *phenyl trithiocarbonate*, CS_3Ph_2, which is a red oil, D_4^0 1·2668, $D_4^{19·5}$ 1·2497. It has the normal molecular weight. Heat decomposes the substance somewhat readily, with formation of hydrogen sulphide and carbon disulphide among other products. When subjected to distillation, the compound evolves vapour at 210—215°/30 mm., and the distillate consists of phenyl disulphide. The action of alcoholic potassium hydroxide, alcoholic ammonia, or aqueous ammonia in a sealed tube, leads to the production of thiophenol, carbon disulphide, a carbonate, and a thiosulphate. As secondary products from the carbon disulphide are formed thiocyanic acid and hydrogen sulphide (when ammonia is used) and xanthic acid (with alcoholic potassium hydroxide).

Thiosulphates give a characteristic blue coloration when treated with a few drops of a 5% solution of sodium nitroprusside which has been exposed to light and air until it has assumed a chestnut-brown colour. The coloration is green in very dilute solutions; it is stable in neutral solutions or in the presence of potassium hydrogen tartrate, but becomes green and finally yellow in the presence of alkali, acid, or oxidisers. The reaction is not given by sulphites or by tetrathionates. The reagent may also be made by treating a fresh solution of sodium nitroprusside with potassium ferricyanide, then with potassium hydroxide, and finally rendering the liquid just acid with potassium hydrogen tartrate. R. V. S.

Sulphur Derivatives of *o*-Cresol. THEODOR ZINCKE and R. BRUNE (*Ber.*, 1911, **44**, 185—197. Compare Zincke and Glahn, Abstr., 1907, i, 698).—*3-Bromo-o-cresol-5-sulphonyl chloride*,

$$OH·C_6H_2BrMe·SO_2Cl,$$

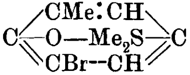
prepared by the action of phosphoryl chloride on potassium bromo-*o*-cresol-sulphonate (Claus and Jackson, Abstr., 1889, 129) at 150°, crystallises from light petroleum in colourless needles, m. p. 94°, and yields an *acetyl* derivative in the form of colourless prisms, m. p. 131°. The *methyl* ester, $OH·C_6H_2MeBr·SO_2Me$, forms colourless plates, m. p. 141—142°; the *ethyl* ester, compact needles, m. p. 113°, and the *anilide*, minute crystals, m. p. 165—166°. Potassium acetate reacts with an acetone solution of the chloride, yielding a polymeric *bromosulphonyl-*p*-toluquinone*,  $\left[SO_2{:}C\begin{matrix}<CH{:}CMe>\\ <CH{=}CBr>\end{matrix}C{:}O\right]_n$, which crystallises from nitrobenzene in small, colourless needles, with no definite m. p. *3-Bromo-5-thiol-o-cresol*, $SH·C_6H_2MeBr·OH$, obtained by reducing the sulphonyl chloride with zinc dust, alcohol, and hydrochloric acid, crystallises from light petroleum in colourless needles, m. p. 51—52°. The *diacetyl* derivative, $C_{11}H_{11}O_3SBr$, forms small, compact plates, m. p. 111—112°. Concentrated ferric chloride solution oxidises the thiol in the presence of glacial acetic acid to *3-bromo-o-cresol 5-disulphide*, $S_2(C_6H_2BrMe·OH)_2$, which crystallises from light petroleum in thick, yellow plates, m. p. 123—124°. The corresponding *acetyl* derivative, $C_{18}H_{16}O_4S_2Br_2$, forms colourless plates,

m. p. 101—102°, and is also formed when the thiol is warmed with acetic anhydride and a little sulphuric acid.

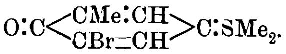
3-*Bromo*-5-*methylthiol*-o-*cresol*, $OH\cdot C_6H_2MeBr\cdot SMe$, obtained by methylating the thiol with methyl iodide and sodium methoxide in the cold, is a colourless oil, b. p. 167—169°/20—21 mm., and yields an *acetyl* derivative, $C_{10}H_{11}O_2SBr$, in the form of glistening, rhombic plates, m. p. 53°. When shaken with water the methyl sulphide yields a yellow, amorphous powder, $C_{32}H_{33}O_4S_4Br$, m. p. about 90° after sintering at 50—60°. Dilute alkali hydroxide solutions react in much the same manner as water. Sodium nitrite reacts with a glacial acetic acid solution of the methyl sulphide, yielding 3-*nitro*-5-*methylthiol*-o-*cresol*, $SMe\cdot C_6H_2Me(NO_2)\cdot OH$, which crystallises in orange-red needles, m. p. 78—79°; its *acetyl* derivative forms yellow needles, m. p. 70°. 3-*Bromo*-o-*cresol* 5-*methylsulphoxide*, $OH\cdot C_6H_2MeBr\cdot SOMe$, obtained by oxidising a glacial acetic acid solution of the methyl sulphide with hydrogen peroxide, crystallises from benzene in well-developed, colourless needles, m. p. 121°; it dissolves in alkalis without decomposition, and yields a perbromide. The corresponding *sulphone*, $OH\cdot C_6H_2MeBr\cdot SO_2Me$, obtained by using excess of hydrogen peroxide, crystallises in colourless needles or prisms, m. p. 168°. 3 : 6-*Dibromo*-5-*methylthiol*-o-*cresol perbromide*, $OH\cdot C_6HMeBr_2\cdot SMeBr_2$, exists in two modifications, namely, orange-red plates from acetic acid and brownish-violet needles from chloroform. Both forms lose bromine, yielding 3 : 6-*dibromo*-5-*methylthiol*-o-*cresol*, $C_8H_8OSBr_2$, which crystallises from light petroleum in colourless needles or rhombic plates, m. p. 111—112°. 3 : 6-*Dibromo*-o-*cresol*-5-*methylsulphoxide*, $OH\cdot C_6HMeBr_2\cdot SMeO$, prepared by the action of water on the perbromide, crystallises from benzene in stout, colourless needles, m. p. 168°, and the corresponding *sulphone*, $C_8H_8O_3SBr_2$, forms colourless needles, m. p. 169°.

3-*Bromo*-o-*cresol*-5-*dimethylsulphinium iodide*, $OH\cdot C_6H_2MeBr\cdot SMe_2I$, prepared by the action of methyl iodide on the thiol derivative in the presence of an excess of alkali, crystallises in felted needles, m. p. 114° (decomp.). The corresponding *chloride*, $C_9H_{12}OSClBr$, forms slender needles, m. p. 151° (decomp.), and the *platinichloride* crystallises in brownish-yellow needles.

The *anhydro*-compound, $C_9H_{11}OSBr$, obtained by the action of moist silver oxide on the sulphinium iodide, crystallises in colourless needles, m. p. 185—187°, after darkening at 170°. It must be represented by one or other of the formulæ :

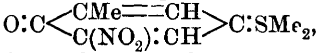


or



$$O:C<\begin{matrix}CMe:CH\\CBr=CH\end{matrix}>C:SMe_2.$$

The corresponding *nitrothionium quinone*,



$$O:C<\begin{matrix}CMe=CH\\C(NO_2):CH\end{matrix}>C:SMe_2,$$

crystallises in glistening, yellow needles, m. p. 245—246°, and when boiled for some time with dilute alkalis yields the nitromethylthiolcresol. The *nitrate*, $C_9H_{11}O_3NS,HNO_3$, forms stout, yellow prisms, m. p. 150—151° (decomp.); the *chloride* forms pale yellow plates, m. p. 99—100° (decomp.), and the *platinichloride*, $2C_9H_{11}O_3NS,H_2PtCl_6$, forms compact, yellow needles. J. J. S.

Action of Magnesium Phenyl Bromide on Heptaldehyde. U. Colacicchi (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 600—605).—*Phenylhexylcarbinol*, $C_{13}H_{20}O$ (from magnesium phenyl bromide and heptaldehyde), is a colourless liquid, b. p. 156°/25 mm., 176°/40 mm., or 275° at the ordinary pressure, D 0·9455, *n* (yellow) 1·501. Its *phenylurethane*, $C_{20}H_{25}O_2N$, forms rosettes of colourless crystals, m. p. 77°. The *phenylthiourethane* crystallises in laminæ, m. p. 147°. Phenylhexylcarbinol, when reduced with iodine and phosphorus, yields the corresponding *iodide*, which is a liquid, b. p. 140°/38 mm., and a *substance* (probably a hydrocarbon) distilling at 290—360°. By oxidation of the carbinol, phenyl hexyl ketone is obtained, identical with that described by Auger (Abstr., 1887, 814). The *semicarbazone* of the ketone, $C_{14}H_{21}ON_3$, forms colourless needles, m. p. 118—119°. The p-*nitrophenylhydrazone*, $C_{19}H_{23}O_2N_3$, crystallises in yellow needles, m. p. 127—128°.

Experiments on the physiological action of the compounds described show that the toxicity of the alcohol is somewhat greater than that of the ketone, both for warm-blooded (*Mus musculus*) and cold-blooded (*Rana esculenta*) animals. Both substances eventually cause paralysis of the central nervous system, and diminish the amplitude of the beats of the heart, which finally stops in diastole. R. V. S.

Dextrorotatory Phytosterols of Anthemis nobilis (Anthesterols). Timothée Klobb (*Compt. rend.*, 1911, **152**, 327—330. Compare Abstr., 1909, i, 471).—The existence of isomeric benzoates and the variable composition of its bromo-derivatives suggest that anthesterol is not a single substance. To throw light on this point, the alcohol was treated with acetic anhydride, when three isomeric acetates were obtained. A. Hexagonal lamellæ, m. p. 245—248°, $[\alpha]_D$ +91·2°; this yields α-anthesterol on hydrolysis. B. Hexagonal lamellæ, m. p. 225—230°, $[\alpha]_D$ +73·9°; β-anthesterol is obtained on hydrolysis. (C) Confused crystals, m. p. 185—195°, giving on hydrolysis needles having a double m. p., 158—160° and 185—190°.

On bromination the acetate, (A) yields two *monobromo*-derivatives, $C_{31}H_{50}OBrAc$, m. p. about 180°, but having $[\alpha]_D$ +133° and +58·8° respectively. (B) gives a *dibromo*-additive product, $C_{31}H_{51}OBr_2Ac$, m. p. 170—175°. (C) forms a mixture of the bromo-acetate from (A), with a substance corresponding in composition with a mixture of the (A) and (B) bromo-derivatives containing 45% of the latter.

The interpretation placed on these results is that anthesterol has the formula $C_{31}H_{52}O,3H_2O$, and is an individual substance homologous with amyrin and paltreubin (Jungfleisch and Leroux, Abstr., 1906, i, 525; 1907, i, 783; 1908, i, 1000). It is not identical with lupeol as suggested by Cohen (Abstr., 1908, i, 882). W. O. W.

Esterification of Benzamide and the Preparation of *N*-Substituted Benzamides. E. Emmet Reid (*Amer. Chem. J.*, 1911, **45**, 38—47).—Bonz (Abstr., 1889, 335) made a study of the reversible reaction: $CH_3\cdot CO\cdot NH_2 + EtOH \rightleftarrows CH_3\cdot CO_2Et + NH_3$, and identified ethylamine among the reaction products. He assumed that the amine was produced by the action of ammonia on the ester previously formed, thus: $CH_3{\cdot}CO_2Et + NH_3 = CH_3{\cdot}CO_2{\cdot}NH_3Et$, but his results are more simply accounted for by supposing that the amide and alcohol react directly to form acetoethylamide:

$$CH_3{\cdot}CO{\cdot}NH_2 + EtOH = CH_3{\cdot}CO{\cdot}NHEt + H_2O.$$

In connexion with certain other work (Abstr., 1910, i, 481, 701), the author studied the action of alcohol on benzamide and found that benzoethylamide could be readily obtained. The work has been continued and extended to other alcohols. The reactions which take place when ethyl alcohol is heated with benzamide are as follows: $C_6H_5{\cdot}CO{\cdot}NH_2 + EtOH \rightleftarrows C_6H_5{\cdot}CO_2Et + NH_3$, $C_6H_5{\cdot}CO{\cdot}NH_2 + EtOH = C_6H_5{\cdot}CO{\cdot}NHEt + H_2O$. The benzoethylamide undergoes hydrolysis according to the reaction:

$$C_6H_5{\cdot}CO{\cdot}NHEt + H_2O \rightleftarrows C_6H_5{\cdot}CO_2H,NH_2Et,$$

which finally reaches equilibrium.

Benzamide was heated with a slight excess of the alcohol in a sealed tube at 220—230° for periods varying from two to seven days. In an experiment with methyl alcohol, 39% of benzomethylamide was isolated, but no methyl benzoate was obtained, and 61% of the amide underwent hydrolysis. In two experiments with ethyl alcohol, the yields of benzoethylamide were 61·1 and 62·6%, of ethyl benzoate 1·27 and 1·58%, whilst the amounts of amide hydrolysed were 38·1 and 36·4%. With propyl alcohol the yield of benzopropylamide was 72·9%, of propyl benzoate 5·2%, and the amide hydrolysed amounted to 23·1%. In the case of *iso*butyl alcohol, 69·4% of benzo*iso*butylamide was obtained and 8·3% of *iso*butyl benzoate, whilst 24·3% of the amide suffered hydrolysis.

The amount of benzamide transformed into the ester seems to increase with the molecular weight of the alcohol. In the case of the experiment with methyl alcohol, a small quantity of water was present, and a large amount of hydrolysis therefore occurred.

The action of alcohols on benzamide affords a convenient method for preparing certain benzoalkylamides, and may also be of service for the preparation of the amines which are obtained as by-products.

E. G.

Study of *o*-Amino-*p*-sulphobenzoic Acid with Special Reference to its Fluorescence. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1911, 45, 58—78).—Aqueous solutions of *p*-aminobenzoic sulphinide exhibit a bluish-purple fluorescence, but solutions in concentrated hydrochloric acid are not fluorescent. Since several difficulties arise in attempting to elucidate the causes of this phenomenon, the author has studied *o*-amino-*p*-sulphobenzoic acid (Hart, Abstr., 1881, 1146), which, on account of its simpler constitution, appeared more suitable for an investigation of the influence of simple chemical changes on fluorescence.

o-Amino-*p*-sulphobenzoic acid crystallises with $\frac{1}{2}H_2O$, and in dilute aqueous solution exhibits a bluish-purple fluorescence which, within certain wide limits, is inversely proportional to the concentration. The intensity of the fluorescence of both the acid and its salts is diminished by heat. The fluorescence of aqueous solutions of the acid is weakened or destroyed by strong acids and alkalis, the power of effecting this change being roughly proportional to the degree of ionisation of the reagent. The intensity of the fluorescence of sodium, potassium, ammonium, calcium, barium, and magnesium *o*-amino-*p*-sulphobenzoates is independent of the nature of the base. Solutions of the acid and of the acid salts are much more fluorescent than those of the normal salts, whilst the fluorescence of solutions of the acid salts is somewhat more intense than that of solutions of the free acid.

Di-silver o-*amino*-p-*sulphobenzoate* exists in two forms, one amorphous and unstable above 27·5°, the other crystalline, stable at 27·5° and at higher temperatures, and less soluble in water than the amorphous variety. By the action of ethyl iodide on the crystalline di-silver salt, a compound, probably o-*ethylamino*-p-*sulphobenzoic acid*, $CO_2H\cdot C_6H_3(NHEt)\cdot SO_3H,H_2O$, m. p. 243° (decomp.), is produced, which forms colourless, rhombic crystals, and exhibits a blue fluorescence in dilute aqueous solution. In one experiment, another *compound*, m. p. 160°, probably either the true diethyl ester or the acid ester of the ethylamino-acid, $CO_2Et\cdot C_6H_3(NHEt)\cdot SO_3H$, was obtained, which forms pale yellow crystals, and, when boiled with water, is converted into the substance melting at 243°. A *barium* salt, probably $[CO_2Et\cdot C_6H_3(NHEt)\cdot SO_3]_2Ba$, has also been prepared.

E. G.

Iminosulphides. I. The Condensation of Thiobenzamide with Benzonitrile.

MOTOOKI MATSUI (*Mem. Coll. Sci. Eng. Kyoto*, 1910, **2**, 401—404).—Under the influence of hydrochloric acid, thiamides combine with nitriles to form iminosulphides of the constitution : $S(CR\colon NH)_2$.

Benziminosulphide, $S(CPh\colon NH)_2$, obtained in the form of its hydrochloride by the action of hydrochloric acid on an ethereal solution of thiobenzamide and benzonitrile, crystallises in light red needles, m. p. 71° ; the *acetyl* derivative crystallises in orange needles, The *hydrochloride*, $C_{14}H_{12}NS,2HCl$, forms orange needles, m. p. 110—111°, and is decomposed by water, yielding the free base. The *picrate*, $C_{14}H_{12}NS,C_6H_3O_7N$, crystallises in light red, prismatic plates, containing one molecule of alcohol; when heated at 80°, the alcohol of crystallisation is lost, and the picrate is obtained as an amorphous, yellow substance, m. p. 114°.

F. B.

Degradation of Amino-acids by Fermentation with Yeast.

OTTO NEUBAUER and KONRAD FROMHERZ (*Zeitsch. physiol. Chem.*, 1911, **70**, 326—350. Compare Abstr., 1909, ii, 750).—Stress is laid on the possible analogy between the conversion of an amino-acid into alcohol by means of yeast and into fatty-acid in the mammalian organism. In each case it is considered that the ketonic acid $R\cdot CO\cdot CO_2H$ is the intermediate product.

It is shown that by the action of yeast on *a*-aminophenylacetic acid, benzoyl alcohol, phenylglyoxylic acid, *l*-mandelic acid, and *l*-acetyl aminophenylacetic acid are formed. Yeast is able to effect a partial reduction of phenylglyoxylic acid to *l*-mandelic acid. The ketonic acid, *p*-hydroxylphenylpyruvic acid, is converted by yeast to a large extent into *p*-hydroxyphenylethyl alcohol. *p*-Hydroxyphenyl-α-lactic acid, on the other hand, is not converted to any extent into *p*-hydroxyphenylethyl alcohol, proving that this alcohol acid is not the intermediate product between keto-acid and alcohol. The conversion of amino-acid into alcohol involves a series of alternate oxidative and reducing changes.

E. F. A.

Transformation of δ-Phenyl-Δ^{α}-pentenoic Acid into the Δ^{γ}-Isomeride. J. Bougault (*Compt. rend.*, 1911, **152**, 196—197).—Fittig (Abstr., 1895, ii, 204) has shown that β-hydroxyvaleric acid is formed on boiling δ-phenyl-Δ^{α}-pentenoic acid with aqueous alkalis, together with a substance which he supposed to be δ-phenyl-Δ^{β}-pentenoic acid. The present author has been unable to obtain the latter substance, but finds that the Δ^{γ}-acid is an important product of the transformation, under the most favourable conditions the yield amounting to 50%. The formation of β-hydroxyvaleric acid was confirmed. An acidic liquid, possibly a mixture, is also produced in small quantity.

W. O. W.

Introduction of the Carboxylic Group into Polynuclear Aromatic Hydrocarbons. Carl Liebermann and M. Zsuffa (*Ber.*, 1911, **44**, 202—210).—The methods of Graebe and Liebermann (*Ber.*, 1869, 2 678), Friedel and Crafts (this Journ., 1877, ii, 725), and Gattermann (Abstr., 1888, 574) for the introduction of the carboxylic group into polynuclear aromatic hydrocarbons give but poor yields, and in many cases do not work. The authors have prepared the following acids by treating the corresponding hydrocarbons with 2·5 times their weight of oxalyl chloride at 160—170°, and extracting with cold sodium carbonate solution; the numbers indicate the percentage yields: anthracene-9-carboxylic acid, m. p. 217° (70—80%); fluorenecarboxylic acid (this Journ., 1877, ii, 493) (7—10%); indenecarboxylic acid, by using a temperature of 140—145° (15%), m. p. 234° (compare Perkin and Révay, Trans., 1893, **65**, 238); acenaphthenecarboxylic acid, also obtained by heating at 180° for fourteen hours (30%) (compare Gattermann, Abstr., 1888, 574); phenanthrene-9-carboxylic acid (yield poor); chrysenecarboxylic acid, by heating for two days at 170°, yield poor.

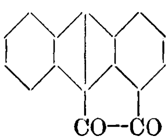
Better yields are obtained when aluminium chloride is added to the hydrocarbon and oxalyl chloride. The mixture becomes quite black even when carbon disulphide is present, but on adding water, the colour changes to yellow or red. The yields are better, but the products less pure.

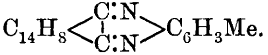
Naphthalene gives a mixture of 80% of α- and β-naphthoic acids, and anthracene yields anthracene-9-carboxylic acid (30%) and aceanthrenequinone (60%).

Benzene and naphthalene are not carboxylated in the absence of aluminium chloride, and when anthracene is heated with excess of oxalyl chloride at 200°, 10-chloroanthracene-9-carboxylic acid is formed (70%) (compare Behla, Abstr., 1886, 248; 1887, 593).

Chrysenecarboxylic acid, $C_{18}H_{11}\cdot CO_2H$, crystallises from alcohol in colourless needles, m. p. 303°, and the *sodium* salt, $C_{19}H_{11}O_2Na$, crystallises from water in long plates.

Aceanthrenequinone (annexed formula) crystallises from benzene in brilliant red prisms, m. p. 270°, and when sublimed has the appearance of alizarin. It combines with sodium hydrogen sulphite, is oxidised by chromic acid to anthraquinonecarboxylic acid, and an acetic acid solution reacts with an alcoholic solution of *o*-toluylenediamine, yielding *aceanthrenetolazin*,





$$C_{14}H_8<\begin{matrix}C:N\\|\\C:N\end{matrix}>C_6H_3Me.$$

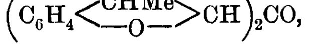
This crystallises in orange-red needles or plates, m. p. 237°, and its alcoholic solution has a green fluorescence. J. J. S.

Preparation of 3 : 5-Di-iodotyrosine from Iodoprotein. Adolf Oswald (*Zeitsch. physiol. Chem.*, 1911, **70**, 310—313).

—3 : 5-Di-iodotyrosine has been isolated among the products of the hydrolysis of iodo-albacid with barium hydroxide (Blum and Vaubel, Abstr., 1898, i, 610). It is suggested that iodine is, in part, attached to tyrosine in the natural iodoproteins. E. F. A.

Conversion of Coumarins into Coumarinic Acids and *o*-Coumaric Acids. II. Karl Fries and W. Volk (*Annalen*, 1911, **379**, 90—110. Compare Abstr., 1908, i, 820).

—Experiments similar to those already recorded (*loc. cit.*) have been performed on 4-methylcoumarin, 3-methylcoumarin, and 3-ethylcoumarin.

The conversion of 4-methylcoumarin into β-methylcoumarinates by aqueous alkalis is slower than that of coumarin into a coumarinate, but, conversely, its conversion by concentrated alkali into *β-methyl-o-coumaric acid*, $OH\cdot C_6H_4\cdot CMe\colon CH\cdot CO_2H$, m. p. 154° (decomp.), proceeds more readily (five hours' boiling with 33% potassium hydroxide) than that of coumarin into *o*-coumaric acid. When 4-methylcoumarin is heated with alcoholic potassium ethoxide at 140—150° for fifteen hours and the product is acidified, 1-(2-*methylcoumaran*)-3-(4-*methylcoumarin*) *ketone* (3-[2-*methylhydrocoumarilyl*]-4-*methylcoumarin*), $C_{20}H_{16}O_4$, m. p. 224°, is obtained, the constitution and behaviour of which are similar to those of the ketone obtained in the same manner from 4 : 7-dimethylcoumarin (*loc. cit.*); when boiled for a short time with dilute aqueous alkali, it loses carbon dioxide and yields *di*-1-(2-*methylcoumaran*) *ketone* (1-[2-*methylhydrocoumarilyl*]-2-*methylhydrocoumarone*),  $\left(C_6H_4<\begin{matrix}CHMe\\O\end{matrix}>CH\right)_2CO$, m. p. 183—185°, solidifying to a glassy mass which has m. p. about 95°, re-solidifies at about 145°, and melts again at 184°. This substance forms yellow solutions in alkalis, and yields an *oxime*, m. p. 213°.

3-Methyl-(or ethyl-)coumarin behaves towards aqueous alkalis and sodium ethoxide like those coumarins which are not alkylated in the pyrone nucleus. After being boiled for five hours with 33% potassium hydroxide, only salts of the alkylcoumarinic acid are formed, since carbon dioxide causes the precipitation of the 3-alkylcoumarin. When boiled for five hours with alcoholic sodium ethoxide, however, the 3-alkylcoumarins yield salts of the α-alkyl-*o*-coumaric acids, although more slowly than is the case with coumarin and its *Bz*-homologues.

*a-Methyl-*o*-coumaric acid*, $OH\cdot C_6H_4\cdot CH:CMe\cdot CO_2H$, m. p. 138° (decomp.), and *a-ethyl-*o*-coumaric acid*, m. p. 181° (decomp.), form yellow solutions in concentrated sulphuric acid, yield alkali salts which exhibit a yellowish-green fluorescence in solution (the alkali salts of *β*-alkyl-*o*-coumaric acids do not show fluorescence), and are not reconverted into the 3-alkylcoumarins very smoothly, in this respect resembling *o*-coumaric acid, but differing from *β*-alkyl-*o*-coumaric acids.

The replacement by methyl groups of hydrogen atoms in the benzene nucleus of coumarins does not affect greatly the behaviour of the resulting alkylcoumarins, except in so far as slight variations in the velocity of formation of the *o*-coumaric acids are concerned. It is very striking, therefore, that the introduction of hydroxy-, methoxy-, or dimethylamino-groups in the *Bz*-nucleus prevents completely the formation of the corresponding *o*-coumaric acids; thus 4-methylumbelliferone, its methyl ether, and 7-dimethylamino-4-methylcoumarin are only converted into the corresponding coumarinates even after prolonged boiling with alcoholic sodium ethoxide or concentrated aqueous potassium hydroxide. 7-Dimethylamino-4-methylcoumarin is decomposed completely by boiling for six hours with 40% potassium hydroxide, *m*-dimethylaminophenol being formed.

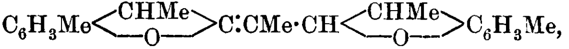
7-Methylcoumarin-4-acetic acid, $C_6H_3Me{<}\substack{C(CH_2\cdot CO_2H)\\ \overline{\quad O\cdot CO \quad}}{>}CH$, m. p. 190° (decomp.; thereby yielding 4:7-dimethylcoumarin), obtained together with its ethyl and *m*-tolyl esters by the interaction of *m*-cresol, ethyl acetonedicarboxylate, and concentrated sulphuric acid at 0°, does not behave like 4-methylcoumarin; with aqueous alkalis it does not form an *o*-coumarate, and with alcoholic sodium ethoxide a ketone is not produced, in both cases a coumarinate being formed which is easily reconverted into the coumarin by acids. The *ethyl ester*, $C_{14}H_{14}O_4$, m. p. 132°, behaves in a similar manner, being hydrolysed by aqueous alkalis and yielding a coumarinate with sodium ethoxide. The m-*tolyl* ester, $C_{19}H_{16}O_4$, m. p. 214°, however, behaves differently. By prolonged boiling with 20% potassium hydroxide, it is partly hydrolysed, partly unchanged, and partly converted into the following *o*-coumaric acid and a substance which yields 2:2:4:6-tetrabromo-3-keto-2:3-dihydrotoluene (Foster, Dissert., Marburg, 1898) by treatment with bromine. By treatment with alcoholic potassium ethoxide at 130—140° for fifteen hours, the *m*-tolyl ester yields, after acidifying the product, the m-*tolyl* ester of *a-acetic-4-methyl-*o*-coumaric acid*,

$$OH\cdot C_6H_3Me\cdot C(CH_2\cdot CO_2\cdot C_6H_4Me):CH\cdot CO_2H,$$

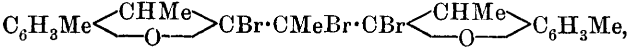
which sinters at 95°, melts and decomposes at about 100°, resolidifies at about 120°, and melts again at 214°, the m. p. of the corresponding coumarin. The acid is remarkably unstable, being converted into the coumarin by acids or organic solvents.

The following two ketones obtained from 4:6-dimethylcoumarin correspond in constitution with those prepared from 4:7-dimethylcoumarin (*loc. cit.*). By treatment with alcoholic potassium ethoxide at 160° for twenty-four hours and acidification of the product, 4:6-dimethylcoumarin yields 1-(2:4-*dimethylcoumaran*)-3-(4:6-*dimethyl-*

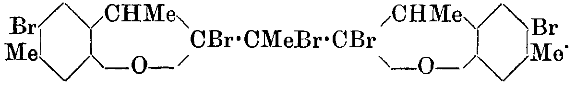
coumarin) *ketone* (3-[2 : 4-*dimethylhydrocoumarilyl*]-4 : 6-*dimethylcoumarin*), $C_{22}H_{20}O_4$, m. p. 275—280°, which is converted by boiling aqueous-alcoholic alkali into an intensely yellow solution, from which, by acidification, the ketone, $C_{21}H_{22}O_3$, m. p. 199°, already described (*loc. cit.*) is obtained. The ketone, $C_{21}H_{22}O_3$, is converted by ethereal magnesium methyl iodide in the usual way into the *compound*,



$C_6H_3Me\left<\begin{matrix}CHMe\\O\end{matrix}\right>C{:}CMe\cdot CH\left<\begin{matrix}CHMe\\O\end{matrix}\right>C_6H_3Me$, m. p. 164°, which reacts with bromine in glacial acetic acid to form the *substance*,



$C_6H_3Me\left<\begin{matrix}CHMe\\O\end{matrix}\right>CBr\cdot CMeBr\cdot CBr\left<\begin{matrix}CHMe\\O\end{matrix}\right>C_6H_3Me$, m. p. 200°. The corresponding compound, $C_{22}H_{24}O_2$, obtained from 4 : 7-dimethylcoumarin (*loc. cit.*), yields by bromination a *substance*, $C_{22}H_{21}O_2Br_5$, m. p. 225°, which has the annexed constitution :



C. S.

Method for the Preparation of Derivatives of α-Cyanoacrylic Acids.

C. H. Clarke and Francis Francis (*Ber.*, 1911, **44**, 273—276).—Instead of condensing aldehydes with cyanoacetic acid or its ester, the authors use substances which will form cyanoacetic acid, for example, potassium bromoacetate and potassium cyanide:

$$CH_2Br\cdot CO_2K + KCN + R\cdot CHO = R\cdot CH{:}C(CN)\cdot CO_2K + KBr + H_2O.$$

The best yields are obtained when the potassium salt of the bromoacetic acid is added to an aqueous solution of the cyanide and aldehyde. Potassium cyanide accelerates the reaction between aromatic aldehydes and salts of cyanoacetic acid, just as sodium ethoxide does (Carrick, Abstr., 1890, 1270; 1892, 1086). The following compounds have been prepared by this method: α-cyanocinnamic acid, α-cyano-β-anisylacrylic acid, α-cyano-β-styrylacrylic acid, α-cyano-β-piperonylacrylic acid, and α-cyano-β-furfurylacrylic acid.

Ethyl α-cyano-β-piperonylacrylate, $C_{13}H_{11}O_4N$, crystallises from alcohol in colourless plates, m. p. 104°. *α-Cyanoferulic acid*,

$$OMe\cdot C_6H_3(OH)\cdot CH{:}C(CN)\cdot CO_2H,$$

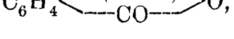
prepared from vanillin, potassium bromoacetate, and potassium cyanide, crystallises from dilute alcohol in pale yellow needles, m. p. 215°. The corresponding *ethyl* ester, $C_{13}H_{13}O_4N$, has m. p. 111°.

α-Cyano-o-coumaric acid, $OH\cdot C_6H_4\cdot CH{:}C(CN)\cdot CO_2H$, could not be obtained crystalline; its *benzoyl* derivative, $C_{17}H_{11}O_4N$, crystallises in needles, m. p. 210°. The acid is hydrolysed with great readiness to coumarinic acid.

J. J. S.

Isomeric Phenylphthalimides and Some Allied Compounds. II.

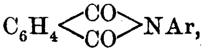
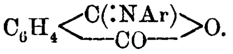
Mitsuru Kuhara and Shigeru Komatsu (*Mem. Coll. Sci. Eng. Kyōtō*, 1910, **2**, 365—386).—By the action of acetyl chloride on phenylphthalamic acid, the authors (Abstr., 1909, i, 484) have previously obtained two isomeric phenylphthalimides. Of these two isomerides, the colourless form was represented by the formula:



$$C_6H_4\left<\begin{matrix}C({:}NPh)\\CO\end{matrix}\right>O,$$

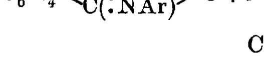
whilst the yellow variety was supposed to possess a peroxide structure.

The authors now consider that the colour of the yellow isomeride is due to the presence of the chromophoric group C:NPh, and have, therefore, assigned to this form the unsymmetrical formula given above. The constitution of the colourless isomeride remains undetermined.

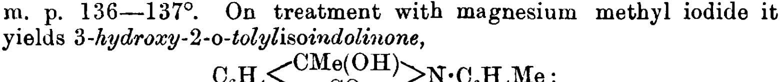
Two isomeric substituted phenylphthalimides, colourless and yellow, are also produced by the action of phthalyl chloride on *o*-toluidine, *p*-toluidine, *m*-4-xylidine, *o*-3-xylidine, *p*-xylidine, and *ψ*-cumidine. The colourless isomerides possess the symmetrical constitution :  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>NAr$, whilst the coloured varieties are represented by the unsymmetrical formula :  $C_6H_4<\genfrac{}{}{0pt}{}{C(:NAr)}{CO}>O$.

The colourless and yellow modifications of *p*-methoxyphenylphthalimide, *p*-ethoxyphenylphthalimide, and *p*-methoxyphenyl-Δ^1-dihydrophthalimide (Piuti and Abati, Abstr., 1903, i, 424) are considered by the authors to be structural isomerides, the yellow forms having an unsymmetrical, and the colourless varieties a symmetrical structure.

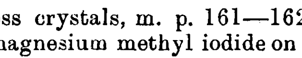
The formulæ assigned by Piutti (Abstr., 1908, i, 783) to the two modifications of *p*-hydroxyphenylmaleimide are to be interchanged.

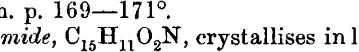
The behaviour of the isomeric arylphthalimides towards alkylmagnesium halides has also been investigated, and it is found that both isomerides yield the same 3-hydroxy-2-aryl-3-alkyl*iso*indolinone :  $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CR(OH)}>NAr$ (compare Sachs and Ludwig, Abstr., 1904, i, 266).

It is suggested that the latter compounds are formed from the *as*-arylphthalimides by a molecular arrangement according to the following scheme :



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{C(:NAr)}>O + RMgX + H_2O \rightarrow \left[C_6H_4<\genfrac{}{}{0pt}{}{CR(OH)}{C(:NAr)}>O\right] \rightarrow C_6H_4<\genfrac{}{}{0pt}{}{CR(OH)}{CO}>NAr.$$

as-o-*Tolylphthalimide*,  $CO<\genfrac{}{}{0pt}{}{O}{C_6H_4}>C:N\cdot C_6H_4Me$, obtained together with *s*-*o*-tolylphthalimide by the action of phthalyl chloride on *o*-toluidine in ethereal solution at − 10°, crystallises in canary-yellow needles, m. p. 136—137°. On treatment with magnesium methyl iodide it yields 3-*hydroxy*-2-o-*tolyl*iso*indolinone*,

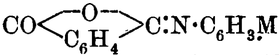


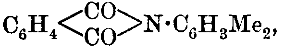
$$C_6H_4<\genfrac{}{}{0pt}{}{CMe(OH)}{CO}>N\cdot C_6H_4Me ;$$

the latter forms colourless crystals, m. p. 161—162°, and is also produced by the action of magnesium methyl iodide on *o*-tolylphthalimide. 3-*Hydroxy*-2-o-*tolyl*-3-*ethyl*iso*indolinone*, $C_{17}H_{17}O_2N$, crystallises in colourless plates, m. p. 169—171°.

as-p-*Tolylphthalimide*, $C_{15}H_{11}O_2N$, crystallises in light yellow needles, m. p. 109—110°, and is formed simultaneously with *s*-*p*-tolylphthalimide by the action of phthalyl chloride on *p*-toluidine ; with magnesium ethyl iodide, both these compounds yield 3-*hydroxy*-2-p-*tolyl*-3-

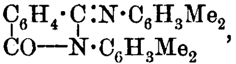
*ethyl*iso*indolinone*, $C_{17}H_{17}O_2N$, which crystallises in colourless needles, m. p. 177—178°.

as-m-4-*Xylylphthalimide*,  $CO\left\langle\begin{matrix}O\\C_6H_4\end{matrix}\right\rangle C{:}N\cdot C_6H_3Me_2$, yellow needles, m. p. 142—143°, m-4-*xylylphthalamide*, $C_6H_4(CO\cdot NH\cdot C_6H_3Me_2)_2$, silky needles, m. p. 202—203°, and s-m-4-*xylylphthalimide*,

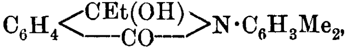


$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle N\cdot C_6H_3Me_2,$$

slender needles, m. p. 154°, are produced by the interaction of phthalyl chloride and *m*-4-xylidine in ethereal solution. The first-named substance is converted by mineral acids or alkali into *s*-*m*-4-xylyl phthalimide, which is readily obtained by heating *m*-4-xylidine with phthalic anhydride or phthalyl chloride.

Di-m-4-*xylylphthaldi-imide*,  $\begin{matrix}C_6H_4\cdot C{:}N\cdot C_6H_3Me_2\\ | \qquad\ \ | \\ CO—N\cdot C_6H_3Me_2\end{matrix}$, is produced, together with *s*-*m*-4-xylylphthalimide, by the interaction of phosphorus pentachloride and *m*-4-xylylphthalamide in chloroform solution; it forms yellow plates, m. p. 149—150°.

3-*Hydroxy*-2-m-4-*xylyl*-3-*ethyl*iso*indolinone*,



$$C_6H_4\left\langle\begin{matrix}CEt(OH)\\CO\end{matrix}\right\rangle N\cdot C_6H_3Me_2,$$

prepared from both *as*-*m*-4-xylylphthalimide and *s*-*m*-4-xylylphthalimide by the action of magnesium ethyl iodide, crystallises in colourless plates, m. p. 176—177°.

3-*Hydroxy*-2-m-4-*xylyl*-3-*methyl*iso*indolinone*, $C_{17}H_{17}O_2N$, has m. p. 161—162°; from methyl- and ethyl-alcoholic solutions it crystallises with one molecule of alcohol.

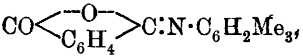
o-3-*Xylylphthalamide*, $C_{24}H_{24}O_2N$, slender needles, m. p. 192—193°, is obtained by the interaction of *o*-3-xylidine and phthalyl chloride in ethereal solution; small quantities of a yellow substance, consisting probably of as-o-3-*xylylphthalimide*, $C_{16}H_{13}O_2N$, and of s-o-3-*xylyl phthalimide*, $C_{16}H_{13}O_2N$, are produced simultaneously. The latter compound crystallises in colourless needles, m. p. 143—144°, and is readily obtained by heating *o*-3-xylidine with phthalic anhydride or phthalyl chloride.

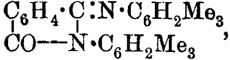
Di-o-3-*xylylphthaldi-imide*, $C_{24}H_{22}ON_2$, prepared by the action of phosphorus pentachloride on *o*-3-xylylphthalamide, crystallises from alcohol in yellow plates, m. p. 123—124°.

p-*Xylylphthalamide*, $C_{24}H_{24}O_2N_2$, silky needles, m. p. 209—210°, s-p-*xylylphthalimide*, $C_{16}H_{13}O_2N$, slender needles, m. p. 147—148°, and as-p-*xylylphthalimide*, $C_{16}H_{13}O_2N$, amber-coloured needles, m. p. 178—181°, are obtained by the action of *p*-xylidine on phthalyl chloride in ethereal solution at a low temperature. The last-named substance is unstable, and readily changes into *s*-*p*-xylylphthalimide, which is more easily obtained by heating *p*-xylidine with phthalic anhydride.

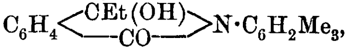
Di-p-*xylylphthaldi-imide*, $C_{24}H_{22}ON_2$, obtained from *p*-xylylphthalamide and phosphorus pentachloride, crystallises in yellow plates, m. p. 133—134°.

ψ-Cumylphthalamide, $C_6H_4(CO\cdot NH\cdot C_6H_2Me_3)_2$, silky needles, m. p.

210—212°, and *as-ψ-cumylphthalimide*,  $\mathrm{CO}{<}^{\mathrm{-O-}}_{\mathrm{C_6H_4}}{>}\mathrm{C{:}N\cdot C_6H_2Me_3}$, yellow needles, m. p. 117—118°, are obtained together with *s*-ψ-cumylphthalimide by the interaction of ψ-cumidine and phthalyl chloride.

Di-ψ-cumylphthaldi-imide,  $\begin{matrix}\mathrm{C_6H_4\cdot C{:}N\cdot C_6H_2Me_3}\\ | \qquad | \\ \mathrm{CO{-}{-}N\cdot C_6H_2Me_3}\end{matrix}$, is formed when ψ-cumylphthalamide is treated with phosphorus pentachloride in chloroform solution; it crystallises in yellow plates, m. p. 136—137°.

3-Hydroxy-2-ψ-cumyl-3-ethylisoindolinone,



$$\mathrm{C_6H_4}{<}^{\mathrm{CEt(OH)}}_{\mathrm{CO}}{>}\mathrm{N\cdot C_6H_2Me_3},$$

colourless plates, m. p. 152—153°, is obtained by the action of magnesium ethyl iodide on both forms of ψ-cumylphthalimide.

F. B.

Spectrometric Examination of Guthzeit's *cyclo*Butane Derivatives. ERICH HARTMANN (*J. pr. Chem.*, 1911, [ii], 83, 190—194).—The stereoisomerides, $C_{30}H_{44}O_{16}$, m. p. 103° and 88° respectively (Guthzeit, Weiss, and Schäfer, Abstr., 1909, i, 933), and the ester, $C_{30}H_{42}O_{16}$, m. p. 86° (Guthzeit and Hartmann, Abstr., 1910, i, 386), have been examined by the spectrograph. The first two esters give almost identical absorption spectra in alcoholic solution; also in the presence of sodium ethoxide (2 mols.) they give spectra identical, not only with each other, but also with that of ethyl sodiodicarboxyglutaconate; when the three solutions have been acidified, they show the spectrum of ethyl dicarboxyglutaconate. The ester, $C_{30}H_{42}O_{16}$, gives an absorption spectrum which is changed by the addition of sodium ethoxide (2 mols.), but is recovered by acidifying the alkaline alcoholic solution.

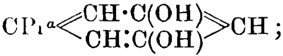
The results, which prove that the first two esters are depolymerised by the addition of sodium ethoxide, whilst the third merely forms a sodium derivative, are in complete harmony with the constitutions ascribed to the three substances (*loc. cit.*).

C. S.

Lichens, and their Characteristic Constituents. XII. OSWALD HESSE (*J. pr. Chem.*, 1911, [ii], 83, 22—96).—A scientific classification of the lichens must be based on a chemical examination of their characteristic constituents. The present paper is very largely a repetition of the author's work in this region during the last fifty years. The new work deals mainly with the divergencies of the author's results from those of other observers.

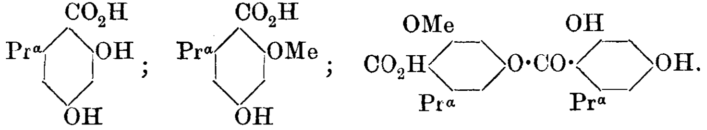
Usnic acid is not a constant constituent of *Evernia prunasti*, as claimed by Zopf (*Flechtenstoffe*, 1907, 356), since the author failed to detect it in several samples of the lichen obtained from different localities. The same statement is true of *Evernia divaricata*.

A large quantity of *E. illyrica*, collected on the Trnovaner Walde, near Görz, has been worked up in the usual way, and the divaricatic acid isolated. It has not the formula $C_{22}H_{26}O_7$, as stated previously, but $C_{21}H_{24}O_7$, which is in agreement with Zopf's analyses. Its decomposition by concentrated hydriodic acid yields methyl iodide, carbon dioxide, and divarinol, not orcinol, as erroneously stated elsewhere (*Biochemisches Handlexicon*, 7, 69). The *potassium, sodium, barium, calcium, copper*, and *silver* salts, the *methyl* and *ethyl* esters, and the *anhydride* are described. The acid, $C_{11}H_{14}O_4$, obtained by the author by boiling divaricatic acid with aqueous barium hydroxide (Abstr., 1898, i, 531), is identical with Zopf's divaricatinic acid, prepared by treating divaricatic acid with potassium hydroxide (Abstr., 1898, i, 489). The *barium* salt, *silver* salt, and *ethyl* ester, m. p. 41°, are described. By treating aqueous sodium divaricatate with an equivalent amount of aqueous ammonia, potassium hydroxide, or sodium hydroxide for forty-eight hours at the ordinary temperature, *divaric acid*, $C_{10}H_{12}O_4$, m. p. 169° (decomp.), is obtained, which in alcoholic solution reddens litmus and develops a purple-violet coloration with ferric chloride. It does not contain a methoxy-group, and is easily decomposed by boiling water, yielding carbon dioxide and divarinol. Pure hydrated divarinol, $C_9H_{12}O_2,H_2O$, has m. p. 44°, and loses its water completely in a desiccator at the ordinary temperature, forming a yellowish-red mass; its *diacetate* has m. p. 12—15°. Divarinol, which resembles orcinol in its behaviour, has the constitution



$\mathrm{CPr}^{\alpha}\begin{matrix}\diagup\mathrm{CH\cdot C(OH)}\diagdown\\ \diagdown\mathrm{CH{:}C(OH)}\diagup\end{matrix}\mathrm{CH}$

; the annexed formulæ are those of divaric acid, divaricatinic acid, and divaricatic acid respectively:



Various samples of *E. furfuracea* have been examined by the author, and found to contain atranorin and evernuric acid, but not farinaceaic acid, as stated by Rave (*Dissert.*, 1908).

Evernia furfuracea, var. *olivetorina* (*Pseudevernia olivetorina*), contains atranorin and olivetoric acid, the *potassium, barium*, and *calcium* salts of which are described. The decomposition of olivetoric acid by boiling aqueous barium hydroxide in the absence of air yields carbon dioxide and a substance, *olivetorol*, $C_{20}H_{26}O_5$, which develops a purple-violet coloration with ferric chloride, and a blood-red coloration with calcium hypochlorite; its further examination has been postponed owing to lack of material.

Since Zopf found *l*-usnic acid, destrictic acid, and a colourless crystalline substance in *Cladonia destricta* (Abstr., 1903, i, 762), whilst the author isolated *l*-usnic acid, squamatic acid, cladestin, and some coloured substances (Abstr., 1905, i, 138), the lichen has been again examined, with the result that *l*-usnic acid, cladestin, squamatic acid, destrictic acid, and two new acids, *destrictasic acid* and *cladestic acid*, have been isolated. Destrictasic acid, $C_{15}H_{24}O_2$, m. p. 202°, sintering at 175°, forms white leaflets from dilute alcohol; its alcoholic solution reddens litmus, but does not develop colorations with ferric chloride or calcium hypochlorite.

The following new facts are stated with respect to cladestin: its m. p. is 242—245°, not 252°, it crystallises anhydrous, and it does not yield ethyl iodide by treatment with hydriodic acid, although it is so changed that its alcoholic solution no longer gives a coloration with ferric chloride. Cladestic acid, $C_{50}H_{74}O_{12}$, is a flesh-coloured, amorphous powder, m. p. 82° (decomp.). It does not contain an alkyloxy-group, has a distinctly acid reaction in alcoholic solution, and develops an intense dark brown coloration with ferric chloride.

Cetraria stuppea contains dilichesteric acid, proto-α-lichesteric acid, and two new substances, called *cornicularin* and *stuppeaic acid.* Cornicularin, $C_{28}H_{44}O_5$, m. p. 230°, is crystalline, does not dissolve in potassium hydroxide or carbonate, and in alcoholic solution gives a dark brown coloration with ferric chloride. Stuppeaic acid, $C_{19}H_{26}O_4$, m. p. 222° (decomp.), is a crystalline powder, dissolves sparingly in the ordinary solvents, gives only a slight brown coloration with ferric chloride, and does not contain an alkyloxy-group. *Cetraria aculeata* contains, in addition to protolichesteric acid and proto-α-lichesteric acid, a new substance called *acanthellin*, $C_{18}H_{34}O_5$, m. p. 188°, which is apparently crystalline, sparingly soluble, and does not give a coloration with ferric chloride.

Stictaic acid, isolated from *Sticta pulmonaria,* probably has the composition $C_{19}H_{14}O_9$, rather than $C_{18}H_{14}O_9$, as stated previously. It is shown that conspersaic acid, isolated from *Parmelia conspersa,* is not identical with salazic acid, as suggested by Zopf (Abstr., 1905, i, 789).

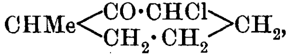
Urceolaria albissima is stated by Zopf (Abstr., 1897, i, 436) to contain zeorin and atranorin, in addition to the lecanoric acid discovered by the author (Abstr., 1899, i, 381), but a repetition of his experiments on 400 grams of the lichen has failed to disclose the presence of these two substances; in one sample, however, atranorin has been discovered. Zopf has stated (Abstr., 1906, i, 672) that the lecanoric acid obtained by the author from *Urceolaria scruposa* (Abstr., 1901, i, 595) is diploschistessic acid ; it is now shown that the latter is a mixture of lecanoric and patellaric acids. C. S.

o-Tolylacetaldehyde and its Derivatives. M. KRONIK (*Chem. Zentr.*, 1910, ii, 1051; from *Kosmos*, 1910, **35**, *Radziszewski-Festband,* 590—593).—*o-Tolylacetaldehyde,* $C_6H_4Me\cdot CH_2\cdot CHO$, is obtained by the dry distillation under reduced pressure of the barium salts of *o*-tolylacetic and formic acids; it forms an oily, yellow liquid, b. p. 219—221°/742 mm., b. p. 142—143°/90 mm., D_4^{18} 1·0241, and when diluted has an odour resembling that of jasmine. The *oxime* forms colourless needles, m. p. 99—100°. The *thiosemicarbazone* crystallises in rhombic plates. N. C.

The Carbonyl Group in the Nascent State. ALFRED W. STEWART (*J. pr. Chem.*, 1911, [ii], **83**, 194—197).—Reply to Petrenko-Kritschenko (Abstr., 1910, i, 177). C. S.

Halogenated Alicyclic Ketones. I. Monohalogenides of *cyclo*Hexanones. ARTHUR KÖTZ and H. STEINHORST (*Annalen*, 1911, **379**, 1—27).—The paper deals with the conditions for the direct introduction of one chlorine or bromine atom into *cyclo*hexanone and its homologues, with the orientation of the halogen atom, and with the influence exerted by one or more alkyl groups in the cyclic ketone on the position of the halogen. It is found that the halogen always enters the ring in the ortho-position to the keto-group, and in the meta- or para-position to a methyl group, when such is present, except in the case of carvomenthone.

The halogenation of the cyclic ketones is effected by Kötz and Götz's process (Abstr., 1908, i, 173), by the action of chlorine, or of bromine vapour mixed with air, in the presence of calcium carbonate and water. The halogenated ketones are deprived of the elements of the hydrogen halogenide by ethereal aniline, and are converted by aqueous potassium carbonate into the corresponding hydroxy-compound, from which the elements of water are removed by anhydrous oxalic acid at 110°; the same *cyclo*hexenone is always obtained by the two processes. Thus *cyclo*hexanone itself has already been shown to yield 2-chloro-(or bromo-)*cyclo*hexanone (Kötz and Götz, *loc. cit.*). 1-Methyl*cyclo*hexan-2-one yields 3-*chloro*-1-*methyl*cyclo*hexan*-2-*one*,



$$\mathrm{CHMe}<\begin{matrix}\mathrm{CO\cdot CHCl}\\ \mathrm{CH_2\cdot CH_2}\end{matrix}>\mathrm{CH_2},$$

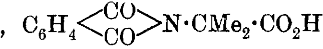
b. p. 98—100°/15 mm., and 3-*bromo*-1-*methyl*cyclo*hexanone*, b. p. 105—107°/12 mm.; the former is converted into 3-*hydroxy*-1-*methyl*-cyclo*hexan*-2-*one*, b. p. 85—87°/13 mm., from which, and also from the bromo-compound, 1-*methyl*-Δ^3-cyclo*hexen*-2-*one*, b. p. 172—173° (*semicarbazone*, m. p. 177—178°), is obtained. 1-Methyl*cyclo*hexan-3-one yields 4-*chloro*-1-*methyl*cyclo*hexan*-2-*one*, m. p. 61—62°, and 4-*bromo*-1-*methyl*cyclo*hexan*-3-*one*, m. p. 83—84°; 4-*hydroxy*-1-*methyl*cyclo*hexan*-3-*one* has b. p. 88—90°/14 mm., and 1-*methyl*-Δ^3-cyclo*hexen*-3-*one*, b. p. 188—190°, forms a *semicarbazone*, m. p. 159—160°. 1-Methyl*cyclo*hexan-4-one yields 3-*chloro*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 99—101°/14 mm., from which 3-*hydroxy*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 90—92°/14 mm., is obtained; the latter is oxidised to β-methyladipic acid, and yields with anhydrous oxalic acid, 1-*methyl*-Δ^2-cyclo*hexen*-4-*one*, b. p. 175—176° (*semicarbazone*, m. p. 184—185°), which is also obtained from 3-*bromo*-1-*methyl*cyclo*hexan*-4-*one*, b. p. 112—113°/14 mm.

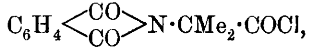
Menthone yields 4-*bromomenthane*-3-*one*, b. p. 120—122°/16 mm., and 4-*chloromenthane*-3-*one*, b. p. 115—117°/15 mm., from which Wallach's Δ^4-menthene-3-one is obtained; an ethereal solution of the last yields with hydrogen chloride, 5-*chloromenthane*-3-*one*, m. p. 135—136°. Carvomenthone yields 1-*chloromenthane*-2-*one*, b. p. 130—132°/14 mm., and 1-*bromomenthane*-2-*one*, b. p. 138—140°/14 mm.; 1-*hydroxymenthane*-2-*one* has b. p. 128—130°/14 mm. The constitutions of the last two compounds are determined by their conversion into carvotanacetone. C. S.

Tetrahydroxybenzenes. GIUSEPPE BARGELLINI and LEDA BINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 595—600).—The preparation is described of some derivatives of 1 : 2 : 3 : 5-tetrahydroxybenzene including 2 : 3 : 4 : 6-tetramethoxyacetophenone, the corresponding tetramethoxychalkone, and 4 : 2′ : 3′ : 4′ : 6′-pentamethoxychalkone.

When 1 : 2 : 3 : 5-tetramethoxybenzene is treated with acetyl chloride in presence of aluminium chloride in carbon disulphide solution, a mixture of the dimethyl (in small quantity), trimethyl, and tetramethyl ethers of 2:3:4:6-tetrahydroxyacetophenone is produced. The first two are soluble in sodium hydroxide; they can be precipitated from it by addition of acid, and separated with the aid of solvents. 2:3:4:6-*Tetrahydroxyacetophenone dimethyl ether*, $C_{10}H_{12}O_5$, is a bright yellow, crystalline powder, m. p. 162—163°. It dissolves in concentrated sulphuric acid with production of an orange-yellow coloration, which on addition of nitric acid becomes intensely red. Its *acetyl* derivative has m. p. 110—112°. 2 : 3 : 4 : 6-*Tetrahydroxyacetophenone trimethyl ether*, $C_{11}H_{14}O_5$, forms slightly yellow, prismatic crystals, m. p. 105—107°, and dissolves in concentrated sulphuric acid, giving a yellow coloration which becomes red on addition of nitric acid. Its *acetyl* derivative, $C_{13}H_{16}O_6$, crystallises in small, colourless needles, m. p. 106°. The *benzoyl* derivative has m. p. 120—122°. 2 : 3 : 4 : 6 *Tetrahydroxyacetophenone tetramethyl ether*, $C_{12}H_{16}O_5$, has m. p. 43—45°, b. p. about 310°, and gives a yellow solution in concentrated sulphuric acid, which becomes intensely red when treated with nitric acid. Its *semicarbazone*, $C_{13}H_{19}O_5N_3$, forms small, colourless needles, m. p. 128—130°. 2′ : 3′ : 4′ : 6′-*Tetramethoxychalkone* (from benzaldehyde) crystallises in tufts of small, very pale yellow needles, m. p. 74—75° (softening at 70°). It dissolves in concentrated sulphuric acid with production of an orange-red coloration. 4 : 2′ : 3′ : 4′ : 6′-*Pentamethoxychalkone*, $C_{20}H_{22}O_6$ (from anisaldehyde), forms small, straw-yellow needles, m. p. 88—90° (previously softening), and dissolves in concentrated sulphuric acid with production of an orange-red coloration.

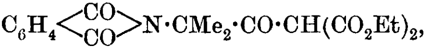
R. V. S.

α-Amino-ketones. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 57—69).—A description is given of the preparation of some α-amino-ketones of the type $X\cdot CO\cdot CR_2\cdot NH_2$, hitherto unknown. *α-Phthalimino*iso*butyric acid*,  $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N\cdot CMe_2\cdot CO_2H$, m. p. 153—154°, obtained from α-amino*iso*butyric acid and phthalic anhydride at 180°, is converted by phosphorus pentachloride into the *chloride*,



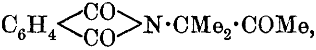
$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N\cdot CMe_2\cdot COCl,$$

m. p. 82—84°. By treatment with benzene and aluminium chloride, and subsequently with cold dilute hydrochloric acid, the chloride is converted into *α-phthalimino*iso*butyrophenone*, m. p. 122—123·5°, which on hydrolysis by hot 10% potassium hydroxide and subsequent treatment with hydrochloric acid yields *α-amino*iso*butyrophenone hydrochloride*, $COPh\cdot CMe_2\cdot NH_2,HCl,\frac{1}{2}H_2O$, sintering at about 137°; the anhydrous salt has m. p. 187—188°; the *picrate*, m. p. 175°. Unlike other α-amino-ketones, the salt of this new amino-ketone does not reduce Fehling's solution. *α-Amino*iso*butyrophenone*, liberated from the hydrochloride by strong potassium hydroxide, has b. p. 254—255°/752 mm., and is the first α-amino-ketone that has been isolated in the pure state, others suffering condensation and oxidation to substituted pyrazines (Abstr., 1908, i, 464).

A suspension of ethyl sodiomalonate in benzene is treated with a benzene solution of α-phthalimino*iso*butyryl chloride, and the yellow solution obtained is boiled for eighteen hours, neutralised by a little hydrochloric acid, and distilled with steam; the yellow residue is extracted with ether (the insoluble yellow, crystalline powder is described in the following abstract), the ethereal filtrate, after being shaken with aqueous sodium carbonate, is evaporated, and the residue is dissolved in lukewarm amyl alcohol, the solution being kept for six hours at the ordinary temperature, whereby *ethyl α-phthalimino*iso*butyrylmalonate*,  $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CMe_2\cdot CO\cdot CH(CO_2Et)_2$, m. p. 76—77·5°, is obtained. When boiled with hydriodic acid, b. p. 127°, for half an hour, the ester is decomposed into phthalic acid, carbon dioxide, ethyl iodide, and *methyl β-amino*iso*propyl ketone hydriodide*,

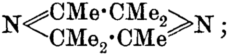
$$CH_3\cdot CO\cdot CMe_2\cdot NH_2,HI,$$

m. p. 169—170°. The *nitrate*, m. p. 132—133·5°, *hydrochloride*, m. p. 210—211°, *platinichloride*, m. p. 201° (decomp.), *aurichloride*, m. p. 165°, giving turbid liquid clarifying at 190°, *picrate*, m. p. 142—143·5°, *benzoyl* derivative, m. p. 124—125°, and *phthalyl* compound,



$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot CMe_2\cdot COMe,$$

m. p. 105—106°, are described. The aqueous solutions of the salts of this α-amino-ketone do not reduce Fehling's solution. Unlike α-amino-*iso*butyrophenone, however, this amino-ketone cannot be isolated in a pure state. When an aqueous solution of its hydriodide is treated with an equivalent amount of *N*-sodium hydroxide, a certain amount of the amino-ketone is obtained together with a crystalline substance with an odour of menthol. The latter is obtained better by shaking the solid hydriodide with an excess of 33% potassium hydroxide; it has m. p. 88—89°, and is the hexahydrate of a *base*, $C_{10}H_{18}N_2$, b. p. 180—881°, m. p. 69—69·5°, which volatilises very readily and appears to be 2 : 3 : 3 : 5 : 6 : 6-*hexamethyl*-3 : 6-*dihydropyrazine*,



$$N<\begin{matrix}CMe\cdot CMe_2\\CMe_2\cdot CMe\end{matrix}>N;$$

its *hydrochloride*, *picrate*, m. p. 232° (decomp.), *platinichloride*, and *aurichloride*, decomp. 180°, are described. By reducing the base with sodium and alcohol, and treating the product with hydrochloric acid and potassium nitrite, *dinitrosohexamethylpiperazine*, $C_{10}H_{20}O_2N_4$, m. p. 248—249° (decomp.), is obtained, which is converted by boiling hydrochloric and a little acetic acids into *hexamethylpiperazine hydrochloride*, $C_{10}H_{22}N_2,2HCl$, from which the hydrated *base*, $C_{10}H_{22}N_2,2H_2O$, m. p. 65—66·5°, is obtained by the action of concentrated potassium hydroxide; the *nitrate*, *platinichloride*, *aurichloride*, *picrate*, decomp. 260°, and *mercurichloride* are mentioned. A by-product of the action of very concentrated potassium hydroxide on methyl β-amino*iso*propyl ketone hydriodide is a basic *substance*, $C_{10}H_{18}N_2$, which forms a *hydrochloride*, $C_{10}H_{18}N_2,2HCl,2H_2O$, m. p. about 171—172°, *platinichloride*, $C_{10}H_{18}N_2,H_2PtCl_6$, *benzoyl* derivative, $C_{10}H_{17}N_2Bz$, m. p. 105°, *picrate*, m. p. 198°, and *aurichloride*. Its constitution has not yet been ascertained; probably it is an aminopyrrole or pyridine derivative.

C. S.

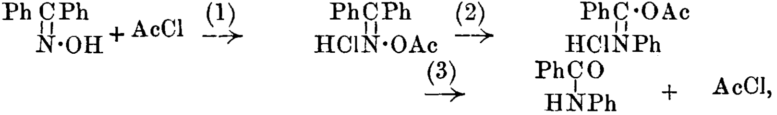
The Beckmann Rearrangement. II. Mitsuru Kuhara and Yoshinori Todo (*Mem. Coll. Sci. Eng. Kyōto*, 1910, 2, 387—396).—The influence of acetyl chloride, chloroacetyl chloride, and benzenesulphonyl chloride on the rate of rearrangement of diphenylketoxime has been determined by heating a chloroform solution of the acid chloride and the oxime in molecular proportions at 60°, and weighing the benzanilide produced.

In $\frac{1}{2}$-molar solutions, diphenylketoxime is almost completely transformed into benzanilide by benzenesulphonyl chloride in five minutes, whilst with chloroacetyl chloride, 61% undergoes change in the same time ; in the case of acetyl chloride the rate of rearrangement is much slower, only 9·4% of the oxime being transformed in fifteen minutes.

The rates of rearrangement thus stand in the order of magnitude of the dissociation constants of the acids, and the conclusion is therefore drawn that the velocity of transformation of the oxime esters, $CPh_2{:}N{\cdot}O{\cdot}CO{\cdot}R$, is dependent on the negative character of the acid residue $R{\cdot}CO{\cdot}O$.

Measurements of the velocity of rearrangement of acetyldiphenylketoxime in the presence of hydrochloric acid, and of diphenylketoxime in the presence of acetyl chloride, both in $\frac{1}{2}$-molar chloroform solutions, indicate that these reactions are unimolecular.

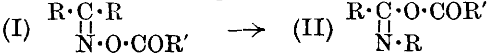
With respect to the mechanism of the rearrangement, the authors propose the following scheme:



$$\underset{\text{N·OH}}{\overset{\text{PhCPh}}{\|}} + \text{AcCl} \xrightarrow{(1)} \underset{\text{HClN·OAc}}{\overset{\text{PhCPh}}{\|}} \xrightarrow{(2)} \underset{\text{HClNPh}}{\overset{\text{PhC·OAc}}{\|}} \xrightarrow{(3)} \underset{\text{HNPh}}{\overset{\text{PhCO}}{|}} + \text{AcCl},$$

in which the changes (1) and (3) take place rapidly, whilst the reaction (2) occurs slowly, thus accounting for the transformation being, apparently, of the unimolecular type.

According to the authors, the primary cause of the change :

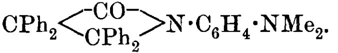


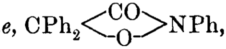
$$\text{(I)}\ \underset{\text{N·O·COR}'}{\overset{\text{R·C·R}}{\|}} \longrightarrow \text{(II)}\ \underset{\text{N·R}}{\overset{\text{R·C·O·COR}'}{\|}}$$

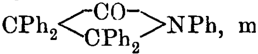
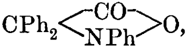
is the negative character of the acid residue $R'CO{\cdot}O$; with strongly negative residues, dissociation of (I) into $R_2C{:}N-$ and $R'CO{\cdot}O$ readily takes place, and these dissociation products then react to form (II).

It has been shown (Kuhara and Kainosho, Abstr., 1907, i, 1027) that the presence of hydrochloric acid is necessary for the rearrangement of acetyldiphenylketoxime, and the authors therefore draw the conclusion that in the case of the oxime-acetates, hydrochlorides of the type $CR_2{:}N{\cdot}OAc,HCl$ are produced ; under the influence of the hydrochloric acid, the tendency of the OAc group to separate from the nitrogen atom is increased to such an extent that a similar dissociation to that mentioned above takes place.

A *compound* of the constitution $OAc{\cdot}CPh{:}NPh$ has been obtained as a viscid, yellow oil by the interaction of the imide-chloride, $CPhCl{:}NPh$, and silver acetate. On passing hydrochloric acid into its cold ethereal solution, the *hydrochloride* separates out as a canary-yellow precipitate, which is converted by excess of the acid into acetylbenzanilide. When the hydrochloride in chloroform solution is heated above 60°, it yields benzanilide. This change corresponds with the last phase of the rearrangement in the authors scheme given above. F. B.

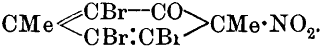
Ketens. XV. Action of Diphenylketen on Nitroso-compounds. HERMANN STAUDINGER and SERGIUS JELAGIN (*Ber.*, 1911, **44**, 365—374. Compare Abstr., 1910, i, 46).—By the action of nitrosodimethylaniline in ethereal solution in 2 mols. of diphenylketen, carbon dioxide is liberated, the green colour at once vanishes, and the Schiff's base first formed combines with diphenylketen to form a *β-lactam* of *β-dimethylaminoanilino-ααββ-tetraphenylpropionic acid*,  $\mathrm{CPh_2}<\begin{array}{c}\mathrm{CO}\\\mathrm{CPh_2}\end{array}>\mathrm{N{\cdot}C_6H_4{\cdot}NMe_2}$. This forms colourless crystals, which sinter at 196°, m. p. above 200° (decomp. to an orange-red liquid). The composition of this lactam was proved by its synthesis from diphenylketen and benzophenone-*p*-dimethylaminoanil.

Nitrosobenzene reacts differently with diphenylketen, forming *anhydrodiphenylglycollylphenylhydroxylamine*,  $\mathrm{CPh_2}<\begin{array}{c}\mathrm{CO}\\\mathrm{O}\end{array}>\mathrm{NPh}$, which separates in well formed, colourless crystals, m. p. 72·5°. It is stable at the melting point, but, on further heating, decomposes explosively into benzophenone and phenylcarbimide. When boiled with concentrated hydrochloric acid, *chlorodiphenylacetophenylhydroxylamine*, $\mathrm{CPh_2Cl{\cdot}CO{\cdot}NPh{\cdot}OH}$, colourless crystals, m. p. 158·5—159·5°, is formed. The four-membered ring-compound is obtained synthetically by the action of chlorodiphenylacetyl chloride on phenylhydroxylamine.

Nitrosobenzene and 2 mols. of diphenylketen also react to form small quantities of the *β-lactam* of *β-anilino-ααββ-tetraphenylpropionic acid*,  $\mathrm{CPh_2}<\begin{array}{c}\mathrm{CO}\\\mathrm{CPh_2}\end{array}>\mathrm{NPh}$, m. p. 191°, which is also formed on condensing benzophenoneanil with diphenylketen. The four-membered ring,  $\mathrm{CPh_2}<\begin{array}{c}\mathrm{CO}\\\mathrm{NPh}\end{array}>\mathrm{O}$, is possibly formed in small quantity during the action of nitrosobenzene on diphenylketen, but decomposes in the cold into benzophenoneanil and carbon dioxide.

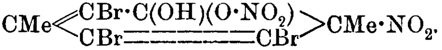
Diphenyl- and dimethyl-nitrosoamines do not react with diphenylketen. E. F. A.

Action of Nitric Acid on Halogen Derivatives of *o*-Alkylated Phenols. II. THEODOR ZINCKE and W. BREITWEISER (*Ber.*, 1911, **44**, 176—184).—The products formed by the action of nitric acid on tribromo-*p*-xylenol are similar to those obtained previously from tetrabromo-*o*-cresol (Abstr., 1907, i, 322). They are three in number, namely: (*a*) 3 : 5 : 6-tribromo-1 : 4-dimethylquinonitrole,



$$\mathrm{CMe}<\begin{array}{c}\mathrm{CBr{-}CO}\\\mathrm{CBr{:}CBr}\end{array}>\mathrm{CMe{\cdot}NO_2}.$$

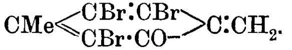
(*b*) An additive compound of the quinonitrole with nitric acid,



$$\mathrm{CMe}<\begin{array}{c}\mathrm{CBr{\cdot}C(OH)(O{\cdot}NO_2)}\\\mathrm{CBr{=\!=\!=}CBr}\end{array}>\mathrm{CMe{\cdot}NO_2}.$$

(*c*) An open-chain compound, $\mathrm{NO_2{\cdot}CHMe{\cdot}CBr{:}CBr{\cdot}CMe{:}CBr{\cdot}CO{\cdot}ONO_2}$, which can also be obtained by the action of sodium carbonate solution on the additive compound.

The quinonitrole is identical with the product described by Auwers (Abstr., 1899, i, 30), but is regarded as an ortho- and not a para-derivative, since the quinole obtained by the action of cold benzene on the nitro-compound does not lose hydrogen bromide and form dibromo-*p*-xyloquinone, and does not yield a *p*-xyloquinone derivative when heated with sodium acetate and acetic anhydride, but loses nitrous acid extremely readily under the influence of moist ether, yielding 3 : 5 : 6-tribromo-4-methyl-*o*-methylenequinone,



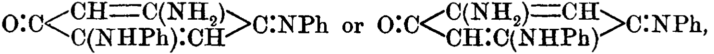
$$CMe{<}\genfrac{}{}{0pt}{}{CBr{:}CBr}{CBr{\cdot}CO{-}}{>}C{:}CH_2.$$

The conversion of the quinonitrole into dibromo-*p*-xyloquinone by boiling with benzene or light petroleum, and of the quinole into dibromo-*p*-xyloquinone by warming with acetic anhydride and concentrated sulphuric acid is accompanied by molecular rearrangements.

3 : 4 : 6-Tribromo-1 : 4-dimethylquinonitrole is most readily prepared by the action of concentrated nitric acid on tribromo-*p*-xylenol in the presence of glacial acetic acid. It reacts with cold methyl alcohol, yielding 3 : 6-*dibromo*-5-*nitro*-p-2-*xylenol*, $NO_2{\cdot}C_6Me_2Br_2{\cdot}OH$, as colourless needles, m. p. 154°, together with a product, m. p. 186—190°, insoluble in alkalis, and with acetic anhydride and a few drops of concentrated sulphuric acid yields *dibromo*-p-*xyloquinol diacetate* in the form of yellowish-white needles, m. p. 218°. 3 : 5 : 6-*Tribromo*-1 : 4-*dimethylquinol*, $C_8H_7O_2Br_3$, crystallises from light petroleum in colourless needles, m. p. 111°.

3 : 5 : 6-*Tribromo*-4-*methyl*-o-*methylenequinone*, $C_8H_5OBr_3$, crystallises from acetic anhydride in yellow plates, m. p. 220—230° (decomp.), and is not chemically active. The *acetyl* derivative of 3 : 6-dibromo-5-nitro-*p*-2-xylenol crystallises in colourless, glistening prisms, m. p. 116°, and 3 : 6-*dibromo*-4-*amino*-p-2-*xylenol* crystallises from benzene in colourless plates, m. p. 186—188°. The additive *compound* of the quinonitrole with nitric acid, $C_8H_7O_6N_2Br_3$, crystallises in colourless, well-developed prisms, m. p. 105—107° (decomp.). The open-chain *compound*, $C_8H_7O_6N_2Br_3$, crystallises in colourless needles, m. p. 141° (decomp.). J. J. S.

Oxidation of Aniline. II. Rikō Majima (*Ber.*, 1911, **44**, 229—234. Compare Willstätter and Majima, Abstr., 1910, i, 748).—By the oxidation of aniline with sodium bromate in aqueous acetic acid solution at 0°, a mixture of 2 : 5-dianilino-*p*-benzoquinoneanil and *amino-anilino*-p-*benzoquinoneanil*,



$$O{:}C{<}\genfrac{}{}{0pt}{}{CH{=}C(NH_2)}{C(NHPh){:}CH}{>}C{:}NPh \text{ or } O{:}C{<}\genfrac{}{}{0pt}{}{C(NH_2){=}CH}{CH{:}C(NHPh)}{>}C{:}NPh,$$

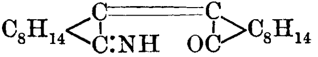
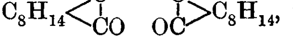
is produced. The latter compound, isolated by means of its sparingly soluble *sulphate*, crystallises in bluish-red prisms. It dissolves in concentrated sulphuric acid with a green colour, has feebly basic properties, and yields 2 : 5-dianilino-*p*-benzoquinoneanil when heated with aniline in glacial acetic acid solution. The *hydrochloride*, $C_{18}H_{15}ON_3,HCl$, forms dark green crystals.

2 : 5-Dianilino-*p*-benzoquinoneimine (Willstätter and Majima, *loc. cit.*) is more conveniently prepared by oxidising aniline with sodium persulphate. When hydrolysed with hydrochloric acid in aqueous alcoholic solution, it yields 2 : 5-dianilino-*p*-benzoquinone. F. B.

Synthesis of β-Menthol-lactoside and its Behaviour in the Organism. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1911, **70**, 256—263. Compare E. and H. Fischer, Abstr., 1910, i, 716).—*Hepta-acetyl-β-menthol-lactoside*, prepared by the interaction of acetobromolactose and menthol in presence of silver carbonate and chloroform, crystallises in long prisms, m. p. 125—130°, $[\alpha]_D^{19}$ $-29\cdot65^\circ$ ($\pm 0\cdot2$). It resists hydrolysis by dilute mineral acids; barium hydroxide converts it into *β-menthol-lactoside*. This crystallises with $4H_2O$ in concentrically-grouped prismatic needles, m. p. 110°, $[\alpha]_D^{16}$ $-38\cdot04^\circ$. It is hydrolysed by mineral acids to menthol and reducing sugar, and by emulsin to menthol, lactose, and some dextrose. Kephir lactose hydrolyses it slowly.

When injected subcutaneously into the organism, it is excreted unchanged; neither mentholglycuronic acid nor menthol-lacturonic acid are formed.

Mentholglycuronic acid ($1\frac{1}{2}H_2O$) sinters at 92°, m. p. 110°, and has $[\alpha]_D^{20}$ $-104\cdot4^\circ$. E. F. A.

Some Derivatives of Dicamphor. VINCENZO CASTELLANA and R. FERRERO (*Gazzetta*, 1910, **40**, ii, 482—491. Compare Angeli, Castellana, and Ferrero, Abstr., 1909, i, 739).—When pernitrosodicamphor is boiled with an excess of alcoholic potassium hydroxide, the *potassium* salt separates as a precipitate. If water is added to dissolve this, the boiling continued for an hour, and then the alcohol removed by distillation, *dicamphenoneimine* remains as an oil, which on cooling solidifies and after recrystallisation forms needles, m. p. 191°. If the ebullition is prolonged for several hours, an amorphous, grey powder having the properties of an *acid* is obtained on acidifying the wash water of the preceding compound. To the imine the structure  $C_8H_{14}\left<\begin{matrix}C=\!=\!=\!=\!=C\\ | \qquad\quad |\\ C{:}NH \quad OC\end{matrix}\right>C_8H_{14}$ is ascribed. It forms a *picrate*, $C_{20}H_{29}ON,C_6H_2(NO_2)_3OH$, m. p. 195°. When warmed with dilute sulphuric acid, the imine yields the corresponding diketone, *dicamphenone*,  $C_8H_{14}\left<\begin{matrix}C=\!=\!=C\\ | \qquad |\\ CO \quad OC\end{matrix}\right>C_8H_{14}$, which crystallises in lemon-yellow needles, m. p. 192—193°, and is identical with the dicamphanehexanedione of Oddo (Abstr., 1897, i, 577). With hydrazine, it yields the azine, as stated by that author, and at the same time a small quantity of a yellow *substance*, m. p. 153°, is formed. The same azine is obtained from hydrazine and pernitrosodicamphor. Its *picrate*, $C_{20}H_{28}N_2,C_6H_3O_7N_3$, has m. p. 220°.

Pernitrosodicamphor when treated with an excess of hydroxylamine yields two products which can be separated with the aid of solvents, and are apparently stereoisomeric *dioximes*, $C_{20}H_{32}O_2N_2$. One is crystalline, and has m. p. about 240° (decomp.); the other is formed in very small amount, and has m. p. about 275—280°.

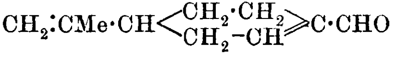
The authors have also prepared pernitrosocamphor and some of its derivatives from inactive camphor, and find them to have similar properties, but somewhat lower melting points: *pernitroso*-i-*camphor* has m. p. 32°; *pernitrosodi*-i-*camphor*, m. p. 163°; i-*dicamphenoneimine*, m. p. 179°. R. V. S.

Behaviour of Iodine towards Terpine Hydrate, Eucalyptol, and Terpineol. CARLO CASANOVA (*Boll. chim. farm.*, 1910, **49**, 957—960. Compare Abstr., 1909, i, 813).—The above terpenes react with iodine on warming, and the liquid compounds produced are heavier than water and give no reaction with starch. They readily decompose in the course of a few hours if exposed to light and air, large quantities of iodine and hydrogen iodide being set free.

R. V. S.

Constituents of Ethereal Oils. Constitution of Perillaldehyde, $C_{10}H_{14}O$. FRIEDRICH W. SEMMLER and B. ZAAR (*Ber.*, 1911, **44**, 52—57).—The aldehyde isolated from *Perilla nankinensis* leaf oil, and described by Schimmel & Co. (Abstr., 1910, i, 758), has been isolated and examined by the authors. In addition to the properties already recorded (*loc. cit.*), the aldehyde, which is called perillaldehyde, shows the following behaviour. The *semicarbazone* has m. p. 199—200°. By reduction with zinc dust and glacial acetic acid on the water-bath, the aldehyde yields perillyl alcohol in the form of its *acetate*, $C_{12}H_{18}O_2$, b. p. 123—126°/13 mm., D^{20} 0·9785, n_D 1·48142, $[\alpha]_D$ $-48°$; the *alcohol*, $C_{10}H_{16}O$, obtained by hydrolysing the ester by alcoholic potassium hydroxide, has b. p. 119—121°/11 mm., D^{20} 0·9640, n_D 1·49964, $[\alpha]_D$ $-68·5°$, and is converted by phosphorus pentachloride in petroleum solution into the *chloride*, $C_{10}H_{15}Cl$, b. p. 99—101°/12 mm., D^{20} 0·9861, n_D 1·49728, $[\alpha]_D$ $-60°$. By treatment with sodium and alcohol, the chloride is converted into *l*-limonene.

Perillaldoxime is changed by boiling acetic anhydride and sodium acetate into *perillonitrile*, $C_{10}H_{13}N$, b. p. 116—118°/11 mm., D^{20} 0·9439, n_D 1·49775, $[\alpha]_D$ $-115°$, which by hydrolysis yields *perillic acid*, $C_{10}H_{14}O_2$, b. p. 164—165°/10 mm., m. p. 130—131°, $[\alpha]_D$ $-20°$ in 25% alcoholic solution. The acid forms a *dibromide*, $C_{10}H_{14}O_2Br_2$, m. p. 166—167°, and is reduced by sodium and boiling amyl alcohol to *dihydroperillic acid*, $C_{10}H_{16}O_2$, b. p. 152—153°/10·5 mm., m. p. 107—109°, $[\alpha]_D$ 0° in 25% alcoholic solution, which forms a *dibromide*, m. p. 116—117°, and a *methyl* ester (from the silver salt and methyl iodide), b. p. 105—106°/11 mm., D^{18} 0·9732, n_D 1·46768, $[\alpha]_D$ 0°, from which *dihydroperillyl alcohol*, $C_{10}H_{18}O$, b. p. 114—115°/10 mm., D^{19} 0·9284, n_D 1·48191, $[\alpha]_D$ 0°, is obtained by the action of sodium in the usual way.

The formation of the preceding derivatives, particularly of *l*-limonene, and the fact that the molecular refraction of perillaldehyde indicates the presence of two ethylenic lingings, afford good evidence of the constitution  $CH_2{:}CMe{\cdot}CH\left<\begin{matrix}CH_2{\cdot}CH_2\\ CH_2{-}CH\end{matrix}\right>C{\cdot}CHO$ for the aldehyde.

C. S.

Curcumin. C. LORING JACKSON and LATHAM CLARKE (*Amer. Chem. J.*, 1911, **45**, 48—58).—Miłobędzka, Kostanecki, and Lampe's statement (Abstr., 1910, i, 629) that curcumin should be represented by the formula $C_{21}H_{20}O_6$, first proposed by Ciamician and Silber (Abstr., 1897, i, 229), instead of $C_{14}H_{14}O_4$, as suggested by Jackson and Menke (*Amer. Chem. J.*, 1884, **4**, 77), is confirmed. Curcumin has m. p. 178°, as found by Jackson and Menke, and not 183°, as stated by Ciamician and Silber. Curcumin dimethyl ether has m. p. 137°, instead of 135°, as recorded by Ciamician and Silber, and can be obtained in a quantitative yield by using a shaking machine instead of applying heat.

The brown coloration produced by the action of hydrogen chloride on curcumin is due to the formation of an additive *compound*, which is dark brown when only a little hydrogen chloride is used, but becomes dark violet when an excess is employed; it is very unstable, and is instantly decomposed by water. A similar *compound*,

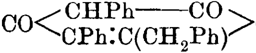
$$C_{21}H_{20}O_6,3HBr,$$

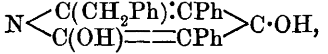
is formed by the action of hydrogen bromide. The reddish-purple substance formed by the action of phosphoryl chloride on curcumin (Jackson and Menke, *loc. cit.*) is probably either the hydrogen chloride additive compound or a similar product containing chlorine and phosphorus, since it is reconverted into curcumin by the action of water. This substance, if left in a desiccator, becomes black, owing to the further action of the phosphoryl chloride.

When an alcoholic solution of curcumin is shaken for a long time with hydroxylamine hydrochloride, a *compound*, m. p. 162°, probably the mono-oxime, is produced, which forms stout, orange-yellow needles. If the mixture is heated on the steam-bath instead of being shaken at the ordinary temperature, a yellowish-white compound, m. p. 163°, is obtained, which is probably identical with the foregoing, although of a different colour. This substance is not identical with the *iso*oxazole described by Ciamician and Silber (*loc. cit.*). E. G.

Pyronone Synthesis by means of the "Tertiary Bases Reaction." II.

Edgar Wedekind [and **Johannes Häussermann**, **W. Weisswange**, and **Moriz Miller**] (*Annalen*, 1911, **378**, 261—292).—The "tertiary bases reaction" (Wedekind and Häussermann, Abstr., 1908, i, 671) has been applied to phenylacetyl chloride, phenylpropionyl chloride, *p*-nitrophenylacetyl chloride, and butyryl chloride; pyronone derivatives are formed, the production of a diketo*cyclo*butane, as in the case of *iso*butyryl chloride (Wedekind and Weisswange, Abstr., 1906, i, 437), not being observed.

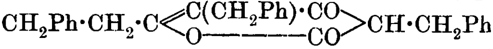
Thus by slowly adding a solution of phenylacetyl chloride (1 mol.) in dry carbon disulphide to a solution of a tertiary base (tripropylamine, pyridine, 1-methylpiperidine, or, best of all, triethylamine) in the same solvent at 0°, moisture being rigorously excluded by passing a slow stream of dry hydrogen through the apparatus, 3 : 5-*diphenyl*-2-*benzyl*-1 : 4 : 6-*pyronone*,  $CO{<}\genfrac{}{}{0pt}{}{CHPh\text{——}CO}{CPh{:}C(CH_2Ph)}{>}O$, m. p. 173—174°, is obtained in 50% yield, its formation being explained in the same way as that of 3 : 5-dimethyl-2-ethyl-1 : 4 : 6-pyronone from propionyl chloride (Wedekind and Häussermann, *loc. cit.*). The substance is remarkably stable to reducing agents, behaves as a monobasic acid (*sodium* salt, $C_{24}H_{17}O_3Na,3EtOH$, colourless crystals from alcohol), but not as an oxonium base, and is decomposed by 20% potassium hydroxide into diphenylacetone, phenylacetic acid, and carbon dioxide. This reaction suggests that the substance might be *s*-triphenylphloroglucinol, produced by the polymerisation of 3 mols. of phenylketen. Its pyronone constitution, however, is indicated by the formation of a *mono-oxime*, m. p. 157° (decomp.), *acetate*, $C_{26}H_{20}O_4$, m. p. 124—125°, and *benzoate*, $C_{31}H_{22}O_4$, m. p. 126°, by the non-formation of triphenylbenzene by reduction with zinc dust, and by its behaviour with concentrated aqueous ammonia at 80—100° and finally at 130—140°, whereby 4 : 6-*dihydroxy*-3 : 5-*diphenyl*-2-*benzylpyridine*,



$$N{\Large\langle}\begin{matrix}C(CH_2Ph){:}CPh\\ C(OH){=\!=\!=}CPh\end{matrix}{\Large\rangle}C\cdot OH,$$

m. p. 260°, is obtained. This substance has acidic properties, does not decolorise bromine, develops a reddish-brown coloration with alcoholic ferric chloride (distinction from the pyronone), and forms a *diacetate*, m. p. 165°. The ready formation of an oxime from diphenylbenzylpyronone is unusual; its oximic structure is proved by the regeneration of hydroxylamine and the pyronone by hydrolysis with concentrated hydrochloric acid.

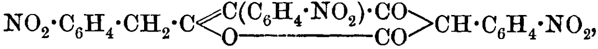
Phenylpropionyl chloride and tripropylamine, reacting under the preceding conditions, yield 3: 5-*dibenzyl*-2-*β*-*phenylethyl*-1 ; 4 : 6-*pyronone*,



$CH_2Ph\cdot CH_2\cdot C{\Large\langle}\begin{matrix}C(CH_2Ph)\cdot CO\\ O\text{———————}CO\end{matrix}{\Large\rangle}CH\cdot CH_2Ph$, m. p. 167—168°, which resembles diphenylbenzylpyronone, but is less acidic, does not form an oxime, and is more readily decomposed by 25% potassium hydroxide at 120°, yielding dibenzylacetone, phenylpropionic acid, and carbon dioxide.

Butyryl chloride and triethylamine react in carbon disulphide to form a pyronone derivative, which is so unstable, however, that its production is indicated only by the formation of dipropyl ketone resulting from its decomposition.

p-*Nitrophenylacetyl chloride*, b. p. 135—138°/0·1 mm., m. p. 47°, obtained from the acid and phosphorus pentachloride, reacts with triethylamine in dry ether cooled by a freezing mixture, 3 : 5-*di*-p-*nitrophenyl*-2-p-*nitrobenzyl*-1 : 4 : 6-*pyronone*,



$$NO_2\cdot C_6H_4\cdot CH_2\cdot C{\Large\langle}\begin{matrix}C(C_6H_4\cdot NO_2)\cdot CO\\ O\text{—————————}CO\end{matrix}{\Large\rangle}CH\cdot C_6H_4\cdot NO_2,$$

m. p. 146° (decomp.), a yellow, microcrystalline powder, being produced, which has pronounced acidic properties and is decomposed by 20% potassium hydroxide at 160°, yielding *p*-nitrophenylacetic acid and pp′-*dinitrodiphenylacetone*, decomp. 205—206° (*phenylhydrazone*, decomp. 110—112°).

The "tertiary bases reaction" has also been applied to *iso*valeryl chloride and crotonyl chloride; the former with ethereal tripropylamine yields ethyl *iso*valerate and *iso*valeric anhydride, whilst the latter with triethylamine in benzene forms crotonic anhydride.

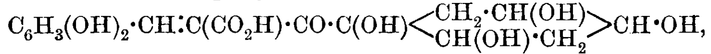
C. S.

"Oxindigo" [2:2′-Diketo-$\Delta^{1:1'}$-dicoumaran]. RICHARD STOERMER and K. BRACHMANN (*Ber.*, 1911, **44**, 315—319).—The yellow substance, m. p. 276° (decomp.), obtained by acidifying the potassium salt of *aci*-nitrocoumaranone and formerly regarded as "leuco-oxindigo" (Abstr., 1909, i, 174), is now found to be 2 : 2′-diketo-$\Delta^{1:1'}$-dicoumaran itself, since it is produced from the potassium salt by the action of iodine in aqueous potassium iodide or alcohol, a reaction in which the formation of "leuco-oxindigo" [2 : 2′-dihydroxy-1 : 1′-dicoumaran] is impossible. The properties of the substance correspond almost exactly with those of 2 : 2′-diketo-$\Delta^{1:1'}$-dicoumaran prepared by Fries and Hasselbach (this vol., i, 150).

The action of chlorine water on potassium *aci*-nitrocoumaranone yields 1-*chloro*-1-*nitrocoumaranone*, $C_8H_4O_4NCl$, m. p. 102°. 1-*Bromo*-1-*nitrocoumaranone*, m. p. 105°, is obtained by shaking the potassium salt with bromine in benzene, or by rapidly adding bromine water to its aqueous solution; when the bromine water is added very slowly, diketo-$\Delta^{1:1'}$-dicoumaran is produced. C. S.

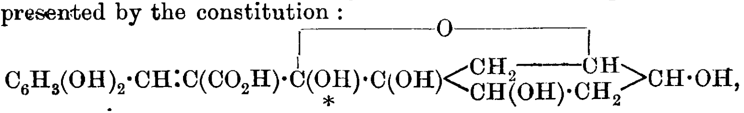
Coffee. IV. K. GORTER (*Annalen*, 1911, **379**, 110—130. Compare Abstr., 1908, i, 186, 345).—The author replies to Lendrich and Nottbohm's criticism (Abstr., 1909, ii, 449) of his method for the estimation of the caffeine in raw coffee (*loc. cit.*), and describes experiments which show that the caffeine in Liberian coffee is all present as potassium caffeine chlorogenate.

All formulæ previously suggested for hemichlorogenic acid are withdrawn and are replaced by the constitution given below for the following reasons: (1) In its fission by acids and alkalis, hemichlorogenic acid behaves like a β-ketonic acid. (2) The non-formation of an oxime, phenylhydrazone, and semicarbazone indicates the absence of a carbonyl group. (3) If the tetrahydropyrone formula previously suggested is correct, the acid should yield 3′ : 4′-dihydroxyflavone by the elimination of $3H_2O$ and of the carboxyl group. This result has not been effected by heating chlorogenic acid with hydriodic acid, with water at 220—230°, or alone at 240—250° in a vacuum. (4) By treatment with bromine (1 mol.) in chloroform in sunlight, penta-acetylhemichlorogenic acid yields a crystalline, additive *compound*, $C_{16}H_{13}O_9Ac_5Br_2$, m. p. 214—215°, which cannot be acetylated, quantitatively regenerates penta-acetylhemichlorogenic acid with alcohol and potassium iodide, and is converted by boiling potassium hydroxide into quinic and bromocaffeic acids. (5) The fact that only five of the six hydroxyl groups in hemichlorogenic acid can be acetylated is proved by showing by Zerewitinoff's method with magnesium methyl iodide in amyl ether that penta-acetylhemichlorogenic acid, which cannot be further acetylated even by acetyl chloride in pyridine, still contains a hydroxyl group. If hemichlorogenic acid were identical with α-quinylcaffeic acid,



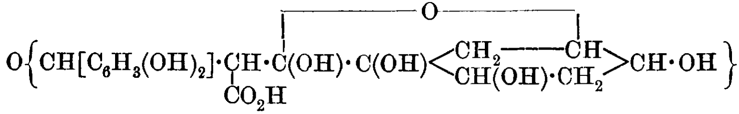
$$C_6H_3(OH)_2\cdot CH\colon C(CO_2H)\cdot CO\cdot C(OH)<\substack{CH_2\cdot CH(OH)\\ CH(OH)\cdot CH_2}>CH\cdot OH,$$

the non-acetylated hydroxyl group would be the tertiary one, a view which is untenable, since this group in quinic acid itself is easily acetylated. (6) Chlorogenic and penta-acetylhemichlorogenic acids are not reduced by zinc dust and acetic acid, and therefore do not contain an ethylenic linking in the $\alpha\beta$-position to a carbonyl group. For these reasons and others already recorded, hemichlorogenic acid is represented by the constitution:



$$C_6H_3(OH)_2\cdot CH\colon C(CO_2H)\cdot \underset{*}{C}(OH)\cdot C(OH)<\substack{CH_2\text{——}CH\\ CH(OH)\cdot CH_2}>CH\cdot OH,$$

in which the * denotes the hydroxyl group which cannot be acetylated. Consequently, chlorogenic acid has the constitution :

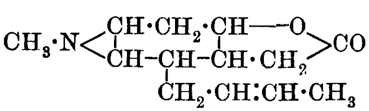


$$O\left\{CH[C_6H_3(OH)_2]\cdot\underset{CO_2H}{CH}\cdot C(OH)\cdot C(OH)<\begin{matrix}CH_2\text{——}CH\\CH(OH)\cdot CH_2\end{matrix}>CH\cdot OH\right\}_2,$$

which is in harmony with the result obtained by reducing the acid by sodium amalgam in a solution which is kept slightly acidic by the continuous addition of sulphuric acid. The product of reduction is *dihydrohemichlorogenic acid*, $C_{16}H_{20}O_9$, m. p. 167—168°, which forms a *penta-acetate*, m. p. 182°, and is decomposed by hydrochloric acid or potassium hydroxide into quinic acid and *dihydrocaffeic acid*, $C_9H_{10}O_4$, m. p. 139°. Its formation is explained by the conversion of the chlorogenic acid into hemichlorogenic acid, which, as an $\alpha\beta$-unsaturated acid, is easily reduced to the dihydro-compound. C. S.

Dioscorine. K. GORTER (*Chem. Zentr.*, 1910, ii, 1228—1229, from *Ann. Jardin Bot. Buitenzorg.*, 1909, [ii], Suppl. 3, 385—392).—From the bulbs of *Dioscorea hirsuta*, Boorsma, and later Schutte (Abstr., 1898, i, 341), isolated a crystalline alkaloid, dioscorine, $C_{13}H_{19}O_2N$. The base was isolated from the bulbs by extraction with alcohol acidified with acetic acid; it can be distilled unchanged in a vacuum. The following salts are described : *hydrobromide*, white crystals, m. p. 213—214° ; *oxalate*, white prisms, m. p. 69·5—70·5° ; *methiodide*, m. p. 213° ; *methochloride aurichloride*, plates, m. p. 188° ; *methochloride platinichloride*, orange tufts, m. p. 218°.

Dioscorine is not acted on by acetic anhydride, and it must be considered to be a tertiary base not containing an OH group. On heating with potassium hydroxide it gives a *potassium* salt, which again yields dioscorine by the action of hydrochloric acid. It must therefore be considered that dioscorine is a γ-lactone. When dioscorine is heated with concentrated potassium hydroxide at 200—250° in the presence of air, methylamine is evolved; dioscorine methiodide gives dimethylamine under similar conditions, a phenol-like substance being also formed. An acid solution of potassium permanganate is at once decolorised by dioscorine. The annexed constitution for dioscorine is suggested. N. C.



$$CH_3\cdot N<\begin{matrix}CH\cdot CH_2\cdot CH\text{——}O\\CH\text{–}\underset{CH_2\cdot CH:CH\cdot CH_3}{CH}\text{–}CH\cdot CH_2\end{matrix}>CO$$

Alkaloid of Eschscholtzia Californica. GEORGES BRINDEJONC (*Bull. Soc. chim.*, 1911, [iv], 9, 97—100).—This plant contains 0·25% of a new alkaloid, ionidine. No other alkaloid is present (compare R. Fischer, Abstr., 1901, i, 743).

An alcoholic extract of the plant deposits potassium nitrate on concentration, and when extracted with warm water deposits resin. From the filtrate after defæcation with lead acetate and addition of alkali, ether extracts *ionidine*, $C_{19}H_{25}O_4N_4$, m. p. 154—156°, which crystallises in short, flattened, colourless, transparent prisms. Its solubility in cold alcohol (90°) is 0·46%, and in water 1 in 2500. The alkaloid is strongly basic, and yields bitter, very soluble, gummy salts with acids. The *aurichloride*, *platinichloride*, and *mercurichloride* are all amorphous. It is precipitated from dilute solutions by iodine, picric acid, or gold chloride, and gives characteristic colour reactions with various reagents, of which the most useful are the following: sulphuric acid gives no coloration, but with sulphuric acid containing a *trace* of nitrous acid, a deep violet tint is produced, and a similar coloration is given with Fröhde's reagent. In both cases the violet tint changes to brown when kept. T. A. H.

Codeine Oxide. Gustav Mossler and Erich Tschebull (*Ber.*, 1911, **44**, 105—109).—By not too prolonged treatment with 1·5% hydrogen peroxide on the water-bath, codeine yields a bimolecular *codeine oxide*, $C_{36}H_{44}O_9N_2,7H_2O$, m.p. 200—202° (decomp.), crystallising in elongated, rectangular plates. The substance loses $6H_2O$ in a vacuum, and $7H_2O$ at 100—110°, and then has m. p. 211—215° (decomp.). It contains two atoms of active oxygen; the monohydrate has $[\alpha]_D -97·6°$ in water and $-105·9°$ in 97% alcohol, the values for the anhydrous substance being $-99·6°$ and $-107·2°$. The molecular weight is determined by the ebullioscopic method in water.

The *hydrochloride*, $C_{18}H_{21}O_4N,HCl,H_2O$, obtained by treating a hot alcoholic solution of the bimolecular oxide with hydrochloric acid, has m. p. 219—220° when anhydrous, and has $[\alpha]_D -105·8°$ in water. By treating its aqueous solution with sodium carbonate. the hydrochloride yields a unimolecular *oxide*, $C_{18}H_{21}O_4N,H_2O$, m. p. 215°, $[\alpha]_D -97·1°$ in water (compare Freund and Speyer, this vol., i, 76). C. S.

Aldehyde Sulphites of Vegetable Alkaloids. Mario Mayer (*Gazzetta*, 1910, **40**, ii, 402—414).—*Brucine benzaldehyde sulphite*,

$$C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_6O,$$

is prepared by treating a suspension of brucine in water with sulphur dioxide until solution is complete, and then shaking the liquid with benzaldehyde. It forms a colourless, crystalline precipitate, m. p. 125° (decomp.). The following similar compounds were prepared in the same way. The analytical figures mostly indicate an excess of alkaloid. *Brucine anisaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_8H_8O_2$, is a white powder, which softens at 108° and decomposes at 115°. *Brucine salicylaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_6O_2$, is a colourless powder, decomposing at 120°. *Brucine heptaldehyde sulphite*,

$$C_{23}H_{26}O_4N_2,H_2SO_3,C_7H_{14}O,$$

is a white, crystalline substance, decomposing at 102°. *Brucine propaldehyde sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_3H_6O$, separates only when the solution is kept in presence of sulphuric acid; it decomposes at 135°. *Brucine acetone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_3H_6O$, is a colourless, crystalline substance, decomposing at 190°. *Brucine benzophenone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_{10}H_{10}O$, is prepared in alcoholic solution; it is a colourless, crystalline substance, decomposing at 120°. *Brucine acetophenone sulphite*, $C_{23}H_{26}O_4N_2,H_2SO_3,C_8H_8O$, forms a yellow, crystalline powder, decomposing at 108°.

Brucinic acid benzaldehyde sulphite, $C_{23}H_{28}O_5N_2,H_2SO_3,C_7H_6O$, crystallises in clusters of small needles, decomposing at 122°.

Brucinic acid ethiodide, $C_{25}H_{33}O_5N_2I,H_2O$, prepared by the method used by Moufang and Tafel (Abstr., 1899, i, 309) for the methyl derivative, is a grey mass, m. p. 205° (decomp.). It yields with sulphur dioxide and benzaldehyde a small quantity of a *substance*, m. p. 145° (decomp.), which does not contain iodine.

Berberine sulphite is obtained by acting on the hydrochloride with a saturated solution of sulphur dioxide in concentrated sodium hydrogen sulphite (compare Perkin, Trans., 1890, 57, 1097). When to a solution of the salt in the cold, benzaldehyde and alcohol are added and the liquid is treated with sulphur dioxide, *berberine benzaldehyde sulphite*, $C_{20}H_{17}O_4N,H_2SO_3,C_7H_6O$, is obtained in golden-yellow, silky needles, which become brown at 180°. *Morphine benzaldehyde sulphite*, $C_{17}H_{19}O_3N,H_2SO_3,C_7H_6O$, is a crystalline substance, m. p. 115° (decomp.). *Narcotine benzaldehyde sulphite*, $C_{22}H_{23}O_7N,H_2SO_3,C_7H_6O$, is a colourless, crystalline powder, m. p. 70° (partial decomp.). *Cocaine benzaldehyde sulphite*, $C_{17}H_{21}O_4N,H_2SO_3,C_7H_6O$, is obtained in alcoholic solution, and forms a colourless, deliquescent mass.

Quinine benzaldehyde sulphite, $C_{20}H_{24}O_2N_2,2H_2SO_3,2C_7H_6O$, prepared in alcoholic solution, is a powder which decomposes at 85°, and at ordinary temperatures and pressures evolves sulphur dioxide. *Cinchonine benzaldehyde sulphite*, $C_{19}H_{22}ON_2,2H_2SO_3,2C_7H_6O$, forms a white powder which decomposes at 90°, and loses sulphur dioxide when kept in a desiccator.

Benzaldehyde anhydrosulphites of the alkaloids are obtained when chloroform or benzene solutions of the alkaloids are treated with dry sulphur dioxide, and benzaldehyde is subsequently added. The anhydrosulphites appear as crystalline or resinous residues when the liquids are evaporated, and have properties similar to those of the sulphites. *Pilocarpine benzaldehyde anhydrosulphite*,

$$C_{11}H_{16}O_2N_2,SO_2,C_7H_6O,$$

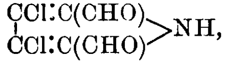
is a colourless, crystalline substance, decomposing at 105°. The *narcotine* compound, $C_{22}H_{23}O_7N,SO_2,C_7H_6O$, is also colourless and crystalline; it decomposes at 80°. The *brucine* compound, $C_{23}H_{26}O_4N_2,SO_2,C_7H_6O$, is crystalline, and has m. p. 105° (decomp.). It dissolves readily in water, the sulphite being precipitated. The *brucinic acid compound*, $C_{23}H_{28}O_5N_2,SO_2,C_7H_6O$, is a crystalline mass, decomposing at 95°. *Strychnine*, although a monoacidic base, yields an anhydrosulphite to which the formula $C_{21}H_{22}O_2N_2,2SO_2,2C_7H_6O$ may be ascribed, although the analytical figures differ somewhat from those required by this formula. The substance is a yellow, resinous mass, m. p. 110°. (decomp.), which continually evolves sulphur dioxide. When dissolved in water it loses sulphur dioxide and benzaldehyde, and on evaporation of the solution a solid resin is obtained, m. p. 95° (decomp.), which is probably *strychnine benzaldehyde sulphite*, $C_{21}H_{22}O_2N_2,H_2SO_3,C_7H_6O$.

It is suggested that the sulphites described in this paper have the structure $C_nH_m\cdot CH<\begin{smallmatrix}-O-\\SO_2\end{smallmatrix}>N{:}R$, $N{:}R$ representing the alkaloid.

R. V. S.

Action of Sulphuryl Chloride on *s*-Dimethylpyrrole.

U. Colacicchi (*Atti R. Accad. Lincei*, 1910, [v], 19, ii, 645—648).—Sulphuryl chloride (2 mols.) reacts with 2 : 5-dimethylpyrrole in ethereal solution at 0°. The liquid, after remaining for two days at the ordinary temperature, was treated with ice, and the residue from the ethereal solution was subjected to steam distillation. No distillate was obtained, but the aqueous residue in the distilling vessel deposited crystals on cooling, from which, by the aid of solvents, two substances were obtained in very small quantity. One of these did not melt at 300°; it behaved as an acid, and gave an unstable *silver* salt, The other substance crystallised in stellate clusters of needles, m. p. 228° (decomp.), had the composition $C_6H_3O_2NCl_2$, and the reactions of an aldehyde. It reduced ammoniacal silver solution, gave a white *substance* with ammonia, yielded a *p-nitrophenylhydrazone*, m. p. 237°. and formed a naphthacinchoninic *derivative*, m. p. 265°, with pyruvic acid and β-naphthylamine. For these reasons the substance is assigned the structure of 3 : 4-*dichloro*-2 : 5-*dialdehydopyrrole*,



$$\begin{matrix}\mathrm{CCl{:}C(CHO)}\\ |\\ \mathrm{CCl{:}C(CHO)}\end{matrix}\!\!>\mathrm{NH},$$

whilst the acid above-mentioned is probably the corresponding dibasic acid, 3 : 4-*dichloropyrrole*-2 : 5-*dicarboxylic acid*. R. V. S.

The Ferriammines. GIUSEPPE A. BARBIERI and G. PAMPANINI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 591—594).—Ferric thiocyanate yields with certain organic bases crystalline compounds containing for every molecule of thiocyanate three molecules of the base. They have a constitution similar to that of the tripyridinechromium chloride of Pfeiffer (Abstr., 1907, i, 872). *Tripyridineferric thiocyanate*, $Fe\genfrac{}{}{0pt}{}{(SCN)_3}{(C_5NH_5)_3}$, is prepared by mixing the calculated quantities of ferric thiocyanate and pyridine in aqueous or, better, in ethereal solution. It forms dark green crystals, which are insoluble in water, but are soluble in various organic solvents with production of either red or violet solutions. *Triquinolineferric thiocyanate*, $Fe(SCN)_3(C_9H_7N)_3$, is similar to the pyridine derivative; it forms crystals which are almost black. *Triantipyrineferric thiocyanate*, $Fe(SCN)_3(C_{11}H_{12}ON_2)_3$, forms red crystals. R. V. S.

Rupture of the Pyridine Ring. FRITZ REITENSTEIN and WILHELM BREUNING (*J. pr. Chem.*, 1911, [ii], **83**, 97—130).—Vongerichten (Abstr., 1900, i, 51; compare Spiegel, *ibid.*, 1901, i, 752) has shown that 1-chloro-2 : 4-dinitrobenzene and pyridine form an additive compound containing a quinquevalent nitrogen atom, and Zincke (Abstr., 1904, i, 448, 921; 1905, i, 241, 923) has proved that this additive compound reacts with primary and secondary arylamines, yielding 2 : 4-dinitroaniline and derivatives of glutaconaldehyde of the type NHPhCl:CH·CH:CH·CH:CH·NHPh, due to the rupture of the pyridine ring (compare Dieckmann, Abstr., 1905, i, 411). It is now shown that other substances containing negative groups can form quaternary ammonium salts with pyridine, for example, diaryloxaliminochlorides, benzanilideimidechloride, phosphorus pentachloride, etc., and that these additive compounds react with primary arylamines, producing a rupture of the pyridine ring and the formation of red dyes of the same type as those described by Zincke. It has not been found possible to isolate definite additive compounds in all the cases studied, but the subsequent formation of a red dye by the action of an amine is regarded as proof of the formation of an additive compound between the pyridine and the compound containing the negative groups.

Di-o-*tolyloxaliminochloride-pyridinium chloride*,

$$C_5NH_5Cl{\cdot}C(:N{\cdot}C_6H_4Me){\cdot}CCl:N{\cdot}C_6H_4Me,$$

obtained by warming a mixture of anhydrous pyridine and di-*o*-tolyloxalimino chloride (Bauer, Abstr., 1907, i, 603) with toluene, extracting the crude product with hot acetone, and crystallising the residue three times from methyl alcohol, forms intensely yellow-coloured plates, m. p. 180°. When boiled with water, acids, or alkalis, it is decomposed, and yields carbylamine derivatives. Its solution in concentrated sulphuric acid has a blood-red colour, and when poured into water yields oxalyl-*o*-toluidide. The *platinichloride*,

$$2C_{21}H_{19}N_3Cl_2,H_2PtCl_6,$$

forms orange-yellow crystals decomposing at 210—212°.

Diphenyloxaliminochloride-pyridinium chloride,

$$C_5NH_5Cl{\cdot}C(:NPh){\cdot}CCl:NPh,$$

prepared in a similar manner from pyridine and diphenyloxalimino chloride, crystallises from methyl alcohol in yellow plates, which turn brown at 200° and melt at 203°.

When the di-*o*-tolyl derivative is warmed for a short time with an alcoholic solution of *p*-toluidine, Zincke's glutacondi-*p*-toluidide hydrochloride is obtained, and with an alcoholic solution of β-naphthylamine the corresponding β-naphthalide. The additive compound of pyridine and bezanilidedi-imidechloride (Wallach, this Journ., 1877, ii, 187) could not be isolated, but by the action of aniline, Zincke's dianilide was obtained, together with anilinobenzylideneaniline (Bernthsen, *Annalen*, 1877, **184**, 353).

A mixture of carbodiphenylimide (Schall, Abstr., 1895, i, 42), pyridine hydrochloride, and *p*-toluidine yields Zincke's *p*-toluidide, and a mixture of phosphorus pentachloride, pyridine, and aniline gives the corresponding anilide.

Pyridine dibromide and potassium cyanide react, yielding the product obtained by König from pyridine cyanogen bromide, and this with aniline yields the glutacondianilide. For the preparation of the anilide it is not necessary to isolate the intermediate compound.

Experiments on the chlorination of pyridine have been carried out. By chlorinating in dry ethereal solution, an unstable, colourless derivative is formed, which readily loses chlorine and reacts explosively with ether, alcohol, or aniline. With water, it yields dichloropyridine hydrochloride, $C_5NH_3Cl_2,HCl,H_2O$, which turns brown at 160° and melts at 168° (decomp.).

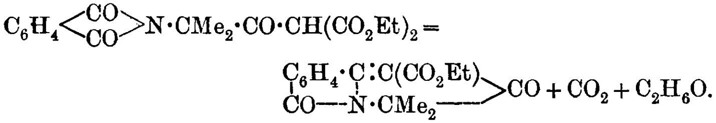
The product of chlorination yields a precipitate with mercuric chloride solution, and when this precipitate is decomposed by boiling with concentrated potassium chloride solution, dichloropyridine distils over, and this forms a *mercurichloride*, $C_5NH_5Cl_4Hg_2$, which crystallises from methyl alcohol in brilliant, colourless needles, m. p. 190°.

When pyridine is chlorinated without the addition of a solvent, but in the presence of zinc chloride or sea-sand, and at low temperatures, a white precipitate is first obtained, but this re-dissolves, and ultimately a dark brown, viscous product is formed. The behaviour of the various chlorinated products towards primary amines has been studied. The white precipitate obtained by chlorinating pyridine in dry ethereal solution when distilled under reduced pressure gave fractions which did not yield dyes with primary arylamines. Similarly, the distillates obtained from the dark viscous liquid, formed by chlorinating pyridine in the presence of zinc chloride, did not give colorations with β-naphthylamine, neither did tri-, tetra-, and penta-chloropyridines. On the other hand, the white precipitate when left in contact with ether and the air underwent partial decomposition, and then reacted with aromatic bases, yielding red dyes of varying composition, and the undistilled dark viscid oil gave a red product with *p*-toluidine melting at 197—198°, with β-naphthylamine a *compound*, $C_{35}H_{27}N_3$, in the form of strongly electrical, dark red needles, m. p. 245°, and with α-methyldihydroindole a product in the form of a cochineal-red precipitate, which has not been analysed.

The *cis*- and *trans*-tolane dichlorides and phosphorus trichloride do not yield dyes with mixtures of pyridine and an aromatic amine.

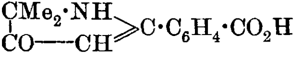
A list of the various amines which react with the chlorinated pyridine is given, together with the colours produced. The characteristic line in the spectra of the various coloured condensation products is also given. J. J. S.

Condensation Product of Ethyl Phthalimino*iso*butyrylmalonate. SIEGMUND GABRIEL (*Ber.*, 1911, 44, 70—91. Compare this vol., i, 212).—The yellow by-product obtained by the interaction of ethyl sodiomalonate and α-phthalimino*iso*butyryl chloride in benzene becomes the main product when 1½ mols. of ethyl sodiomalonate are employed. (In the former method of preparation [*loc. cit.*] the yellow by-product is mixed with a colourless *substance*, m. p. 168—168·5°, which is shown to be *α-phthaliminoisobutyric anhydride* by its formation also from α-phthalimino*iso*butyric acid and its chloride at 170°.) The same *substance*, $C_{16}H_{15}O_4N$, yellow prisms, m. p. 176—177°, is produced when ethyl α-phthalimino*iso*butyrylmalonate is boiled with sodium in benzene. It no longer yields phthalic acid by hydrolysis with hydrochloric acid, and its behaviour, described below, points to the constitution of an ethyl benzoylenedimethylpyrrolonecarboxylate (I), obtained in accordance with the equation :

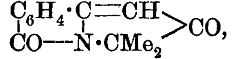


$$C_6H_4{<}{}^{CO}_{CO}{>}N\cdot CMe_2\cdot CO\cdot CH(CO_2Et)_2 = \begin{matrix} C_6H_4\cdot C{:}C(CO_2Et) \\ CO\text{---}N\cdot CMe_2\text{---} \end{matrix}{>}CO + CO_2 + C_2H_6O.$$

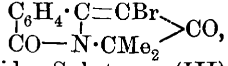
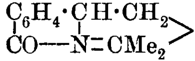
When the ester is hydrolysed by equal volumes of water and concentrated sulphuric acid, it yields *3-keto-2 : 2-dimethyl-2 : 3-dihydropyrrole-5-o-benzoic acid*, $\begin{matrix} CMe_2\cdot NH \\ CO\text{---}CH \end{matrix}{>}C\cdot C_6H_4\cdot CO_2H$ (II) [*hydrobromide*, $C_{13}H_{13}O_3N,HBr,H_2O$, m. p. 200° (decomp.)], which readily suffers ring closure at its m. p., 191° (decomp., rapidly heated), or by prolonged boiling



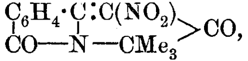
with mineral acids, yielding *benzoylenedimethylpyrrolone* (III),



$$\begin{array}{l} C_6H_4\cdot C{=}CH \\ CO{-}{-}N\cdot CMe_2 \end{array}\Big>CO,$$

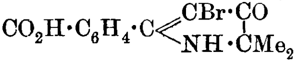
m. p. 125—126°. This is reconverted into (II) by warm alkalis, and forms *benzoylene-4-bromodimethylpyrrolone* (IV),  $\begin{array}{l} C_6H_4\cdot C{=}CBr \\ CO{-}N\cdot CMe_2 \end{array}\Big>CO$, m. p. 224—225°, with bromine in glacial acetic acid. Substance (III) is reduced by hydriodic acid and red phosphorus to *benzoylene-dimethylpyrrolidone* (VII),  $\begin{array}{l} C_6H_4\cdot CH\cdot CH_2 \\ CO{-}{-}N{=}CMe_2 \end{array}\Big>CO$, m. p. 172—173°, which is also formed from (I) and from (II) by the same reducing agent. Substance (VII), unlike (III), is not ruptured by warm alkalis, forms a *phenylhydrazone*, m. p. 215—217·5°, and an *oxime*, 220—221·5°, and yields a *nitro*-compound, $C_{13}H_{12}O_4N_2$, m. p. 172—173° (decomp.), with warm fuming nitric acid.

When substance (III) is treated with fuming nitric acid below 20°, it is converted into *benzoylene-4-nitrodimethylpyrrolone* (V),

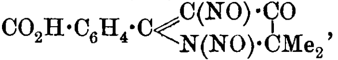


$$\begin{array}{l} C_6H_4\cdot C{:}C(NO_2) \\ CO{-}{-}N{-}{-}CMe_3 \end{array}\Big>CO,$$

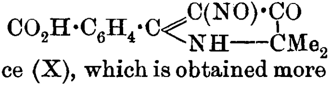
m. p. 264—265° (decomp.), which is reduced by hydriodic and glacial acetic acids, partly to substance (VII), partly to *benzoylene-4-amino-dimethylpyrrolone* (VI), $C_{13}H_{12}O_2N_2$, orange-red prisms, m. p. 212°.

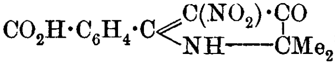
By treatment with methyl-alcoholic hydrogen chloride, substance (II) yields the *hydrochloride*, m. p. 199—199·5° (decomp.), of its methyl ester, an aqueous solution of which is reconverted into (II) by an excess of sodium carbonate. Bromine in glacial acetic acid converts (II) into 4-*bromo*-3-*keto*-2 : 2-*dimethyl*-2 : 3-*dihydropyrrole*-5-o-*benzoic acid* (VIII),  $CO_2H\cdot C_6H_4\cdot C\Big<\begin{array}{l} CBr\cdot CO \\ NH\cdot CMe_2 \end{array}$, m. p. 223° (slowly heated), which is re-converted into (II) and another (unexamined) substance by 20% potassium hydroxide on the water-bath; is almost unattacked by aniline at 150^c (substance IV is produced in this experiment), and reacts with alcoholic ammonia at 100° to form a *substance*, $C_{13}H_{12}O_2N_2$ (XI), m. p. 303—304°, and with methylamine to form a *substance*, $C_{13}H_{11}MeO_2N_2$ (XIII), m. p. 222—223°, the constitutions of which are discussed below.

By the action of cold hydrochloric acid and potassium nitrite, substance (II) is changed into 1 : 4-*dinitroso*-3-*keto*-2 : 2-*dimethyl*-2 : 3-*dihydropyrrole*-5-o-*benzoic acid* (IX),



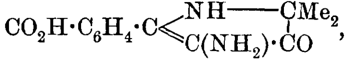
$$CO_2H\cdot C_6H_4\cdot C\Big<\begin{array}{l} C(NO)\cdot CO \\ N(NO)\cdot CMe_2 \end{array},$$

m. p. about 160° (decomp.), which is converted by warm aqueous sodium carbonate into 4-*nitroso*-3-*keto*-2 : 2-*dimethyl*-2 : 3-*dihydropyrrole*-5-o-*benzoic acid* (X),  $CO_2H\cdot C_6H_4\cdot C\Big<\begin{array}{l} C(NO)\cdot CO \\ NH{-}{-}CMe_2 \end{array}$, m. p. 182° (decomp.). This substance (X), which is obtained more conveniently by treating (II) with 50% alcohol, 50% acetic acid, and potassium nitrite, forms a *silver* salt, $C_{13}H_{11}O_4N_2Ag,H_2O$, decomp. 260—270°, and is regarded as containing the nitroso-group in position 4 for the following reasons. It yields substance (VIII) with alcoholic bromine, is converted by nitric acid, D 1·2, into the 4-*nitro-acid* (X*a*),

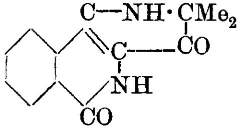


$$CO_2H\cdot C_6H_4\cdot C{<}\begin{matrix}C(NO_2)\cdot CO\\ NH\text{———}CMe_2\end{matrix},$$

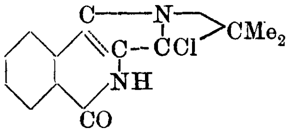
m. p. 262—264° (decomp) (which is changed into V by boiling acetic anhydride), and is reduced, as also is (X*a*), by hydriodic and glacial acetic acids to substance (XI). This substance forms yellow crystals, gives a bluish-green fluorescent solution in boiling water, and a malachite-green solution in concentrated sulphuric acid, from which a blue powder is precipitated by the addition of water. Its insolubility in aqueous ammonia proves the absence of a carboxyl group, and its formation from substances (VIII) and (X) is explained by the formation of the same (unisolated) intermediate compound,

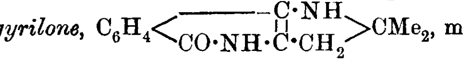


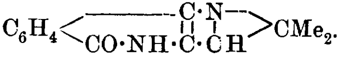
$$CO_2H\cdot C_6H_4\cdot C{<}\begin{matrix}NH\text{———}CMe_2\\ C(NH_2)\cdot CO\end{matrix},$$



from which substance (XI) (annexed constitution) is obtained by the elimination of water. The substance, which is called *gyrolone*, is isomeric with substance (VI); in fact, (VI) can be converted into gyrolone by the action of alcoholic potassium hydroxide and treatment of the product with aqueous ammonium chloride. That the solubility of gyrolone in alkali hydroxides is due to the presence of the acidic imino-group is indicated by the fact that substance (XIII), which contains NMe, is insoluble in these solvents; (XI) is converted into (XIII) by methyl-alcoholic potassium hydroxide and methyl iodide. By treatment with phosphoryl chloride on the water-bath, gyrolone is converted into a *substance*, $C_{13}H_{11}ON_2Cl$, pale yellow needles, which sublimes under diminished pressure, has m. p. 196°, develops a malachite-green coloration in concentrated sulphuric acid, is insoluble in aqueous ammonia, but dissolves in alkali hydroxides; these properties point to the annexed constitution. The substance, which is called *chlorogyrilone*, is converted by methylation into the same *N-methyl* homologue, $C_{13}H_{10}MeON_2Cl$, m.p. 128—128·5°, as is obtained by the action of phosphoryl chloride on substance (XIII).



By reduction with hydriodic acid, b. p. 127°, and red phosphorus, chlorogyrilone is converted into a *base*, $C_{13}H_{16}O_2N_2$, citron-yellow needles, m. p. 196—198°, which loses H_2O in a vacuum, yielding *dihydrogyrilone*,  $C_6H_4{<}\begin{matrix}\text{————}C\cdot NH\\ CO\cdot NH\cdot C\cdot CH_2\end{matrix}{>}CMe_2$, m. p. 190—198°, clarifying completely at 210°, a solution of which in dilute sulphuric acid reduces gold and silver salts and also Fehling's solution. The product of the oxidation, $C_{13}H_{12}ON_2$, m. p. 212° (decomp.) (the *hydrochloride*, *chromate*, *aurichloride*, and *platinichloride* are mentioned), is obtained best by oxidising a solution of dihydrogyrilone or of its hydrate in hydrochloric acid with an excess of bromine; the substance probably has the constitution



$$C_6H_4<\begin{matrix}\text{———————C·N——}\\ \quad\quad\quad\quad\quad\; \| \;\;\; | \\ \text{CO·NH·C·CH}\end{matrix}>CMe_2.$$

When a solution of gyrilone in fuming hydrochloric acid is heated at 135° for two hours and the resulting green powder is distilled in a vacuum, a *substance*, $C_{15}H_{12}ON_2$, isomeric with gyrilone, but devoid of basic properties, is obtained. It crystallises in yellow leaflets, melts and decomposes above 300°, and sublimes when heated carefully on a watch-glass; its constitution is as yet unascertained. C. S.

Transformation of Naphthalimide into Naphthastyril. ELIE E. PISOVSCHI (*Bull. Soc. chim.*, 1911, [iv], 9, 86—88).

—As the processes described by Francesconi and Recchi (Abstr., 1901, i, 721), and by Ullmann and Cassirer (Abstr., 1910, i, 201), do not give good yields, the following new process, which gives a quantitative yield, has been devised.

Naphthalimide (40 grams) dissolved in 600 c.c. of sodium hydroxide solution (3%) is treated at 40° with 480 c.c. of sodium hypochlorite solution containing 5·5% by weight of active chlorine, and the mixture warmed for thirty minutes at 65°. To this, 172 c.c. of sodium hydrogen sulphite solution (30%) are added, and the cooled mixture filtered and the filtrate diluted to 2750 c.c. From this, naphthastyril is precipitated in three fractions by (*a*) adding acetic acid, (*b*) adding dilute sulphuric acid, and (*c*) concentrating the mother liquors. The product may be crystallised from acetic acid.

Dilute solutions of naphthastyril in organic solvents show a green fluorescence. The solution in sulphuric acid is yellow (compare Ekstrand, Abstr., 1886, 715; 1889, 52). T. A. H.

Diacetyl. Diacetylmonophenylhydrazones and their Condensations. OTTO DIELS and ANTON KOLLISCH (*Ber.*, 1911, 44, 263—268. Compare Abstr., 1903, i, 400; 1905, i, 509; 1907, i, 480; 1909, i, 455).

—Although diacetylphenylhydrazone is not decomposed when boiled with hydrochloric acid, the corresponding phenylmethylhydrazone is readily transformed into 1-acetyl-2-methylindole when well shaken with warm hydrochloric acid. The phenylhydrazone and the phenylmethylhydrazone condense readily with ethyl oxalate, yielding hydrazones of ethyl diacetyloxalate, but so far it has not been found possible to remove the hydrazo-group from the condensation products.

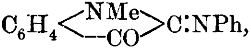
Diacetylphenylmethylhydrazone, $COMe\cdot CMe{:}N\cdot NMePh$, is formed, together with a small amount of the corresponding osazone, by the action of phenylmethylhydrazine on diacetyl in acetic acid solution. It is a deep yellow oil, has b. p. 154—155°/14 mm. (corr.) and D^{20} 1·0809, and condenses with ethyl oxalate in the presence of dry sodium ethoxide and anhydrous ether, yielding the *phenylmethylhydrazone* of *ethyl diacetyloxalate*,

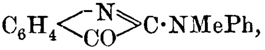
$$CO_2Et\cdot CO\cdot CH_2\cdot CO\cdot CMe{:}N\cdot NMePh,$$

which crystallises from methyl alcohol in red needles, m. p. 88° after sintering. The corresponding *phenylhydrazone*, $C_{14}H_{16}O_4N_2$, crystallises from alcohol in golden-yellow plates, m. p. 148—149° (corr.).

1-*Acetyl*-2-*methylindole*, $C_6H_4<\substack{CH\\NMe}>CAc$, crystallises from light petroleum in stout, colourless plates, m. p. 72°, and yields a *picrate*, $C_{17}H_{14}O_8N_4$, in the form of long, orange needles, m. p. 117°, and a *phenylhydrazone*, $C_{17}H_{17}N_3$, in the form of long, nearly colourless, needles, m. p. 117—118°. J. J. S.

Isatinanils. IV. Cases of Desmotropism. Rudolf Pummerer [with F. Grube] (*Ber.*, 1911, **44**, 338—345. Compare Abstr., 1910, i, 511).—Isatin-2-anil crystallises from benzene in brownish-violet prisms, m. p. 126°, but is precipitated by sodium carbonate from solutions of its salts in brown, crystalline flakes, which crystallise from dilute alcohol in large, yellowish-brown plates, m. p. 126°. At about 110°, partial transference into the violet form is observed. The two modifications are not identical, the yellow leaflets representing isatin-2-anil, $C_6H_4<\substack{NH\\CO}>C:NPh$, and the violet prisms, isatin-2-anilide, $C_6H_4<\substack{N\\CO}>C\cdot NHPh$. The violet form immediately gives red solutions; the yellow form yields yellowish-brown solutions in anhydrous solvents at low temperatures, which soon become red.

1-*Methylisatin*-2-*anil*,  $C_6H_4<\substack{NMe\\CO}>C:NPh$, is obtained by the action of sodium methoxide and methyl iodide; it crystallises in yellowish-red prisms, m. p. 132°, and is hydrolysed by acids to 1-methylisatin and aniline.

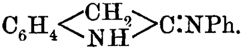
Isatin-2-*methylanilide*,  $C_6H_4<\substack{N\\CO}>C\cdot NMePh$, prepared by the interaction of isatin chloride with methylaniline in benzene solution, crystallises in long, bluish-violet plates, m. p. 103—104°. It is hydrolysed into isatin and methylaniline.

In the case of both isomerides the introduction of methyl causes a deepening of the colour. There is a considerable difference in the basicity of the two forms; the methyl-anil does not react with concentrated sodium hydrogen sulphite solution, whereas the methyl-anilide forms almost quantitatively a sparingly soluble bisulphite compound.

A similar isomerism has been studied in the case of thioindigo-scarlet-2-anil, which is red, and thioindigoscarletanilide, which is greenish-brown (compare following abstract). In this example the anil form is more stable, and has been studied in solution. It is best converted into the anilide by means of acids, boiling with pyridine being the most satisfactory method of effecting the reverse change. E. F. A.

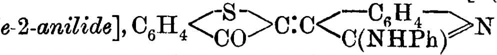
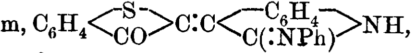
Indirubinanils: Substances with Reactive Carbon Double Bonds. Rudolf Pummerer [with Maximilian Goettler] (*Ber.*, 1911, **44**, 346—356. Compare preceding abstract; also Abstr., 1910, i, 511).—Isatin-2-anil reacts in alkaline solution with indoxyl, forming indirubin-2-anil, in which the anil residue, being no longer in the neighbourhood of a CO group, is firmly fixed. In a similar manner indirubin-*p*-dimethylamino-2-anil and the corresponding sulphur compound have been prepared: both are blue dyes.

Thioindigo-scarlet-*p*-dimethylamino-2-anil on prolonged heating with 1% hydrogen chloride is decomposed quantitatively into aminodimethylaniline and thioindigo-scarlet, but the indirubin compound under similar treament only gives small quantities of indirubin, the main part being converted into a reddish-brown compound, $C_{15}H_{11}O_2N$, which has not been further investigated.

Indirubin-2-anil is decomposed by indoxyl into an indigo dye and *oxindoleanil*,  $C_6H_4{<}{\substack{CH_2\\NH}}{>}C{:}NPh$. The reaction is quantitative, and takes place rapidly in hot dilute acetic acid.

The carbon double bond in indirubinanil is opened by the action of phenylhydrazine, and isatin-2-phenylhydrazone is formed.

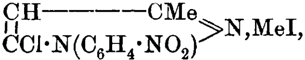
Oxidoleanil forms colourless flakes, m. p. 90—92°; it rapidly becomes violet on exposure to moist air. The *hydrochloride* forms short, lancet-shaped crystals, m. p. 219—220°. When warmed with nitrosobenzene, isatindianil is formed.

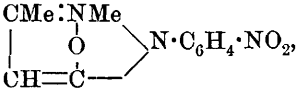
The brown modification of *thioindigo-scarlet-2-anilide* [3(1′)-*thionaphthenyl-ψ-indole-2-anilide*],  $C_6H_4{<}{\substack{S\\CO}}{>}C{:}C{<}{\substack{C_6H_4\\C(NHPh)}}{>}N$ (see preceding abstract), formed by the interaction of isatin-2-anil with 2-hydroxythionaphthen, crystallises in long, narrow, brown prisms, m. p. 226—227°. The red *anil* form,  $C_6H_4{<}{\substack{S\\CO}}{>}C{:}C{<}{\substack{C_6H_4\\C(:NPh)}}{>}NH$, prepared by boiling the brown form in dry pyridine, crystallises in carmine-red prisms with a coppery lustre.

3(1′)-*Thionaphthenyl-ψ-indole*-p-*dimethylamino-2-anil* crystallises in lustrous, violet-black plates, m. p. 220—221°.

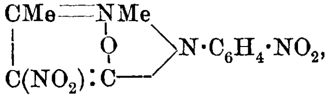
Indirubin-p-*dimethylamino-2-anil* forms bluish-violet plates, m. p. 257—258°. The *sulphate* forms rectangular violet-black plates of metallic lustre, m. p. 255—256°. E. F. A.

1-Nitro- and 1-Amino-derivatives of Antipyrine, Thiopyrine, and Anilopyrine.

AUGUST MICHAELIS [with WALTER GRAFF, RICHARD GESING, and HEINRICH BOIE] (*Annalen*, 1911, **378**, 293—351).—A previous attempt to prepare *p*-nitroantipyrine from methyl iodide and 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole failed, because the two reagents yielded an iodo-*p*-nitrophenylmethylpyrazole methiodide, from which the *p*-nitroantipyrine could not be obtained by the action of alkalis or of silver oxide (Michaelis and Behn, Abstr., 1900, i, 693). Success has now been attained by treating the chloro-*p*-nitrophenylmethylpyrazole with an excess of methyl sulphate at 110° and treating the neutralised aqueous solution of the methosulphate with potassium iodide, whereby 5-*chloro*-1-p-*nitrophenyl*-3-*methylpyrazole methiodide*,  $\begin{matrix}CH\text{———}CMe\\ \Vert \\ CCl\cdot N(C_6H_4\cdot NO_2)\end{matrix}{>}N,MeI$, yellow crystals, m. p. 196°, is obtained; an aqueous solution of this methiodide, by treatment with



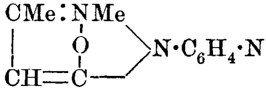
silver oxide and subsequent evaporation, yields p-*nitroantipyrine* (1-p-*nitrophenyl*-2 : 3-*dimethyl*-5-*pyrazolone*) (annexed formula), yellow prisms, m. p. 132°. *p*-Nitroantipyrine, which can also be prepared, although less satisfactorily, by warming an aqueous solution of the preceding methiodide with the calculated quantity of hydroxylamine hydrochloride and sodium carbonate, forms a *hydrochloride*, $C_{11}H_{11}O_3N_3,HCl$, m. p. 191·5°, which is decomposed by water; *platinichloride*, large, red crystals; *hydriodide*, m. p. 163° (decomp.), and *picrate*, m. p. 101°. The methine hydrogen atom in position 4 exhibits its customary activity. Thus, by treatment with sodium nitrite in glacial acetic acid, *p*-nitroantipyrine yields p-*nitro*-4-*nitrosoantipyrine*, a green, crystalline powder, which becomes yellow at 176° and has m. p. 188—189°. p-4-*Dinitroantipyrine* (annexed formula), colourless needles, m. p. 276°, is prepared by the action of nitric and sulphuric acids on antipyrine, by treating *p*-nitroantipyrine with nitric acid, or by heating 5-*chloro*-4-*nitro*-1-p-*nitrophenyl*-3-*methylpyrazole*, m. p. 181° (obtained by the action of nitric and sulphuric acids on 5-chloro-1-phenyl-3-methylpyrazole) with methyl sulphate at 115—120° and decomposing the resulting methosulphate with sodium carbonate.



4-*Bromo*-p-*nitroantipyrine*, obtained from the nitroantipyrine and bromine in chloroform solution, has m. p. 173°. By reduction with tin and hydrochloric acid, *p*-nitroantipyrine yields *p*-aminoantipyrine, m. p. 210°, which does not condense with aldehydes; its *hydrochloride*, $C_{11}H_{13}ON_3,2HCl$, has m. p. 220° (decomp.). The *acetyl* derivative, m. p. 221°, forms 4-*nitroso*-p-*acetylaminoantipyrine*, green needles, m. p. 237° (decomp.), with potassium nitrite in acetic acid solution, and 4-*bromo*-p-*acetylaminoantipyrine*, m. p. 240°, with bromine in chloroform. p-*Benzoylaminoantipyrine*, m. p. 261°, yields 4-*nitroso*-p-*benzoylaminoantipyrine*, m. p. 214°, and 4-*bromo*-p-*benzoylaminoantipyrine*, m. p. 237°, by similar processes. p-*Benzenesulphonylaminoantipyrine*, m. p. 251°, obtained from *p*-aminoantipyrine and benzenesulphonyl chloride in alcoholic solution, yields a 4-*nitroso*-compound, m. p. 211° (decomp.), and a 4-*bromo*-compound, m. p. 235°. p-4-*Diaminoantipyrine*, m. p. 279°, obtained by reducing dinitroantipyrine by tin and hydrochloric acid, forms a *diacetyl* derivative, m. p. 291°, which has only a slight antipyretic action.

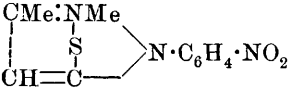
The following compounds of *m*-nitroantipyrine and of *o*-nitroantipyrine are obtained, in the main, by processes similar to those mentioned above. 5-*Chloro*-1-m-*nitrophenyl*-3-*methylpyrazole methiodide*, m. p. 222°, yellow needles. m-*Nitroantipyrine*, m. p. 98°, yellow needles, forms a *hydrochloride*, m. p. 188°, which is decomposed by water; *platinichloride*, $2C_{11}H_{11}O_3N_3,H_2PtCl_6,2H_2O$, m. p. 140°; *hydriodide*, m. p. 171°; *picrate*, m. p. 165°, and *nitrate*, m. p. 143°. m-*Nitro*-4-*nitrosoantipyrine*, green crystals, decomp. 165°, complete at 188—190°. m-4-*Dinitroantipyrine*, prepared from *m*-nitroantipyrine and nitric acid with cooling, decomposes at 203°. 4-*Bromo*-m-*nitro*-

antipyrine, m. p. 184°. m-*Aminoantipyrine*, m. p. 148°, does not react with aldehydes, phenylthiocarbimide, or carbon disulphide; it forms a *hydrochloride*, $C_{11}H_{13}ON_3,2HCl$, m. p. 228°, which is very unstable; *platinichloride*, $2C_{11}H_{13}ON_3,H_2PtCl_6,2H_2O$, decomp. above 200°, and an *acetyl* derivative, $C_{13}H_{15}O_2N_3,H_2O$, m. p. 127° (hydrated), 167° (anhydrous), which has only a slight antipyretic action. 4-*Bromo*-m-*acetylaminoantipyrine* has m. p. 217°. m-*Benzoylaminoantipyrine* has m. p. 119°. m-*Dimethylaminoantipyrine* (*ψ-pyramidone*) (annexed formula), obtained by heating *m*-aminoantipyrine and methyl sulphate nearly at the b. p. for half an hour and basifying the aqueous solution of the resulting methosulphate, is an oil which forms a *platinichloride*, reddish-brown needles, m. p. 270° (decomp.). *m*-4-*Diaminoantipyrine*, m. p. 170°, forms a *hydrochloride*, $C_{11}H_{14}ON_4,2HCl$, m. p. 245°, and a *diacetyl* derivative, m. p. 273°.

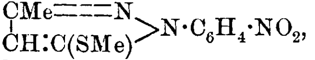


5-*Chloro*-1-o-*nitrophenyl*-3-*methylpyrazole methiodide*, m. p. 183°, yellow prisms, is converted by silver oxide in the preceding manner into o-*nitroantipyrine*, m. p. 188°, which forms a *hydrochloride*, m. p. 201°, and *platinichloride*, $2C_{11}H_{11}O_2N_3,H_2PtCl_6,2H_2O$, m. p. 133° (hydrated), decomp. above 300° (anhydrous). o : 4-*Dinitroantipyrine*, white needles, has m. p. 244°. o-*Aminoantipyrine* has m. p. 165°.

2 : 5-*Thio*-1-m-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (m-*nitrothiopyrine*) (annexed formula), m. p. 204°, yellow leaflets, obtained by treating a suspension of 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole methiodide in chloroform with a concentrated alcoholic solution of potassium sulphide (the use of aqueous solutions is to be avoided, since the hydrogen sulphide liberated reduces the nitro-group to the amino-group), forms a *hydrochloride*, $C_{11}H_{11}O_2N_3S,HCl$, m. p. 147°, which is decomposed by water, *platinichloride*, m. p. 225°, *hydriodide*, m. p. 185°, *methiodide*, m. p. 209°, and *trioxide*, $C_{11}H_{11}O_5N_3S$, m. p. above 350°, the last being obtained by passing chlorine through a hot aqueous solution of the nitrothiopyrine.



5-*Methylthiol*-1-m-*nitrophenyl*-3-*methylpyrazole* (m-*nitro-ψ-thiopyrine*),



$$\begin{matrix} CMe{=\!=\!=}N \\ CH{:}C(SMe) \end{matrix}{>}N\cdot C_6H_4\cdot NO_2,$$

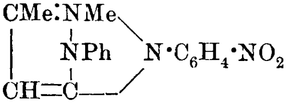
m. p. 84°, white needles, is obtained by carefully heating *m*-nitrothiopyrine methiodide under reduced pressure; by oxidation by potassium permanganate in glacial acetic acid, it yields the *sulphone*,

$$C_{11}H_{11}O_4N_3S,$$

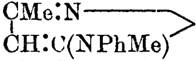
m. p. 135°. m-*Aminothiopyrine*, m. p. 199°, obtained by reducing the nitrothiopyrine by tin and hydrochloric acid, forms a *hydrochloride*, m. p. 226°, and *platinichloride*, an amorphous, red powder. The following compounds are obtained by methods similar to the preceding: 2 : 5-*thio*-1-o-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (o-*nitrothiopyrine*), m. p. 190°, blood-red-crystals, forms a *hydrochloride*, m. p. 125°, *platinichloride*, decomp. 230°, *hydriodide*, m. p. 152°, *methiodide*, m. p. 181°, and *trioxide*, m. p. 298°. o-*Nitro-ψ-thiopyrine* and its sulphone have m. p. 61° and 160° respectively. o-*Aminothiopyrine*,

m. p. 172°, forms a *platinichloride*, decomp. 300°. 2 : 5-*Thio*-1-p-*nitrophenyl*-2 : 3-*dimethylpyrazolone* (p-*nitrothiopyrine*), m. p. 241°, red crystals, is obtained by treating a hot aqueous solution of 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole methiodide with concentrated aqueous sodium sulphide; it forms a *hydrochloride*, m. p. 175°, *methiodide*, m. p. 196°, and *trioxide*, decomp. above 370°. *p*-Nitro-ψ-thiopyrine (Michaelis and Besson, Abstr., 1904, i, 780) forms a *hydrochloride*, m. p. 85°, and a *sulphone*, m. p. 154°; 4-*bromo*-p-*nitro*-ψ-*thiopyrine* has m. p. 120°. p-4-*Dinitrothiopyrine*, m. p. 240°, yellow crystals, obtained in a similar manner to the dinitroantipyrine, forms a *methiodide*, m. p. 154—155°, which by heating under reduced pressure yields the *dinitro*-ψ-*thiopyrine*, m. p. 123°; the corresponding *sulphone* has m. p. 177°. p-*Aminothiopyrine*, m. p. 255—256°, obtained by the reduction of *p*-nitrothiopyrine, forms a *hydrochloride*, $C_{11}H_{13}N_3S,2HCl$, an *acetyl* derivative, m. p. 271°, and *benzoyl* derivative, m. p. 265°. p-*Amino*-ψ-*thiopyrine*, m. p. 132°, white leaflets, obtained by the reduction of *p*-nitro-ψ-thiopyrine, forms a *hydrochloride*, $C_{11}H_{13}N_3S,2HCl$, m. p. 221°, and an *acetyl* derivative, m. p. 137°. p-4-*Diaminothiopyrine*, m. p. 207°, obtained in a similar manner to the diaminoantipyrine, forms a *diacetyl* derivative, m. p. 273°. p-4-*Diamino*-ψ-*thiopyrine*, m. p. 115°, white needles, is obtained by the reduction of the dinitro-ψ-thiopyrine; its *diacetyl* derivative has m. p. 235°.

2 : 5-endo*Anilo*-1-m-*nitrophenyl*-2 : 3-*dimethylpyrazole* (m-*nitroanilopyrine*) (annexed formula), m. p. 110°, reddish-brown needles, is obtained by heating 5-chloro-1-*m*-nitrophenyl-3-methylpyrazole methiodide and aniline (2 mols.) at 125° for two hours. It reduces Fehling's solution and silver salts, and is a strong base; the *hydriodide*, m. p. 166°, *platinichloride*, *picrate*, *thiocyanate*, m. p. 168°, *methiodide*, m. p. 222°, *ethiodide*, m. p. 176°, and *propiodide*, m. p. 130°, are described. By treatment with benzoyl-chloride in benzene, *m*-nitroanilopyrine forms a *benzoyl chloride*, which is isolated as the *platinichloride*, $2(C_{17}H_{16}O_2N_4,C_6H_5\cdot COCl)PtCl_4$, m. p. 235°; from this, by aqueous potassium iodide, the *benzoyliodide*, m. p. 198°, is obtained; the *acetyliodide*, $C_{17}H_{16}O_2N_4,CH_3\cdot COI$, has m. p. 214°. When heated at 200°, *m*-nitroanilopyrine hydrochloride loses methyl chloride, and is converted into 5-*anilino*-1-m-*nitrophenyl*-3-*methylpyrazole*, m. p. 122—123°, yellow needles.

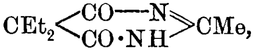


2 : 5-endo*Anilo*-1-o-*nitrophenyl*-2 : 3-*dimethylpyrazole* (o-*nitroanilopyrine*), m. p. 111°, dark red prisms, is obtained in a similar manner to the meta-compound, using 4 mols. of aniline at 110°. It is likewise a strong base, forming a *platinichloride*, m. p. 206°, *hydriodide*, m. p. 198°, *picrate*, m. p. 167°, *thiocyanate*, m. p. 193°, *methiodide*, m. p. 97°, *ethiodide*, m. p. 177°, *propiodide*, m. p. 168°, *acetyliodide*, m. p. 225°, *benzoyliodide*, m. p. 197°, and *benzoyl chloride*, m. p. 124°; by heating the last at 50—80°/40 mm., 5-*benzoylanilino*-1-o-*nitrophenyl*-3-*methylpyrazole*, m. p. 156—157°, white prisms, is obtained. 1-*Azo*-o-*anilopyrine*, $N_2(C_6H_4\cdot C_3N_2Me_2{:}NPh)_2$, red needles, m. p. 225°, is prepared by heating an alcoholic solution of *o*-nitroanilopyrine with aluminium amalgam and a little water on the water-bath.

2 : 5-endo*Anilo*-1-p-*nitrophenyl*-2 : 3-*dimethylpyrazole* (p-*nitroanilopyrine*), m. p. 168°, dark red crystals, is prepared by heating 5-chloro-1-*p*-nitrophenyl-3-methylpyrazole with methyl sulphate and treating the resulting methosulphate with aniline at 125—130° for five hours; the *hydriodide* has m. p. 192°, and the *methiodide*, m. p. 182°. By heating the latter at 200° under reduced pressure, p-*nitro-ψ-anilopyrine*,  $\left.\begin{array}{l}CMe{:}N \\ CH{:}C(NPhMe)\end{array}\right>N\cdot C_6H_4\cdot NO_2$, m. p. 100°, yellow needles, is obtained. p : 4-*Dinitroanilopyrine*, m. p. 192°, yellow leaflets, is prepared by heating 5-chloro-4-nitro-1-*p*-nitrophenyl-3-methylpyrazole with methyl sulphate at 115—120° for six hours, and treating the resulting methosulphate with an excess of aniline at 130° for four hours. *p*-Nitroanilopyrine yields p-*aminoanilopyrine*, m. p. 175°, by reduction with tin and hydrochloric acid, and p-*azoanilopyrine*, m. p. 224°, dark red crystals, by reduction in alcohol-chloroform solution by aluminium amalgam and water. C. S.

Action of Diethylmalonyl Chloride on Some Substances Containing Nitrogen. Martin Freund and Karl Fleischer (*Annalen*, 1911, **379**, 27—36. Compare Abstr., 1910, i, 490).—When warmed with acetamide (2 mols.), diethylmalonyl chloride yields 4 : 6-*diketo*-2-*methyl*-5 : 5-*diethyltetrahydropyrimidine hydrochloride*,

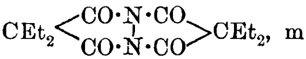
$$C_9H_{14}O_2N_2,HCl,$$

decomp. 253°, white needles, from which dilute aqueous ammonia liberates the *base* itself,  $CEt_2<\begin{array}{l}CO—N \\ CO\cdot NH\end{array}>CMe$, m. p. 125°. The constitution follows from the ready decomposition of the base into diethylmalonamide by warm alkalis. It separates from methyl alcohol in long needles, $C_9H_{14}O_2N_2,MeOH$, m. p. 135—140°, which at 100—110° lose methyl alcohol and are converted into a vitreous, yellow mass, which has pronounced acidic properties, and is probably the enolic form of the base, since it is converted by 20% hydrochloric acid into the preceding hydrochloride. Formamide and propionamide do not form pyrimidines with diethylmalonyl chloride.

By the prolonged interaction of benzamide and diethylmalonyl chloride with warming, diethylmalonamic acid, together with a little cyaphenine, are produced. By short, careful heating, however, the two substances yield *benzoyldiethylmalonamic acid*,

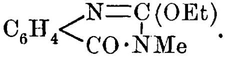
$$NHBz\cdot CO\cdot CEt_2\cdot CO_2H,$$

m. p. 127—128° (decomp.), together with *diethylacetylbenzamide*, $NHBz\cdot CO\cdot CHEt_2$, m. p. 138—139°, which is also formed by heating the preceding acid above its m. p.

When warmed with diethylmalonyl chloride, benzylidenesemicarbazone is converted into 3 : 5-*diketo*-1 : 2-*diethylmalonyl*-4 : 4-*diethylpyrazolidine*,  $CEt_2<\begin{array}{c}CO\cdot N\cdot CO \\ \vert \\ CO\cdot N\cdot CO\end{array}>CEt_2$, m. p. 202—203°. This is converted by warm dilute sodium hydroxide and subsequent acidification into *bisdiethylmalonhydrazinic acid*, $N_2H_2(CO\cdot CEt_2\cdot CO_2H)_2$, m. p. 233—234° (decomp.), which is very stable to alkalis and to sulphuric acid, but is converted by careful heating into *bis-a-ethylbutyrylhydrazide*, $N_2H_2\cdot CO\cdot CHEt_2$, m. p. 234°.

[With Max Rothschild.]—Benzylidenesemicarbazone and dipropylmalonyl chloride yield the corresponding 3 : 5-*diketo*-1 : 2-*dipropylmalonyl*-4 : 4-*dipropylpyrazolidine*, $C_{18}H_{28}O_4N_2$, m. p. 189°. C. S.

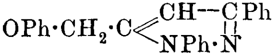
[Benzoylenecarbamide.] Hermann Finger and H. Günzler (*J. pr. Chem.*, 1911, [ii], **83**, 198—199).—The substance designated as ethyl cyanoanilide-*o*-carboxylate (Finger and Zeh, Abstr., 1910, i, 382) has been described previously by Griess under the name ethoxycyanoaminobenzene (4-keto-2-ethoxy-1 : 4-dihydro-1 : 3-benzdiazine); he also mentions its conversion into benzoylenecarbamide. If this constitution is correct, the substance obtained from it by the action of methyl sulphate and described as *o*-carbethoxyphenylmethylcarbodi-imide (Finger, Abstr., 1910, i, 383) may very possibly be 4-keto-2-ethoxy-3-methyl-3 : 4-dihydro-1 : 3-benzdiazine,



$$C_6H_4<\begin{matrix}N{=}C(OEt)\\ CO\cdot NMe\end{matrix}.$$

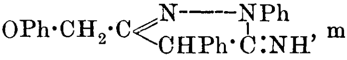
C. S.

Condensation of Esters of Alkyloxy-acids with Cyanides and Ketones. Reinhold von Walther (*J. pr. Chem.*, 1911, [ii], **83**, 171—182).—[With H. Litter.]—*Phenoxyacetylacetophenone*, $OPh\cdot CH_2\cdot CO\cdot CH_2\cdot COPh$, m. p. 79—80°, white needles, obtained by acidifying the product of the condensation of equimolecular quantities of ethyl phenoxyacetate and acetophenone in the presence of sodium ethoxide, gives a red coloration with alcoholic ferric chloride, does not react with phenylcarbimide or with benzoyl chloride and sodium hydroxide, but condenses with phenylhydrazine to form 1 : 3-*diphenyl*-5-*phenoxymethylpyrazole*,

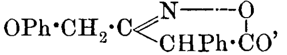


$OPh\cdot CH_2\cdot C<\begin{matrix}CH{-}CPh\\ NPh\cdot N\end{matrix}$, m. p. 88°, which is reduced by sodium and alcohol to 1 : 3-diphenyl-5-methylpyrazoline, phenol being eliminated. 3-*Phenyl*-5-*phenoxymethylpyrazole*, m. p. 104°, is obtained by boiling an alcoholic solution of phenoxyacetylacetophenone with aqueous hydrazine, whilst 3-*phenyl*-5-*phenoxymethylisooxazole*, m. p. 61°, is produced in a similar manner with hydroxylamine hydrochloride.

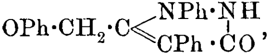
[With P. Herschel.]—α-*Phenoxyacetylphenylacetonitrile*, $OPh\cdot CH_2\cdot CO\cdot CHPh\cdot CN$, m. p. 125—126°, prepared from ethyl phenoxyacetate, phenylacetonitrile, and sodium ethoxide, dissolves in aqueous ammonia, and reacts with phenylhydrazine in boiling glacial acetic acid to form 5-*imino*-1 : 4-*diphenyl*-3-*phenoxymethylpyrazolone*,



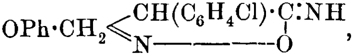
$OPh\cdot CH_2\cdot C<\begin{matrix}N{-\!-}NPh\\ CHPh\cdot C{:}NH\end{matrix}$, m. p. 120—121°, the *hydrochloride*, *platinichloride*, m. p. 192° (decomp.), *picrate*, m. p. 163°, *benzoyl* derivative, m. p. 163—169°, and *acetyl* derivative, m. p. 174—175°, of which are described. Phenoxyacetyl phenylacetonitrile reacts with dry ammonia at 150° to form β-*amino*-γ-*phenoxy*-α-*phenylcrotononitrile*, $OPh\cdot CH_2\cdot C(NH_2){:}CPh\cdot CN$, m. p. 88—89°, and with aniline, *p*-toluidine, and α-naphthylamine to form corresponding β-anilino-, β-*p*-toluidino-, and β-naphthylamino-derivatives, m. p. 131°, 118°, and 145—150° respectively; also, by saturating its solution in hot glacial acetic acid with hydrogen chloride it yields *γ-phenoxy-α-phenylacetoacetamide*, $OPh\cdot CH_2\cdot CO\cdot CHPh\cdot CO\cdot NH_2$, m. p. 151—152°, which reacts with hydroxylamine hydrochloride in boiling acetic acid to form *4-phenyl-3-phenoxymethyl*iso*oxazolone*,



$$OPh\cdot CH_2\cdot C\Big<\substack{N\text{———}O\\ CHPh\cdot CO}$$

m. p. 160—162° (decomp.), and with phenylhydrazine to form *2:4-diphenyl-3-phenoxymethylpyrazolone*,  $OPh\cdot CH_2\cdot C\Big<\substack{NPh\cdot NH\\ CPh\cdot CO}$, m. p. 145°, a substance which is soluble in sodium hydroxide, carbonate, or hydrogen carbonate. Ethyl phenoxyacetate condenses with *p*-chlorophenylacetonitrile to form *p-chloro-α-phenoxyacetylphenylacetonitrile,*

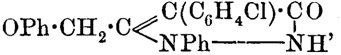
$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CN,$$

m. p. 168°, from which the following substances are produced by reactions similar to the preceding: *5-imino-1-phenyl-4-*p*-chlorophenyl-3-phenoxymethylpyrazolone*, m. p. 107° (*hydrochloride*, *picrate*, m. p. 165°, *acetyl* derivative, m. p. 219°, *benzoyl* derivative, m. p. 219—220°); *β-amino-γ-phenoxy-α-*p*-chlorophenylcrotononitrile*, m. p. 132°; the corresponding *β-anilino-* and *β-*p*-toluidino*-derivatives have m. p. 122° and 135° respectively. *p*-Chloro-α-phenoxyacetylphenylacetonitrile, unlike the non-halogenated cyanide, reacts with hydroxylamine hydrochloride in boiling alcohol to form *5-imino-4-*p*-chlorophenyl-3-phenoxymethyl*iso*oxazolone*,  $OPh\cdot CH_2\Big<\substack{CH(C_6H_4Cl)\cdot C{:}NH\\ N\text{————————}O}$, m. p. 108°. Also, it does not form an amide, but with alcoholic hydrogen chloride yields *ethyl γ-phenoxy-α-*p*-chlorophenylacetoacetate*,

$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CO_2Et,$$

m. p. 70°; the *methyl* ester has m. p. 87°. With phenylhydrazine in boiling alcohol, the ester yields a *phenylhydrazide*,

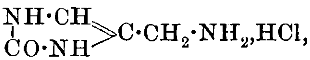
$$OPh\cdot CH_2\cdot CO\cdot CH(C_6H_4Cl)\cdot CO\cdot NH\cdot NHPh,$$

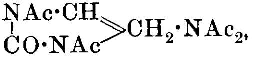
m. p. 125—126°, which is easily converted by alcoholic sodium hydroxide into the *pyrazolone*,  $OPh\cdot CH_2\cdot C\Big<\substack{C(C_6H_4Cl)\cdot CO\\ NPh\text{———}NH}$, m. p. 166°.

C. S.

Reaction Products of Potassium *iso*Cyanate and Diaminoacetone Hydrochloride. Amino- and Carbamido-propyleneureine [Carbamidomethylglyoxalone].

ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 625—628).—It is shown that when potassium *iso*cyanate and diaminoacetone hydrochloride interact, the products are not those described by Rügheimer (Abstr., 1892, ii, 952), but 4-carbamidomethylglyoxalone and aminopropyleneureine [4-aminomethylglyoxalone] hydrochloride.

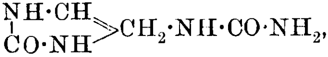
Aminomethylglyoxaline hydrochloride,  $\substack{NH\cdot CH\\ CO\cdot NH}\Big>C\cdot CH_2\cdot NH_2,HCl$, crystallises in small needles which are very soluble in water. The free base has not yet been isolated, but some of its compounds and derivatives are described. The *nitrate* and normal and acid *sulphates* all form small, colourless needles with no definite melting point. The

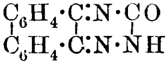
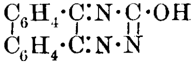
triacetyl derivative forms needles, m. p. 141°. The *tetra-acetyl* derivative,

$\left.\begin{array}{l}\mathrm{NAc\cdot CH}\\ \mathrm{CO\cdot NAc}\end{array}\right>\mathrm{CH_2\cdot NAc_2}$, crystallises in plates, m. p. 163—164°.

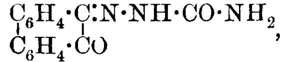
The *carboxymethyl* derivative forms leaflets, m. p. 238°, and when boiled with acetic anhydride yields a *monoacetyl* derivative,

$$\mathrm{C_3N_2H_3\cdot CH_2\cdot NHAc},$$

m. p. 215°. The *diacetyl* derivative crystallises in needles, m. p. 125—126°. The corresponding *carboxyethyl* derivative forms, small glittering crystals, m. p. 208°. It yields a *monoacetyl* compound, m. p. 218—219°, and a *diacetyl* compound, m. p. 101—102°.

4-*Carbamidomethylglyoxalone*,

$\left.\begin{array}{l}\mathrm{NH\cdot CH}\\ \mathrm{CO\cdot NH}\end{array}\right>\mathrm{CH_2\cdot NH\cdot CO\cdot NH_2}$, was obtained from diaminoacetone hydrochloride with 2 molecules of potassium *iso*cyanate, and also from aminomethylglyoxalone hydrochloride with 1 molecule of the *iso*cyanate. It forms snow-white leaflets, decomposing at 220°, and gives no precipitate with silver nitrate or mercuric chloride unless ammonia is added, but is precipitated by mercuric nitrate. N. C.

Phenanthrene Series. XXIX. Phenantriazines. Julius Schmidt, Otto Schairer, and Ernst Glatz (*Ber.*, 1911, 44, 276—282. Compare Thiele and Bihan, Abstr., 1899, i, 47).—Hydroxyphenantriazine,

$\begin{array}{l}\mathrm{C_6H_4\cdot C{:}N\cdot CO}\\ \mathrm{C_6H_4\cdot C{:}N\cdot NH}\end{array}$ or

$\begin{array}{l}\mathrm{C_6H_4\cdot C{:}N\cdot C\cdot OH}\\ \mathrm{C_6H_4\cdot C{:}N\cdot N}\end{array}$, is formed when phenanthraquinonemonoxime is boiled for ten hours with an alcoholic solution of semicarbazide hydrochloride, hydroxylamine being formed at the same time. Substituted derivatives of phenanthraquinonemonoxime react in much the same manner, and by using the 4-nitro-derivative it has been found possible to isolate the semicarbazone of the monoxime as an intermediate product. It has not been found possible to obtain the phenantriazine directly from phenanthraquinonemonosemicarbazone.

Phenanthraquinonesemicarbazone,

$\begin{array}{l}\mathrm{C_6H_4\cdot C{:}N\cdot NH\cdot CO\cdot NH_2}\\ \mathrm{C_6H_4\cdot CO}\end{array}$, crystallises from alcohol in golden, crystalline nodules or in long, brilliant golden-yellow needles containing 0·5 mol. of ethyl alcohol. Both forms have m. p. 220° (decomp.).

3-*Hydroxyphenantriazine*, $\mathrm{C_{15}H_9ON_3}$, crystallises from alcohol in pale yellow nodules, m. p. 285° (decomp.), and does not give the usual reactions for ketones.

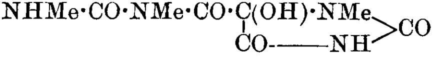
4-*Nitrophenanthraquinonemonosemicarbazone*, $\mathrm{C_{15}H_{10}O_4N_4}$, forms a yellow, crystalline powder, m. p. 210—211° (decomp.).

4-*Nitrophenanthraquinoneoximesemicarbazone*, $\mathrm{C_{15}H_{11}O_4N_5}$, forms a yellowish-green powder, m. p. 240° (decomp.), and yields 8-*nitro*-3-*hydroxyphenantriazine*, $\mathrm{C_{15}H_8O_3N_4}$, as a yellow powder, m. p. 285° (decomp.), when heated with alcohol and concentrated hydrochloric acid.

3-*Bromophenanthraquinoneoximesemicarbazone* form pale yellow, crystals, m. p. 274—275°, and 7-*bromo*-3-*hydroxyphenantriazine* yellow crystals, m. p. 304°.

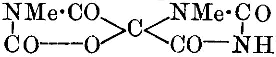
3-*Nitrophenanthraquinoneoximesemicarbazone* has m. p. 249—250° (decomp.), and 7-*nitro*-3-*hydroxyphenantriazine* forms ochre-yellow crystals, m. p. 273—274° (decomp.). J. J. S.

Hypocaffeine and its Decomposition. HEINRICH BILTZ and PAUL KREBS (*Ber.*, 1911, **44**, 282—305. Compare Abstr., 1910, i, 521, 524, 526).—The products described by Fischer (Abstr., 1882, 217; 1883, 356) under the names of hypocaffeine, caffoline, and acecaffeine have been re-examined. The formula for hypocaffeine is shown to be $C_8H_{10}O_4N_4$, and not $C_6H_7O_3N_3$, as suggested by Fischer. A 60% yield of the compound is formed when trimethyluric-acid-glycol ether is decomposed by an alcoholic solution of hydrogen chloride in the absence of water; when aqueous hydrochloric acid is used, the yield is only 30%, and *apo*caffeine is also formed. The formulæ for the silver and barium salts are $C_8H_9O_4N_4Ag$ and $(C_8H_9O_4N_4)_2Ba$ respectively. When trimethyluric-acid-glycol ether is decomposed by concentrated sulphuric acid, *apo*caffeine and not hypocaffeine is formed. Caffoline has the formula $C_7H_{12}O_3N_4$, and in the conversion of hypocaffeine into caffoline by warming with barium carbonate solution a molecule of water is added and one of carbon dioxide eliminated, and the conversion of caffoline into acecaffeine by boiling with acetic anhydride and hydrolysing the resulting acetyl derivative also consists in the addition of water and the removal of carbon dioxide and ammonia. These conclusions have been confirmed by molecular-weight determinations and the methylation of hypocaffeine to oxytetramethyluric acid (Fischer, Abstr., 1898, i, 180). In the conversion of the glycol ether into hypocaffeine, trimethyluric-acid-glycol is probably first formed; this is, however, unstable, and is ruptured at the 3 : 4 position, yielding 5-hydroxy-1-methylhydantoyl-7 : 9-dimethylcarbamide,

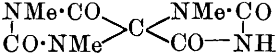


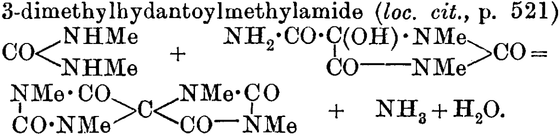
$$\begin{array}{l}NHMe\cdot CO\cdot NMe\cdot CO\cdot C(OH)\cdot NMe\\ \qquad\qquad\qquad\qquad\qquad\quad CO——NH\end{array}\!\!>CO$$

by the hydrolytic decomposition of this in the 8 : 9 position, and (*a*) subsequent formation of a lactone, *apo*caffeine,



$$\begin{array}{l}NMe\cdot CO\\ CO——O\end{array}\!\!>C<\!\!\begin{array}{l}NMe\cdot CO\\ CO—NH\end{array},$$

is formed, or (*b*) ring formation between carbon No. 5 and nitrogen No. 9, hypocaffeine,  $\begin{array}{l}NMe\cdot CO\\ CO\cdot NMe\end{array}\!\!>C<\!\!\begin{array}{l}NMe\cdot CO\\ CO—NH\end{array}$, is obtained. According to Baeyer's nomenclature (*Ber.*, 1900, **33**, 3771), hypocaffeine is thus 1 : 7 : 9-*trimethyl*-spiro-5 : 5-*hydantoin*, and oxytetramethyluric acid, the corresponding 1 : 3 : 7 : 9-tetramethyl derivative. This constitution of oxytetramethyluric acid has been confirmed by its synthesis from dimethylcarbamide and 5-hydroxy-1 : 3-dimethylhydantoylamide or 5-hydroxy-1 : 3-dimethylhydantoylmethylamide (*loc. cit.*, p. 521) (*allo*-caffuric acid),

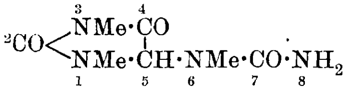


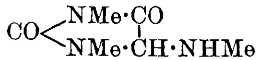
$$CO<\!\!\begin{array}{l}NHMe\\ NHMe\end{array} + \begin{array}{l}NH_2\cdot CO\cdot C(OH)\cdot NMe\\ \qquad\qquad\quad CO——NMe\end{array}\!\!>CO = \begin{array}{l}NMe\cdot CO\\ CO\cdot NMe\end{array}\!\!>C<\!\!\begin{array}{l}NMe\cdot CO\\ CO—NMe\end{array} + NH_3 + H_2O.$$

Hypocaffeine is not formed when methylcarbamide is fused with 5-hydroxy-1 : 3-dimethylhydantoylamide, or yet by heating dimethylcarbamide with caffuric acid alone or in presence of solvents, but can be synthesised together with oxytetramethyluric acid by heating dimethylcarbamide with 5-hydroxy-1-methylhydantoylmethylamide at 150° for eight to ten minutes whilst hydrogen chloride is passed through the mixture.

A *spiro*-dihydantoin is not formed by the decomposition of 7 : 9-dimethyluric-acid-glycol, as the rupture then occurs at the 8 : 9 position only. These facts are in perfect harmony with Biltz's views on the stability of the C·N union (*loc. cit.*, p. 324), when methyl is attached to the nitrogen. The formation of *spiro*-hydantoins is to be expected only when the uric acid is alkylated in position 3. Fischer's hypoethyltheobromine (Abstr., 1883, 357) is undoubtedly 1 : 9-*dimethyl-7-ethyl* spiro-5 : 5-*dihydantoin*.

Further support for the constitutional formula for hypocaffeine is afforded by an examination of the decomposition products of caffoline, namely, dimethylcarbamide or cholesterophan and methylcarbamide, from which it is argued that caffoline must be 1 : 3 : 6-*trimethylallantoin* (annexed formula), the formula of which is in harmony with most of the properties described by Fischer.


$$^{2}\mathrm{CO}<\begin{matrix}\overset{3}{\mathrm{N}}\mathrm{Me}\cdot\overset{4}{\mathrm{C}}\mathrm{O}\\ \underset{1}{\mathrm{N}}\mathrm{Me}\cdot\underset{5}{\mathrm{C}}\mathrm{H}\cdot\underset{6}{\mathrm{N}}\mathrm{Me}\cdot\underset{7}{\mathrm{C}}\mathrm{O}\cdot\underset{8}{\mathrm{N}}\mathrm{H}_2\end{matrix}$$

Caffoline and acetic anhydride yield acetylacecaffeine, carbon dioxide, and acetamide: $C_7H_{12}O_3N_4 + (CH_3\cdot CO)_2O = C_8H_{13}O_3N_3 + CO_2 + CH_3\cdot CO\cdot NH_2$, and the acetyl derivative when heated with concentrated hydrochloric acid yields acecaffeine hydrochloride, from which the free base is formed by the action of magnesium oxide and extracting the dry mass with benzene. The constitution 5-*methylamino*-1 : 3-*dimethylhydantoin*,  $\mathrm{CO}<\begin{matrix}\mathrm{NMe}\cdot\mathrm{CO}\\ \mathrm{NMe}\cdot\mathrm{CH}\cdot\mathrm{NHMe}\end{matrix}$, is suggested for acecaffeine, and this agrees with its basic properties, with the readiness with which it can be oxidised to cholesterophan, and with the formation of methylamine, dimethylcarbamide, and glyoxylic acid on hydrolysis.

Caffoline can be synthesised by evaporating an aqueous solution of acecaffeine hydrochloride and potassium cyanate to dryness on the water-bath.

Free acecaffeine condenses readily with alkyl carbimides or thiocarbimides, yielding alkylated allantoins and thioallantoins, and this appears to be an extremely convenient method for the preparation of these types of compounds.

It is pointed out that the oxidation of uric acid and its monomethyl derivatives cannot be due to the intermediate formation of *spiro*-hydantoins, as, according to such a scheme, both 1-methyl and 9-methyluric acids should yield 3-methylallantoin, and the 3-methyl and 7-methyl acids should yield 1-methylallantoin, whereas Fischer and Ach (Abstr., 1900, i, 63) have shown that 3-methylallantoin is formed from the 1- and 7-methylated acids, and 1-methylallantoin from the 3- and 9-methylated acids.

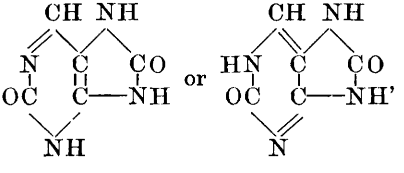
Hypocaffeine has m. p. 185—186° (corr.), and 1 : 3 : 6-trimethylallantoin (caffoline), m. p. 197° (corr.). Hypocaffeine can also be obtained from 5-chloro-1 : 3 : 7-trimethyl*iso*uric acid (Abstr., 1911, i, 168) and the corresponding 5-alkyloxy-compounds, but this method is not so convenient as Fischer's. In the alkylation of silver hypocaffeine by methyl iodide, the yield of oxytetramethyluric acid is only about 25—30%, and appreciable quantities of free hypocaffeine are formed. This is attributed to the conversion of a portion of the methyl iodide into hydrogen iodide and ethylene. When ethyl iodide is used, the silver compound is not alkylated. It has not been found possible to oxidise trimethyluric acid to a trimethylallantoin.

1 : 3 : 6 : 8-*Tetramethylallantoin*, $C_8H_{14}O_3N_4$, is readily formed when acecaffeine and methylcarbimide in benzene solution are sealed in a glass tube and left for twelve hours; it is also formed by the action of barium hydroxide solution on oxytetramethyluric acid. It absorbs water rapidly, yielding a monohydrate, which crystallises in rectangular prisms, m. p. 92°, after sintering at 85°. The anhydrous compound has m. p. 112—113°.

8-*Phenyl*-1 : 3 : 6-*trimethylallantoin*, $C_{13}H_{16}O_3N_4$, obtained from phenylcarbimide and acecaffeine in benzene solution and in the absence of moisture, crystallises from ethyl acetate, and has m. p. 197—198°. 7-*Thio*-1 : 3 : 6 : 8-*tetramethylallantoin*, $C_8H_{14}O_2N_4S$, crystallises from benzene in prisms, m. p. 158—159°. 7-*Thio*-1 : 3 : 6-*trimethyl*-8-*ethylallantoin*, $C_9H_{16}O_2N_4S$, has m. p. 135°, and is not readily desulphurised. J. J. S.

Purines. II. An Isomeride of Xanthine; 2 : 8-Dioxypurine. CARL O. JOHNS (*Amer. Chem. J.*, 1911, **45**, 79—87).—In an earlier paper (Abstr., 1909, i, 192) an account was given of 2:8-dioxy-6-methylpurine, which was prepared by the condensation of 5 : 6-diamino-2 : 4-methylpyrimidone with carbamide. 2 : 8-Dioxypurine has now been obtained in a similar manner.

2 : 8-*Dioxypurine* (annexed formulæ), obtained in a yield of 92% of the theoretical by heating a mixture of 5 : 6-diamino-2-pyrimidone (Johnson, Johns, and Heyl, Abstr., 1906, i, 771) and carbamide at 180—190°, resembles xanthine (2 : 6-dioxypurine) in many respects, and gives the murexide reaction. If carbon dioxide is passed into a solution of the substance in potassium hydroxide, or if a solution in a mineral acid is poured into water, the free base is precipitated. 2 : 8-Dioxypurine can be distinguished from xanthine by means of its *sodium* salt, which forms stout prisms containing $4H_2O$. The *hydrochloride*, *dinitrate*, and *ammonium* and *potassium* salts are also described; the last-mentioned crystallises with $2H_2O$.



5 : 6-Diamino-2-pyrimidone can be obtained in a yield of 65% of the theoretical by reducing 5-nitrocytosine with ferrous hydroxide; its *hydrochloride*, $C_4H_6ON_4,2HCl$, *sulphate*, $C_4H_6ON_4,H_2SO_4,H_2O$, and *nitrate*, $C_4H_6ON_4,4HNO_3$, are described. When this compound is heated with sulphuric acid of 20% strength in a sealed tube at 140—150°, it is converted into *iso*barbituric acid. E. G.

Quadriurates. RUDOLF KOHLER (*Zeitsch. physiol. Chem.*, 1911, **70**, 360—387).—Attempts were made to prepare the quadriurates first described by Bence Jones (this Journ., 1862, **15**, 201) by mixing saturated sodium biurate solution with a primary phosphate, and by introducing uric acid into hot acetate solutions of varying concentration. The salts were also sought for in snake excrement. The salts have not the composition $H_2C_5H_2O_3N_4,MHC_5H_2O_3N_4$ attributed to them by Bence Jones, but appear to be a mixture of primary urate and uric acid in the proportion of 1 : 1. By varying the concentration of the acetate solution, mixtures varying in concentration to biurate may be obtained. It is shown that this is in agreement with theoretical considerations.

The hydrolysis by water is not characteristic of the so-called quadriurates, as some do not show it at all, whereas some biurates are hydrolysed. It is due to the partial absorption of acid during the formation of the salt: this passes out into water and causes decomposition. The same reasoning applies to the decomposition of snake excrement by water, and to simultaneous precipitation of biurate and uric acid from human urine, as witnessed by the decrease in acidity after the formation of sediment. E. F. A.

Action of Azoimide on the Carbylamines. E. OLIVERI-MANDALÀ and B. ALAGNA (*Gazzetta*, 1910, **40**, ii, 441—444. Compare Abstr., 1910, i, 343).—By the action of azoimide on the corresponding carbylamines, other homologous tetrazoles can be prepared in the manner already described for 1-methyltetrazole. 1-*Ethyltetrazole*, $C_3H_6N_4$, is a liquid, b. p. 155—156°/14 mm.; it forms a stable *platinichloride*, $(C_3H_6N_4)_2PtCl_4$. 1-Phenyltetrazole (compare Freund and Paradies, Abstr., 1901, i, 770) has m. p. 65—66°. R. V. S.

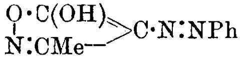
The Course of the Sandmeyer Reaction. GUSTAV HELLER and WALTER TISCHNER (*Ber.*, 1911, **44**, 250—255. Compare Abstr., 1910, i, 240).—The authors have investigated the velocity of decomposition of benzenediazonium chloride, and also of *o*- and *p*-toluenediazonium chlorides, in aqueous hydrochloric acid solution in the presence of cuprous chloride by measuring the rate of evolution of nitrogen.

It is found that the velocity depends not only on the temperature and concentration both of the acid and of the diazonium compound, but also to a great extent on the nature of the diazonium compound itself, slight changes in the constitution producing considerable differences in the course of the decomposition; catalytic influences also play a considerable part in determining the rate of decomposition.

In the case of benzenediazonium chloride, free nitrous acid and also excess of cuprous chloride influence the decomposition in a marked, but irregular, manner. With *p*-toluenediazonium chloride, the velocity at the beginning of the reaction is very small, and then gradually increases; this increase is followed by a gradual diminution in the rate of decomposition, and, finally, by a rapid rise to a maximum, when the reaction quickly comes to an end.

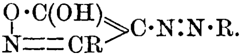
In the case of *o*-toluenediazonium chloride, the rate of decomposition is very slow at first, then rises rapidly to a maximum in about two hours, and slowly diminishes. F. B.

o-Arylazo-compounds of Heterocyclic Phenols: 3-Methyl-4-arylazo-5-hydroxy*iso*oxazole.

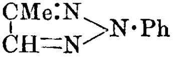
CARL BÜLOW and ARNULF HECKING (*Ber.*, 1911, **44**, 238—250).—Knorr and Reuter's 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole,  $\begin{array}{l}\text{O}\cdot\text{C(OH)}\\ \text{N:CMe}-\end{array}\!\!>\text{C}\cdot\text{N:NPh}$ (Abstr., 1894, i, 371; compare Schiff, Abstr., 1896, i, 83), can be readily prepared by the addition of an aqueous solution of sodium acetate and hydroxylamine hydrochloride to a boiling alcoholic solution of ethyl benzeneazoacetoacetate. It dissolves in alkalis, and is reprecipitated by carbon dioxide. The *silver* salt, $C_{10}H_8O_2N_3Ag$, when slowly heated, has m. p. 208—210° (decomp.). The sodium salt, $C_{10}H_{18}O_2N_3Na,H_2O$, was prepared by Schiff and Viciani (Abstr., 1897, i, 444), who considered it to be sodium β-oximino-α-phenylhydrazonoacetoacetate,

$$HO\cdot N:CMe\cdot C(N\cdot NHPh)\cdot CO_2Na.$$

The authors find, however, that this sodium salt loses one molecule of water of crystallisation when kept in a vacuum over sulphuric acid, and is readily hydrolysed with the formation 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole; when treated with hydrochloric acid, it yields the original heterocyclic phenol (compare Schiff and Viciani, *loc. cit.*).

These facts are in contradiction to the view that the solubility of 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole in alkalis is due to the rupture of the *iso*oxazole ring with the formation of salts of oximinophenylhydrazonoacetoacetic acid, and support the contention of Bülow and Haas (Abstr., 1910, i, 902) that the products obtained by the action of diazonium salts on 3-substituted *iso*oxazolones are azo-derivatives of heterocyclic phenols:  $\begin{array}{l}\text{O}\cdot\text{C(OH)}\\ \text{N}{=\!=}\text{CR}\end{array}\!\!>\text{C}\cdot\text{N:N}\cdot\text{R}.$

The *iso*oxazolones themselves are also represented by the hydroxylic and not the ketonic formulæ.

When 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole is boiled with concentrated potassium hydroxide solution, 2-phenyl-4-methyl-2:1:3-triazole,  $\begin{array}{l}\text{CMe:N}\\ \text{CH}{=\!=}\text{N}\end{array}\!\!>\text{N}\cdot\text{Ph}$ (von Pechmann, Abstr., 1888, 1287), and α-methylglyoxal-α-oxime-β-phenylhydrazone are produced. The authors consider that the first stage in this reaction consists in the rupture of the *iso*oxazole ring and the formation of

$$NaO\cdot N:CMe\cdot C(N_2Ph):C(ONa)_2,$$

which then loses sodium carbonate, yielding the oxime-hydrazone.

α-Methylglyoxal-α-oxime-β-phenylhydrazone,

$$HON:CMe\cdot CH:N\cdot NHPh,$$

forms yellow crystals, m. p. 147—148°, which become yellowish-brown on keeping; it reduces silver nitrate and Fehling's solutions, and gives an intense reddish-violet coloration when its solution in concentrated sulphuric acid is treated with ferric chloride or potassium dichromate. When heated with phenylhydrazine, it is converted into methylglyoxalosazone, NHPh·N:CMe·CH:N·NHPh (von Pechmann, Abstr., 1887, 1103).

4-p-*Nitrobenzeneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{10}H_8O_4N_4$, is prepared by the interaction of equal molecular quantities of nitric acid and 4-benzeneazo-5-hydroxy-3-methyl*iso*oxazole in concentrated sulphuric acid solution; it forms felted needles, m. p. 176—177°, dissolves in strong sulphuric acid with a greenish-yellow colour, and does not give the Bülow reaction for hydrazones.

4-*Dinitrobenzeneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{10}H_7O_6N_5$, prepared in a similar manner from two mols. of nitric acid, crystallises in yellow leaflets, m. p. 184—185°.

4-o-*Tolueneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{11}H_{11}O_2N_3$, is prepared by the gradual addition of an aqueous solution of hydroxylamine and sodium acetate to a boiling alcoholic solution of ethyl *o*-tolueneazoacetoacetate; it has m. p. 154—155°, and dissolves in alkalis with a yellow colour.

4-*p*-Tolueneazo-5-hydroxy-3-methyl*iso*oxazole, $C_{11}H_{11}O_2N_3$, obtained in a similar manner from ethyl *p*-tolueneazoacetoacetate, crystallises in yellow needles, m. p. 203°(Schiff: 202°).

4-m-*Xyleneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{12}H_{13}O_2N_3$, forms orange-yellow needles, m. p. 124—125°; its salts with alkalis are decomposed by carbon dioxide.

4-α-Naphthaleneazo-5-hydroxy-3-methyl*iso*oxazole, $C_{14}H_{11}O_2N_3$, crystallises in brick-red leaflets, m. p. 172—173° (Schiff: 168—170°), and dissolves in concentrated sulphuric acid with a deep bluish-red colour.

4-*β-Naphthaleneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{14}H_{11}O_2N_3$, forms stout, brownish-yellow needles, m. p. 201—202°; its solutions in strong sulphuric acid have a reddish-orange colour.

By the interaction of sodium acetate, hydroxylamine hydrochloride and ethyl *o*-carboxybenzeneazoacetoacetate in alcoholic solution, *ethyl α-o-carboxybenzeneazo-β-oximinoacetoacetate*,

$$HON{:}CMe{\cdot}CH(N_2{\cdot}C_6H_4{\cdot}CO_2H){\cdot}CO_2Et,$$

is produced. The latter compound has m. p. 207—208°, and yields 4-o-*carboxybenzeneazo-5-hydroxy-3-methyl*iso*oxazole*, $C_{11}H_9O_4N_3$, yellow leaflets, m. p. 232°, when boiled in glacial acetic acid solution.

Ethyl nitrocarboxybenzeneazoacetoacetate, $C_{13}H_{13}O_7N_3$, obtained by nitrating ethyl carboxybenzeneazoacetoacetate, crystallises in felted, yellow needles, m. p. 188—189°; the *oxime*, $C_{13}H_{14}O_7N_4$, has m. p. 222°, and could not be converted into the corresponding *iso*oxazolone.

F. B.

The State of Aggregation of Matter. I—III. SAMUEL B. SCHRYVER (*Proc. Roy. Soc.*, 1910, *B*, **83**, 96—123).—I. *Action of Salts in Heterogeneous Systems and the Nature of the Globulins.*—When formaldehyde acts on a solution of Witte's peptone, a precipitate is formed. This precipitation can, however, as Sollman has shown, be inhibited by the presence of salts. The titration of the mixture by alkali, even in the absence of precipitate formation, shows that the formaldehyde has acted on the amino-groups with the formation of methyleneimino-peptones. The inhibitory action of salts on precipitate formation can, however, be explained if the methyleneimino-peptones undergo polymerisation or condensation to form more complex molecules, and behave in the same way as methyleneasparagine behaves, according to the investigations of Schiff. If the unpolymerised or uncondensed methyleneimino-peptones are of such complexity as to form colloidal solutions, they can adsorb salt molecules from solution, which sterically inhibit their reactions with one another and prevent the formation of the insoluble complexes. A quantitative investigation of the inhibitory action of a large number of salt solutions showed that (with certain explicable exceptions), those which possessed the greatest power in this respect were the best solvents of the globulins. This suggested an explanation of the nature of these substances which are soluble in salt solution, but insoluble in water. The author gives reasons for supposing that the undissolved globulins are aggregates formed by the combination of a carboxyl group in one molecule with an amino-group in another, by means of which a salt is formed which undergoes a slight, but definite, hydrolysis in the presence of water. Owing to adsorptions of salt, the dissociated globulin molecules are sterically inhibited from reaggregation; the more readily a salt is adsorbed, the greater the solvent or (diaggregating) capacity as regards the globulin. The results indicate that owing to their adsorption capacities, chemical reactions of colloids do not follow the ordinary laws of mass action. The solvent capacity of salts for globulins can be correlated with two physical properties of their aqueous solutions, namely, their surface tensions and their viscosities; the higher the surface tension and the viscosity of a salt, the smaller its solvent capacity for the globulins. The influence of the former property can be deduced from a general study of adsorption phenomena, and of the latter by an extension of Noyes and Whitney's and of Nernst's generalisations on the rate of action in heterogeneous systems, with the assumption of the existence of a diffusion layer at the limiting surfaces. Salts also exert similar action in systems other than those containing proteins. Thus, the critical solution temperature of phenol and salt solutions is shown to be a function of the surface tension of the latter. Furthermore, the solubility of certain crystalline substances in salt solutions, especially of amphoteric substances, is shown to follow similar laws to the globulins. The surface tensions and viscosities of a series of salt solutions, together with the solubility of edestin and serum-globulin in these solutions, are tabulated.

II. *Action of Formaldehyde on Witte's Peptone.*—It is shown that the precipitate is formed from the more complex constituents of the peptones. Owing to the acidic nature of the methyleneimino-peptones, the salts of the weaker acids exert a greater inhibitory capacity on precipitate formation than would be deduced from their surface tensions and viscosities, as double decomposition can take place.

III. *The Solubility of Phenol and Certain Crystalline Substances in Salt Solutions.*—The solubilities of *dl*-leucine, *dl*-phenylalanine, caffeine, benzamide, and *p*-toluidine in the series of salt solutions employed in the investigations on the globulins are tabulated.

S. B. S.

Organic Colloids. S. J. Levites (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 4—8).—Observations are recorded in reference to the solubility and precipitability of proteins and the adsorption of tannin by gelatin.

Glutin is readily soluble in solutions of iodides and thiocyanates; casein in solutions of potassium iodide, sodium thiocyanate, potassium nitrate, and sodium phosphate. Aqueous pyridine is a good solvent for various proteins. Glutin and casein are both insoluble in water and in anhydrous pyridine, but dissolve in water-pyridine mixtures, the maximum solubility corresponding with a solvent of the composition $C_5H_5N + 2H_2O$. Glutin and Witte's peptone are readily soluble in formamide, and the solutions can be diluted with water without precipitation. The formamide and aqueous pyridine solutions of the proteins are very viscous.

In regard to the precipitation of proteins, it has been found that Witte's peptone and gelatin are precipitated by cadmium iodide in very dilute solution. Solutions of zinc and cadmium sulphates only give rise to a slight opalescence when added to Witte's peptone, and have no effect on a gelatin solution.

From experiments on the adsorption of tannin by gelatin from tannin solutions of different concentrations, it has been found that the proportion of adsorbed substance diminishes as the concentration increases. For a given solution the adsorption increases with the period of swelling of the gelatin. In presence of an electrolyte (potassium aluminium sulphate), the adsorption of tannin by gelatin is diminished, and the influence of the concentration of the tannin solution on the magnitude of the adsorption is very greatly reduced.

H. M. D.

Methylation of Gelatin. Zdenko H. Skraup and B. Böttcher (*Monatsh.*, 1910, 31, 1035—1050).—The authors find that gelatin contains a small quantity of methyl in the form of the groups ·OMe and ⁝NMe, and that the percentage of methyl, in both forms, increases on methylation.

When hydrolysed, the methyl derivative yields histidine and arginine in quantities amounting to 10% of those furnished by gelatin itself, traces of glutamic acid, and no lysine; leucine, alanine, glycine, pyrrolidinecarboxylic acid, and phenylalanine were also found amongst the products of hydrolysis. The hexone bases and glutamic acid are thus destroyed on methylation, whereas the leucine, alanine, etc., remain unchanged.

Comparing these results with those obtained in the case of casein (Abstr., 1909, i, 748), the authors draw the conclusion that the arrangement of the glutamic acid residue in the latter compound is different from that in gelatin.

Methylgelatin, prepared by boiling a solution of gelatin in alcoholic potassium hydroxide with methyl iodide, forms an amorphous, yellow mass, which, when powdered, is almost white; it is soluble in water, and is precipitated on the addition of ammonium sulphate. The xanthoprotein reaction is more marked than with ordinary gelatin. F. B.

The Pepsin-chymosin Question. J. F. B. VAN HASSELT (*Zeitsch. physiol. Chem.*, 1910, **70**, 171—185).—The experiments quoted bear against the view that pepsin and rennin (chymosin) are one and the same substance. It is possible to obtain preparations which exhibit only one action; anti-substances also inhibit differently the two enzymatic actions. W. D. H.

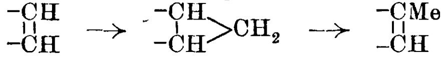
Diastase and Commercial Lecithin Preparations. HERMAN LAPIDUS (*Biochem. Zeitsch.*, 1910, **30**, 39—55).—The amount of action was determined by estimating the reducing sugars formed (calculated as maltose, for which the author has worked out tables). Wohlgemuth's iodine method was not available, owing to the action of this substance on the lecithin. The lecithin inhibits the action of ptyalin to a marked extent, but not to a relatively greater extent when small amounts of saliva are employed as compared with its inhibitory action on larger amounts of saliva. There does not appear, therefore, to be any evidence of combination between saliva and lecithin. The inhibitory influence is more marked at room temperature than at body temperature. The action of lecithin on pancreas diastase is similar, although here there is not such a marked difference between the action at room temperature and body temperature. With serum diastase, the results obtained are somewhat complicated, as the amount of diastase in the serum alters (increases) with age and diminishes after extraction with ether. The lecithin in this case diminishes the action at room temperature; at body temperature it sometimes increases and sometimes diminishes the action. Generally the action is weakly inhibitory. If, however, the serum which has been extracted with ether is employed, lecithin markedly increases the diastatic action. The above experiments were carried out with ox-serum. In human serum (from placenta) the diastatic action was weak, but was increased by addition of lecithin. Similar results were obtained with syphillitic sera, in which the diastatic action is stronger than in the normal.
S. B. S.

Hæmoglobin as a Peroxydase. GABRIEL BERTRAND and FELIX ROGOSINSKI (*Compt. rend.*, 1911, **152**, 148—151; *Bull. Soc. chim.*, 1911, [iv], **9**, 149—152. Compare Wolff and Stoecklin, Abstr., 1910, i, 802).—The peroxydase character of oxyhæmoglobin is also shared by carboxyhæmoglobin and cyanohæmoglobin; it appears, therefore, not to be due to the ability of oxyhæmoglobin to part with oxygen, but to depend on the presence of iron in the molecule. W. O. W.

Extraction of Zymase by Simple Maceration. A. VON LEBEDEFF (*Compt. rend.*, 1911, **152**, 49—51).—It is not necessary to employ Buchner's method to obtain a preparation of zymase from yeast. The solution obtained by macerating one part of dried yeast with 2·5—3 parts of water, on filtering through paper after being allowed to remain overnight, has greater activity and stability than that prepared by the usual method. W. O. W.

Organic Chemistry.

Action of Formaldehyde on Petroleum Distillates: Formation of Liquid Condensation Products. Alexander M. Nastukoff and K. L. Maljaroff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1596—1604).—On treating the fraction of ordinary kerosene of b. p. 200—250° with its own volume of formalin and 0·75 time its volume of sulphuric acid, the authors obtained, in addition to solid condensation products, also liquid condensation products of b. p. above 250°. These products, amounting to 19% of the weight of the kerosene, have very high formolite numbers (compare Abstr., 1904, i, 801). The fraction of the liquid products b. p. 186—188°/50 mm. has the formula $C_{15}H_{28}$, the formolite number 105, $D^{21·5}_{21·5}$ 0·8498, and n_D^{23} 1·4703; its viscosity is 2·07 compared with that of the original kerosene fraction as unity, or, in Engler degrees, 6·57 at 21°. The reaction of formation of these liquid products is regarded as a union of the methylene group of the formaldehyde with the $-C{:}C-$ group of the original naphthene or olefine, the instability of the trimethylene ring thus formed leading to the re-formation of a double linking, thus:



$$\begin{matrix}-CH\\ \| \\ -CH\end{matrix} \longrightarrow \begin{matrix}-CH\\ | \\ -CH\end{matrix}\!\!>\!CH_2 \longrightarrow \begin{matrix}-CMe\\ \| \\ -CH\end{matrix}$$

The solid condensation products mentioned above are soluble in benzene, toluene, etc., and are termed soluble formolites. T. H. P.

Methyl*iso*propylethylene [δ-Methyl-Δ^β-amylene]. A. Gorsky (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1356—1358).—By converting methyl*iso*butylcarbinol, obtained by the action of acetaldehyde on magnesium *iso*butyl chloride, into the corresponding iodide or chloride, and treating the latter with alcoholic alkali hydroxide, the author obtains an hexene, C_6H_{12}, b. p. 57—58·5°/760 mm., D_4^{20} 0·6706, n_D^{20} 1·3883. If, however, the methyl*iso*butylcarbinol is prepared by reducing mesityl oxide in aqueous ether by means of sodium, the hexene has the constants: b. p. 57—59°/740 mm., D_4^{20} 0·6703, n_D^{20} 1·3884. This hydrocarbon, which gives *iso*butyric acid on oxidation, and is probably δ-methyl-Δ^β-amylene, is accompanied by a small proportion of another, possibly δ-methyl-Δ^α-amylene. T. H. P.

Action of Hypochlorous Acid on Ethylene Hydrocarbons. [Mlle] A. Umnova (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1530—1543).—The action of hypochlorous acid on βδ-dimethyl-Δ^β-amylene yields: (1) *γ-chloro-βδ-dimethyl-Δ^α-amylene*, $CH_2{:}CMe\cdot CHCl\cdot CHMe_2$, a colourless liquid, b. p. 44—45°/30 mm, D_0^0 0·9229, D_0^{20} 0·9083. The corresponding alcohol, *βδ-dimethyl-Δ^α-penten-γ-ol*,

$$CH_2{:}CMe\cdot CH(OH)\cdot CHMe_2,$$

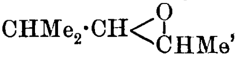
is a viscous liquid, b. p. 77—79°/21 mm., 154—156°/ordinary pressure, D_0^0 0·8599, D_0^{20} 0·8427, giving an *acetyl* derivative, $C_9H_{16}O_2$, b. p. 169—171°. On heating with 0·5% sulphuric acid solution, the alcohol in converted into di*iso*propyl ketone. (2) The *chlorohydrin*, $OH\cdot CMe_2\cdot CHCl\cdot CHMe_2$, which was not obtained pure, and is apparently formed as an intermediate product. These results are analogous to those obtained by Lwoff (*J. Russ. Phys. Chem. Soc.*, 1884, 16, 469), Scheschukoff (Abstr., 1884, 1276; 1885, 645), and Kondakoff (Abstr., 1886, 136), by treating various unsaturated hydrocarbons with gaseous chlorine.

γ-Chloro-βδ-dimethyl-Δ^{α}-amylene is also obtained by the action of chlorine on βδ-dimethyl-Δ^{β}-amylene.

The action of hypochlorous acid on βδδ-trimethyl-Δ^{β}-amylene yields (1) *γ-chloro-βδδ-trimethyl-Δ^{α}-amylene*, $CH_2{:}CMe\cdot CHCl\cdot CMe_3$, b. p. 53—54°/20 mm., D_0^0 0·9199, D_0^{20} 0·9042, n_D^{20} 1·4473. The corresponding alcohol, $CH_2{:}CMe\cdot CH(OH)\cdot CMe_3$(?), b. p. 75—77°/12 mm., 173—175°/ordinary pressure, D_0^0 0·8685, D_0^{20} 0·8556, forms an *acetyl* derivative, $C_{10}H_{18}O_2$, b. p. 187—188°, 83—85/20 mm. This alcohol could not be converted into the isomeric ketone by means of dilute sulphuric acid, so that its structure is somewhat uncertain. (2) Possibly a chlorohydrin, which could not be isolated. γ-Chloro-βδδ-trimethyl-Δ^{α}-amylene is also obtained by the action of chlorine on βδδ-trimethyl-Δ^{β}-amylene.

δ-Iodo-β-methylpentane, $CHMeI\cdot CH_2\cdot CHMe_2$, prepared by the action of hydrogen iodide on methyl*iso*butylcarbinol, has b. p. 75—77°/60 mm., D_0^0 1·4412, D_0^{20} 1·4201.

δ-Methyl-Δ^{β}-amylene, $CHMe{:}CH\cdot CHMe_2$, obtained by the action of alcoholic potassium hydroxide on the preceding compound, has b. p. 58—59°, D_0^0 0·6874, D_0^{20} 0·6695.

The action of hypochlorous acid on δ-methyl-Δ^{β}-amylene yields the chlorohydrin, $OH\cdot CHMe\cdot CHCl\cdot CHMe_2$, which was not isolated in a pure state, but was converted, by distilling with potassium hydroxide, into the *oxide*,  $CHMe_2\cdot CH{<}\begin{matrix}O\\ |\\ CHMe\end{matrix}$, a colourless liquid, b. p. 99—100°. The corresponding *β-methylpentane-γδ-diol*,

$CHMe_2\cdot CH(OH)\cdot CHMe\cdot OH$,

has m. p. 48—49°, b. p. 194—196°. T. H. P.

Course of the Intramolecular Transformations of Alkyl Bromides and the Question of the Cause of Equilibrium in Reversible Reactions.

ARTHUR MICHAEL and HANS LEUPOLD (*Annalen*, 1911, **379**, 263—332. Compare Faworsky, Abstr., 1907, i, 741).—The vapour densities of *iso*butyl bromide and *tert.*-butyl bromide have been determined by Blackman's and by V. Meyer's method. The results by both methods prove that at 184° only 3% of the *iso*butyl derivative, but about 50% of the tertiary compound, is dissociated. Using the Blackman apparatus, the volume of vapour of the tertiary compound agreed with the normal vapour density during the first minute, but gradually increased during half an hour owing to slow dissociation. The authors confirm Meyer and Pond's conclusion (Abstr., 1885, 1033; compare Konowaloff, *ibid.*, 1886, 9) that the dissociation is not affected by the nature of the walls of the glass vessel or by the introduction of asbestos, sand, or powdered glass. When mercury is present, a small amount of a white solid, probably mercuric bromide, is formed in the case of the tertiary compound, but the amount is so small that it does not affect the volume of vapour. An interesting observation was made during the determination of the vapour density of *iso*butyl bromide by Victor Meyer's method. In our experiment the stopper of the small Hofmann bottle stuck, and the bromide was not vaporised until the liquid had been some minutes in the hot tube. The result indicated appreciable dissociation, due to the partial conversion of the *iso*- into the *tert.*-butyl bromide.

Formation of the tertiary bromide cannot be detected after heating the *iso*bromide at 80° for three hundred hours or even after boiling (b. p. 91·2—91·5°) for fifty hours. At 92—95°, however, in sealed tubes 3% is tranformed after thirty hours, and at 110° the reaction proceeds fifteen times as quickly as at 92—95°. The rate of transformation appears to depend on the diameter of the tube in which the liquid compound is heated; with narrow tubes the reaction proceeds much more slowly than with wider ones at all temperatures between 110 and 235°. The velocity does not depend on the dimensions of the gaseous phase, as stated by Eltekoff, but on the size of the liquid surface. The reaction proceeds much less readily when all the substance is in the form of vapour; for example, when the *iso*butyl bromide is heated at 140° for fourteen hours in the form of vapour no appreciable amount of tertiary bromide is formed, whereas after one hour at the same temperature in the liquid form (diam. of tube 6 mm.) 55% of the tertiary compound is formed. The equilibrium between the *iso*- and *tert.*-bromides is reached when 74% of tertiary compound is formed, and this equilibrium holds for practically all temperatures between 140° and 262°. At the higher temperatures, even at 235°, decomposition occurs, as proved by the darkening in colour and the evolution of hydrogen bromide on opening the tubes, but the amount of this decomposition does not appear to be appreciable (1% after two hours). The conversion of *tert.*-butyl bromide into the *iso*butyl bromide proceeds extremely slowly, even after fourteen hours at 140° in the liquid condition the formation of the *iso*-compound could not be detected, whereas the *iso*bromide under similar conditions has reached the equilibrium point. The transformation of the tertiary compound begins at 184°, and even after thirty-five hours only 7% is transformed into the *iso*-compound. At 235° and 262° equilibrium is attained after ten and two hours respectively, and the equilibrium mixture has the same composition as when the *iso*bromide is heated, namely, 74% of tertiary and 26% of *iso*bromide. In this reaction the liquid surface does not appear to have any appreciable affect.

The conversion of propyl into *iso*propyl bromide has been studied, but as the temperatures required are much higher, the results are not so favourable. The reaction begins at 184°, and after one hour at 237° and 262° the amounts of *iso*propyl bromide are 17% and 20% respectively; as distinct signs of decomposition were observed, attempts were not made to determine the equilibrium point. The influence of the size of the liquid surface is observable, but not marked, and at 237° and 262° the transformation takes place more readily in the gaseous than in the liquid phase. This may be due to the partial decomposition of the propyl bromide (compare Aronstein, Abstr., 1883, 172). The transformation of *iso*propyl into propyl bromide takes place extremely slowly whether examined in the gaseous or liquid condition.

The transformation of active amyl bromide into the tertiary compound takes place quickly at 184°, and at this temperature is influenced to an appreciable extent by the dimensions of the liquid surface, but at 237° the effect of this factor is not so marked. At 184° the velocity of transformation is much smaller with the vapour than with the liquid, whereas at 237° and 262° the reverse is true.

Transformation of inactive primary *iso*amyl bromide could not be detected at 262°, and the investigation of Wichnegradsky's secondary *iso*amyl bromide (*Annalen*, 1877, **190**, 328), which is a mixture of secondary and tertiary bromide, showed that the mixture is comparatively stable, as after ten hours at 184° only 6% of the secondary compound was transformed. Tertiary amyl bromide at 166° is fairly rapidly transformed into a mixture of secondary and primary active *iso*amyl bromides. The dimensions of the liquid surface have an appreciable effect, and equilibrium appears to be attained when 12% of secondary and 7% of primary bromide are formed.

The conclusion is drawn that dissociation does not play an important part in the transformations, as many of these begin at temperatures at which dissociation does not take place, and in many cases the transformation proceeds more slowly in the vapour phase, where dissociation is marked, than in the liquid phase, where the dissociation is less. The reactions are regarded as intramolecular changes, and an attempt is made to explain the changes by reference to Michael's entropy law, to intramolecular neutralisation, and to the relative affinities of the atoms.

It is suggested that the influence of the liquid surface may be due to the fact that in the conversion of the liquid into vapour an intermediate state is formed, which is extremely sensitive to energy changes.

One of the most interesting points established is that the velocity of transformation of the butyl bromides is not in harmony with the dynamical views of equilibrium in the case of a balanced reaction. In the case of *iso*- and *tert.*-butyl bromides, equilibrium is reached at any temperature between 140° and 265° when 74% of tertiary and 26% of *iso*-bromide is present, and hence the values of K and K' for the transformation of *iso*- into tertiary and tertiary into *iso*bromide should be in the ratio 3 : 1, whereas the ratio is much greater. It is shown that when a mixture of 74% tertiary and 26% *iso*butyl bromide is heated at 110°, 140°, or 237°, no apparent change occurs in the liquid state, but that at 237° in the state of vapour a diminution of tertiary bromide is noticed, probably due to decomposition.

It is suggested that the equilibrium is static, and not dynamic, and that it does not depend on the two velocity constants, but merely on the relative amounts of the two bromides. Such a mixture may correspond with the maximum of entropy under the conditions of the experiment.

Full details are given for the preparation of the various alkyl bromides, and methods have been worked out for estimating the amounts of the isomerides present in mixtures. *tert.*-Butyl bromide can be estimated in the presence of the *iso*bromide by shaking for fifteen minutes with fifty times its weight of water, filtering, and estimating the hydrobromic acid in the filtrate by means of standard silver nitrate and ammonium thiocyanate. A mixture of *n*- and *iso*-propyl bromide is shaken with *N*/10-aqueous silver nitrate solution for three hours, when the whole of the *iso*-compound is decomposed together with about 2·7% of the *n*-compound. With mixtures of primary, secondary, and tertiary *iso*amyl bromides, the amount of tertiary compound can be determined by shaking with water, and then the secondary by shaking with silver nitrate solution for three hours.

J. J. S.

Boiling Points of Aqueous Solutions of *iso*Propyl Alcohol and of Trimethylcarbinol.

ANTONY G. DOROSCHEWSKY and E. V. POLJANSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1448—1452).—For the b. p./760 mm. of *iso*propyl alcohol and trimethylcarbinol, the authors find the respective values 82·44° and 82·55°, which are in good agreement with those obtained by Young and Fortey (Trans., 1902, **81**, 735). The boiling points of aqueous solutions containing from 0 to 100% of *iso*propyl alcohol or trimethylcarbinol were determined at 700 mm., 760 mm. and 800 mm., the results being tabulated along with the corresponding values of *dt*/*dp*.

For the aqueous solutions of these alcohols, as with those of methyl, ethyl, and propyl alcohols, the ratio of the absolute boiling points at two definite pressures is constant. Thus with *iso*propyl alcohol, the mean values of $T/760 : T/700$, $T/760 : T/800$, and $T/800 : T/700$ are 1·0060, 0·9963, and 1·0097 respectively, the limiting values being 1·0058—1·0062, 0·9962—0·9966, and 1·0095—1·0100. For trimethylcarbinol these ratios have the values 1·0059 (1·0058—1·0060), 0·9963 (0·9962—0·9966), and 1·0095 (1·0094—1·0096) (compare Abstr., 1910, ii, 266).

T. H. P.

Oxide from Decamethyleneglycol.

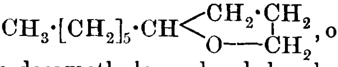
I. V. EGOROFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1655—1665).—Attempts to prepare the hydroxy-acid, $OH\cdot[CH_2]_9\cdot CO_2H$, from ethyl sebacate resulted in the formation of a considerable proportion of the glycol, $OH\cdot[CH_2]_{10}\cdot OH$. In order to convert this glycol into the unsaturated hydrocarbon,

$$CH_2{:}CH\cdot[CH_2]_6\cdot CH{:}CH_2,$$

(1) the corresponding dibromo-compound was treated with alcoholic potassium hydroxide solution, and (2) the glycol itself was treated with sulphuric acid. But neither reaction gave rise to the hydrocarbon, the diethyl ether of decamethylene glycol being obtained in the first case and an oxide in the second.

ακ-Dibromodecane, $CH_2Br\cdot[CH_2]_8\cdot CH_2Br$, has m. p. 27°.

The *diethyl ether* of *decamethyleneglycol*, $OEt\cdot[CH_2]_{10}\cdot OEt$, is an oily liquid, b. p. 257—260°, D_0^0 0·8500.

Decamethylene αδ-oxide,  $CH_3\cdot[CH_2]_5\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CH_2\end{matrix}$, obtained by the action of sulphuric acid on decamethylene glycol, has b. p. 197—199°, D_0^0 0·8694. The action of phosphorus pentachloride or pentabromide on the oxide shows that the latter readily undergoes conversion into the unsaturated alcohol, $OH\cdot CH_2\cdot[CH_2]_2\cdot CH{:}CH\cdot[CH_2]_4\cdot CH_3$. In the case of the pentachloride, this alcohol is then transformed into an unsaturated halogen derivative, but with the pentabromide the hydrogen bromide developed readily combines with the unsaturated compound, giving $a\delta$-dibromodecane, $C_{10}H_{20}Br_2$, as a yellow oil. T. H. P.

New Method for the Preparation of Ketone-Alcohols. OTTO DIELS and JACOB MARTIN JOHLIN (*Ber.*, 1911, **44**, 403—410).—Ketone-alcohols of the type $OH\cdot CMeR\cdot COMe$ are obtained in the form of their phenylmethylhydrazones by the interaction of magnesium alkyl halides and diacetylphenylmethylhydrazone. The reaction takes place according to the following scheme:

$$COMe\cdot CMe{:}N\cdot NMePh + RMgX + H_2O \longrightarrow CMeR(OH)\cdot CMe{:}N\cdot NMePh.$$

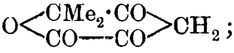
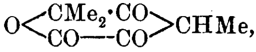
On boiling the phenylmethylhydrazones with water and benzaldehyde, the keto-alcohols are obtained in the free condition.

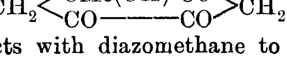
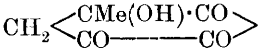
β-Methylbutan-β-ol-γ-one (trimethylketol), $OH\cdot CMe_2\cdot COMe$, is a colourless liquid, b. p. 142°/750 mm., D^{13} 0·9595 (compare Schmidt and Austen, Abstr., 1903, i, 2); the *phenylmethylhydrazone*, $OH\cdot CMe_2\cdot CMe{:}N\cdot NMePh$, is a yellow liquid, b. p. 144—145°/12 mm., D^{20} 1·0179.

γ-Methylpentan-γ-ol-δ-one (*dimethylethylketol*), $OH\cdot CMeEt\cdot COMe$, a colourless liquid, b. p. 154°/750 mm., D^{13} 0·9496, is purified by converting it into the *semicarbazone*, $OH\cdot CMeEt\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2$, m. p. 150°, and distilling this in steam with phthalic anhydride; the *phenylmethylhydrazone*, $OH\cdot CMeEt\cdot CMe{:}N\cdot NMePh$, is a yellow, oily liquid, b. p. 158—159°/12 mm., D^{13} 1·0146.

β-Phenylbutan-β-ol-γ-one (*phenyldimethylketol*), $OH\cdot CMePh\cdot COMe$, forms a colourless, oily liquid, b. p. 122—123°/8 mm., D^{17} 1·0801; the *phenylmethylhydrazone*, $OH\cdot CMePh\cdot CMe{:}N\cdot NMePh$, crystallises in white prisms, m. p. 68°.

Attempts to prepare ketoses of the type $OH\cdot CRR'\cdot CO\cdot CH_2\cdot OH$, by brominating the above ketone-alcohols and replacing the bromine by the hydroxyl group, were unsuccessful.

The interaction of equal molecular quantities of ethyl oxalate, β-methylbutan-β-ol-γ-one, and sodium ethoxide leads to the formation of a compound, which the authors consider to be a *lactone* of the following structure:  $O<\genfrac{}{}{0pt}{}{CMe_2\cdot CO}{CO\text{—}CO}>CH_2$; it crystallises in prisms, m. p. 113°, gives a dark purple coloration with ferric chloride, and, on treatment with diazomethane in ethereal solution, yields a crystalline *methyl* derivative,  $O<\genfrac{}{}{0pt}{}{CMe_2\cdot CO}{CO\text{—}CO}>CHMe$, having m. p. 89°.

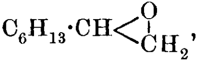
When the condensation of β-methylbutan-β-ol-γ-one and ethyl oxalate is effected by means of two molecules of sodium ethoxide, an *isomeride*, having the formula  $CH_2<\genfrac{}{}{0pt}{}{CMe(OH)\cdot CO}{CO\text{———}CO}>CH_2$ (?), is obtained; this has m. p. 179°, and reacts with diazomethane to form a *methyl* derivative,  $CH_2<\begin{matrix}CMe(OH)\cdot CO\\ CO\text{———}CO\end{matrix}>CHMe$, which crystallises in slender needles, m. p. 70°, having the appearance of glass wool. F. B.

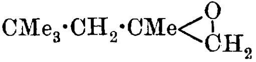
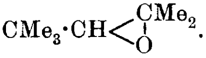
Action of Ultra-violet Light on Glycerol. Henri Bierry, Victor Henri, and Albert Ranc (*Compt. rend.*, 1911, **152**, 535—536. Compare Abstr., 1910, i, 652).—When exposed to ultra-violet light in the presence of air, glycerol is decomposed with production of glyceraldehyde and other unidentified substances which combine with phenylhydrazine. If the decomposition takes place in presence of an alkali, β-acrose is formed. In both cases the yields are small, but may be improved by the addition of salts of iron, cobalt, and especially uranium, which act as catalysts (compare Neuberg, Abstr., 1908, i, 915; Berthelot and Gaudechon, this vol., ii, 170).

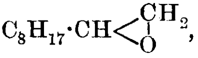
W. O. W.

Oxidation of Unsaturated Compounds with Organic Peroxides. I. Nikolaus Prileschaeff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1387—1418).—Most of this paper has been already published (Abstr., 1910, i, 86), the new work being as follows:

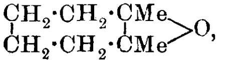
Measurements of the velocity of decomposition of benzoylhydroperoxide were made in chloroform, ether, and carbon tetrachloride at 25°. In the first two of these solvents the reaction is of the first order, the values of K being 0·06507 (chloroform) and 0·06469 (ether). In carbon tetrachloride the decomposition proceeds much more rapidly.

Octylene oxide,  $C_6H_{13}\cdot CH<\begin{matrix}O\\ |\\ CH_2\end{matrix}$, readily reacts with acetyl chloride, giving the *compound*, $C_8H_{16}O,AcCl$, b. p. 117—118°/21 mm., D_0^0 1·0066, D_{15}^{15} 0·9951. With zinc chloride, the oxide readily undergoes isomerisation, giving a compound, b. p. 172—173°, showing intense aldehydic properties and forming a semicarbazone, m. p. 67°. The glycol, $C_8H_{16}(OH)_2$, b. p. 135—136°/20 mm., formed on hydration of the oxide, is a vaselin-like mass, m. p. 45—46°, and gives a *diacetyl* derivative, b. p. 139—140°/24 mm., D_0^0 0·9874, D_{16}^{16} 0·9739.

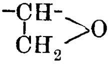
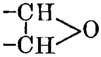
The interaction of di*iso*butylene and benzoylhydroperoxide results in the formation of the two oxides:  $CMe_3\cdot CH_2\cdot CMe<\begin{matrix}O\\ |\\ CH_2\end{matrix}$ and  $CMe_3\cdot CH<\begin{matrix}CMe_2\\ |\\ O\end{matrix}$.

The glycol formed from decylene oxide,  $C_8H_{17}\cdot CH<\begin{matrix}CH_2\\ |\\ O\end{matrix}$, forms a vaselin-like mass, and yields a *diacetyl* derivative, $C_{10}H_{20}O_2Ac_2$, b. p. 163°/22 mm., D_0^0 0·9330, D_{16}^{16} 0·9195. Under the influence of zinc chloride, the oxide undergoes isomerisation to an aldehyde, b. p. 209—210°/762 mm. or 125—126°/50 mm.

$\beta\gamma$-Dimethyl-Δ^β-butylene and benzoylhydroperoxide yield $\beta\gamma$-dimethyl Δ^β-butylene oxide.

Dimethylcyclohexene oxide,  $\begin{matrix}CH_2\cdot CH_2\cdot CMe\\ |\qquad\qquad |\\ CH_2\cdot CH_2\cdot CMe\end{matrix}>O$, prepared from dimethyl*cyclo*hexene and benzoylhydroperoxide, has b. p. 150—151°/

756·6 mm., D_0^0 0·9340, D_4^{16} 0·9201, n_D^{16} 1·44676. The corresponding *glycol*, $C_8H_{14}(OH)_2$, m. p. 92—92·5°, gives a *monoacetyl* derivative, b. p. 128—129/22 mm., D_0^0 1·0680, D_4^{16} 1·0545, n_D^{16} 1·4689.

These results show that benzoylhydroperoxide may be used as a reagent for hydrocarbons of the ethylene series, and that, under the conditions employed by the author, it allows of the estimation of the double linkings in a hydrocarbon with considerable accuracy. The character of the unsaturated complex present in the hydrocarbon is also indicated, since, under the isomerising influence of acids, oxides containing the group  $\begin{matrix}-CH-\\ | \\ CH_2\end{matrix}\!>\!O$ yield aldehydes, $\cdot CH_2\cdot CHO$, whilst those containing  $\begin{matrix}-CH\\ | \\ -CH\end{matrix}\!>\!O$ yield ketones, $-CH_2\cdot CO-$.

Oxidation of phenylacetylene by means of benzoylhydroperoxide yields phenylacetic acid. T. H. P.

Two-Component Systems. I. Ether–Hydrobromic Acid, Ether–Chlorine, and Ether–Bromine.

Douglas McIntosh (*J. Amer. Chem. Soc.*, 1911, **33**, 71—75).—Studies of these two-component systems were made in connexion with the investigation of the compounds formed by organic substances containing oxygen with the halogens and halogen acids. The results are tabulated and plotted as curves.

On adding liquid hydrogen bromide to ether, the f. p. (−118°) is slightly depressed, and then the compound, $C_4H_{10}O,HBr$, separates; further addition raises the m. p., and at −40° the ether hydrobromide melts. On adding more of the acid, the f. p. falls until the eutectic point is reached, when a mixture of solid hydrogen bromide and a compound separates; this occurs at about −115°, and the liquid contains 12% of ether. The f. p. then rises to −86°, the m. p. of hydrogen bromide. Ethyl ether forms two compounds with hydrogen bromide, namely, $C_4H_{10}O,HBr$ (Archibald and McIntosh, Trans., 1904, **85**, 919) and $C_4H_{10}O,2HBr$, in which the oxygen may be regarded as sexavalent; the latter compound has m. p. −46°, but the f.-p. curve shows no break at this temperature.

With chlorine, ether yields the compound $C_4H_{10}OCl_2$ (Trans., 1905, **87**, 784), which melts at −51°; further addition of chlorine lowers the m. p. to −103°. Pure chlorine melts at −101·5°.

Ether unites with bromine to form the compound $C_4H_{10}OBr_2$ (*loc. cit.*). The addition of bromine depresses the f. p. of this compound, and at −119·5°, solid ether and ether dibromide separate. The dibromide melts at −38°, and, on adding more bromine, the compound $C_4H_{10}OBr_3$, m. p. 23°, is produced (Schutzenberger, *Annalen*, 1864, **129**, 50). On continuing to add bromine, the f. p. falls, and at −20° bromine and the tribromide separate. E. G.

Influence of the Medium on the Formation of Oxonium Dibromides of Simple Ethers.

Wladimir W. Tschelinzeff and W. K. Konowaloff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1614—1630. Compare Abstr., 1909, i, 353).—The authors have studied the formation of the oxonium dibromide corresponding with ethyl ether in benzene, light petroleum (b. p. 81—82°/746·7 mm., D_4^{20} 0·7789), chloroform, carbon tetrachloride, ethyl bromide, ethylene dibromide, bromobenzene, and carbon disulphide at 20°, at which temperature the reaction occurs practically instantaneously in absence of solvent. The reactions were followed calorimetrically, the heats of solution of ether, bromine, and the oxonium dibromide in the various solvents being determined separately.

The results show that all these solvents exert intense retarding influences on the reaction. Such influence is conditioned by the friction between the molecules of bromine and ether and the solvent, this being complicated by the different mutual actions occurring between the reacting and resultant compounds and the solvent. The formation of a new phase in the shape of a layer of the dibromide observed in four of the eight cases exerts only a very small influence on the subsequent velocity of the reaction. In the order of increasing magnitude of their retarding effects, the solvents are carbon disulphide, carbon tetrachloride, ethyl bromide, light petroleum, ethylene dibromide, chloroform, benzene, bromobenzene. T. H. P.

Uranyl Nitrate and the Nature of its Ethereal Solution. PAUL LEBEAU (*Compt. rend.*, 1911, **152**, 439—441. Compare Löwenstein, Abstr., 1909, ii, 736).—Uranyl nitrate appears to form at least two compounds with ethyl ether, these being deposited in crystals when an ethereal solution of the salt is dried over calcium nitrate and cooled at about −10° and −70° respectively. The dihydrate remains when the ether is removed from these compounds by a current of dry air. W. O. W.

Action of Magnesium and Aliphatic Halogen Derivatives on Ethyl Chlorocarbonate. I. MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1582—1589).—The author has studied the formation of triethylcarbinol from magnesium, ethyl chlorocarbonate and ethyl bromide (or iodide), and that of tripropylcarbinol from magnesium, ethyl chlorocarbonate, and propyl bromide. The results show that this method affords a good means of obtaining tertiary aliphatic alcohols. The following complex compounds, formed in the second phase of the reaction (compare Reformatsky, *J. Russ. Phys. Chem. Soc.*, 1903, **35**, 1157; Houben, Abstr., 1903, i, 825), have been obtained: (1) $C_7H_{15}\cdot O\cdot MgBr$; (2) $CEt_3\cdot O\cdot MgI,Et_2O$, which was obtained crystalline; (3) when propyl bromide was employed, the complex could not be isolated in a pure state. T. H. P.

Preparation of Aluminium, Chromium, and Iron Formates. GEORG MUTH (D.R.-P. 228668).—The usual method of preparing aluminium, chromium, and iron formates by treating the metallic hydroxide with free formic acid is expensive, and the following alternative is recommended. The metallic hydroxides in the form of a paste are treated with an aqueous solution of aluminium fluoride (50%), the calculated quantity of sodium formate added and the insoluble sodium aluminium fluoride separated by filtration; the solution is concentrated, and the product obtained in a pure condition:

$$Al_2F_6 + Al_2F_6 + 6H\cdot CO_2Na = Al_2F_6,6NaF + Al_2(CO_2H)_6$$
$$Al_2F_6 + Cr_2F_6 + 6H\cdot CO_2Na = Al_2F_6,6NaF + Cr_2(CO_2H)_6.$$

F. M. G. M.

Direct Esterification by Catalysis; Preparation of Benzoic Esters PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **152**, 358—261).—The reactions that take place when a mixture of an alcohol and acid are passed over a heated catalyst of the type MO may be represented by the equations: (1) $MO + 2R\cdot CO_2H = (R\cdot CO_2)_2M + H_2O = MO + R\cdot CO\cdot R + H_2O + CO_2$; (2) $MO + 2C_nH_{2n+1}\cdot OH \rightleftarrows M(O\cdot C_nH_{2n+1})_2 + H_2O$; (3) $M(O\cdot C_nH_{2n+1})_2 = MO + H_2O + C_nH_{2n}$; (4) $M(O\cdot C_nH_{2n+1})_2 + 2R\cdot CO_2H = MO + 2R\cdot CO_2\cdot C_nH_{2n+1}$.

The formation of an ester according to (4) is limited by decomposition of the unstable salt by water, whereby the alcohol is regenerated. All the possible products are formed when acetic acid and alcohol are acted on by thoria at 400°. If the acid employed, however, is one that does not readily decompose according to (1), the principal reaction is that of ester formation, (2) and (3) being negligible. Thus, methyl, ethyl, propyl, *iso*butyl, *iso*amyl, and allyl benzoates are obtained in practically theoretical yield by passing a mixture of the acid (1 mol.) and the alcohol (12 mols.) over thoria at 350°. The mixture of vapours is best obtained by allowing a solution of the acid in the alcohol to drop through a capillary tube. *iso*Propyl benzoate has also been obtained in good yield in spite of the readiness with which *iso*propyl alcohol forms propylene. *cyclo*Hexanol gave a good yield of benzoate.

Similar results have been obtained with the toluic acids, but the method is less advantageous in these cases, owing to the sparing solubility of the acids. W. O. W.

Direct Esterification and Hydrolysis by Catalysis. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **152**, 494—497. Compare preceding abstract).—Titanium oxide is even more effective than thorium oxide in bringing about esterification when the vapour of an alcohol and an acid is passed over it at 280—300°. This is especially the case with acetic and propionic acids. The equilibrium limit of ester formation is very rapidly attained when the acid and alcohol are in molecular proportions. Thus, with acetic acid and *iso*butyl alcohol 69·5% of ester was formed, and with *iso*butyric acid and ethyl alcohol 71% was produced. These values are slightly higher than Menschutkin's for esterification at 155°. The process is complete with large excess of acid or alcohol.

This method cannot be applied to the preparation of formates, owing to the decomposition undergone by the acid; it has been successful, however, in the case of the acetates, propionates, butyrates, *iso*butyrates, *iso*valerates, and benzoates of methyl, ethyl, propyl, butyl, *iso*butyl, *iso*amyl, and benzyl alcohols. *Benzyl* iso*valerate* has b. p. 245°. The same syntheses can be effected by thorium oxide below 300°, but less advantageously.

Complete hydrolysis occurs when an ester is mixed with excess of water vapour and passed over titanium oxide at 280—300°.

W. O. W.

Preparation of Derivatives of ββ-Dialkylpropionic Acids. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P. 228667).—The preparation of some ββ-dialkylpropionamides has been previously described; it is now shown that therapeutically active amides can be obtained by the action of alkalicyanoacetic ester on halogenated dialkylcarbinols, followed by hydrolysis and subsequent elimination of carbon dioxide. Ethyl cyanoacetate (113 parts) was mixed with absolute alcohol (200 parts), and slowly treated with sodium ethoxide (23 parts Na) in the same solvent; methylpropylcarbinyl bromide (151 parts) was then added, the mixture boiled until neutral, the alcohol removed by distillation, and the oily *ethyl methylpropylcarbocyanoacetate* [*α-cyano-β-methylhexoate*],

$$C_3H_7\cdot CHMe\cdot CH(CN)\cdot CO_2Et,$$

separated by treatment with water; it has b. p. 175°/35 mm. The foregoing ester was hydrolysed with alcoholic sodium hydroxide, and the *α-cyano-β-methylhexoic acid* separated by the addition of acid; this, on prolonged warming with somewhat concentrated acid, yielded *α-methylbutylmalonamic acid*, $CHMePr\cdot CH(CO\cdot NH_2)\cdot CO_2H$, which, at a temperature of 180°, was converted, by loss of carbon dioxide, into *β-methyl*-n-*hexoamide*, $C_3H_7\cdot CHMe\cdot CH_2\cdot CO\cdot NH_2$, m. p. 99°.

F. M. G. M.

Direct Synthesis of the Glycerides. ITALO BELLUCCI and R. MANZETTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 125—128).—The authors find that the direct synthesis of the glycerides may be effected with nearly theoretical yield by heating together equivalent quantities of glycerol and the fatty acid at a moderate temperature under reduced pressure. In these circumstances the water formed is removed, and the reaction rapidly proceeds to completion. In an instance cited, a yield of 95—98% of triolein was obtained in a few hours by heating together the theoretical quantities of oleic acid and glycerol under a pressure of 2 cm., the temperature being gradually raised from 160° to 260°, and special arrangements being made to prevent volatilisation of the reagents. The glycerides obtained in this way are pure, except for traces of glycerol and acid, which can be removed readily by washing them with water, and subsequently treating them in ethereal solution with calcium hydroxide. R. V. S.

Condensation of Halogen Compounds with Ethyl ββ-Dimethylglycidate. GEORGES DARZENS (*Compt. rend.*, 1911, **152**, 443—446).—The action of organomagnesium halides on ethyl ββ-dimethylglycidate has not led to the isolation of any definite compounds. If the corresponding zinc derivatives are employed, however, esters of the type $CHMe_2\cdot CR(OH)\cdot CO_2Et$ are obtained. Thus, on warming the ester with methyl iodide in toluene solution, in presence of the zinc–copper couple, and treating the product in the usual way, an 80% yield of *ethyl α-hydroxy-αβ-dimethylbutyrate*,

$$CHMe_2\cdot CMe(OH)\cdot CO_2Et,$$

is obtained. This is a liquid with a camphoraceous odour, b. p. 76°/20 mm., 172—173° under ordinary pressure. The acid resulting from hydrolysis has m. p. 70°; Perkin (Trans., 1896, **69**, 1486) gives m. p. 75—77°, but his compound may be isomeric with the author's.

From ethyl ββ-dimethylglycidate and ethyl iodide, *ethyl α-hydroxy-β-methyl-α-ethylbutyrate* was prepared. This has b. p. 76°/16 mm., 180—181° under ordinary pressure; the corresponding *acid* has m. p. 76°, b. p. 140°/22 mm. Allyl bromide gave *ethyl α-hydroxy-β-methyl-α-allylbutyrate*, b. p. 90°/21 mm., 198—199° under ordinary pressure; the corresponding *acid* has m. p. 57°, b. p. 147°/21 mm.

The molecular transformation involved in the formation of these substances may be explained by supposing that the glycidic ester first undergoes change into a pyruvic ester, which then acts normally with the zinc compound. Ethyl dimethylpyruvate was detected amongst the products of the reaction. W. O. W.

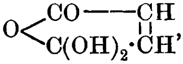
Action of the Chlorides of α-Alkyloxy-acids on Mixed Organo-metallic Zinc Compounds. Edmond É. Blaise and L. Picard (*Compt. rend.*, 1911, **152**, 446—447. Compare this vol., i, 175).—A discussion of the action of organo-zinc halides on higher homologues of the acid chlorides dealt with in a previous communication.

α-Ethoxyhexoic acid on treatment with thionyl chloride furnishes *α-ethoxyhexoyl chloride*, b. p. 69°/9 mm.; *γ-ethoxyheptane*, b. p. 151°/750 mm., results when this is acted on by zinc ethyl iodide. Esters of α-alkyloxy-αα-dialkyl acids are best prepared by treating ethyl oxalate with phosphorus pentachloride, and allowing a zinc alkyl halide to act on the product. The reaction proceeds in accordance with the equation: $OEt\cdot CCl_2\cdot CO_2Et + 2ZnRI = ZnI_2 + ZnCl_2 + OEt\cdot CR_2\cdot CO_2Et$. The ester is contaminated with ethyl oxalate, which may be removed by shaking with ammonia. *α-Ethoxy*iso*butyric acid*, $OEt\cdot CMe_2\cdot CO_2H$, b. p. 99°/14 mm., was prepared in 84% yield by this process. *α-Ethoxy-α ethylbutyric acid* has b. p. 120·5°/13 mm. It was not possible to prepare the chlorides of these acids by the action of thionyl chloride, this reagent leading to profound decomposition. W. O. W.

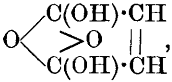
Synthesis of β-Hydroxy-α-ethylbutyric Acid. I. Matschurevitsch (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1576—1582).—β-Hydroxy-α-ethylbutyric acid, previously prepared by Waldschmidt (Abstr., 1878, 136) and by Marshall and Perkin (Trans., 1891, **59**, 870), may be obtained by Reformatsky's method by the interaction of acetaldehyde, ethyl α bromobutyrate, and zinc. Obtained in this way, the acid has the properties given by Waldschmidt, except that the silver salt is found to be unstable and readily soluble in water. On distillation, the acid is converted into α-ethylcrotonic acid. T. H. P.

Interchange of Alkyl Groups in Acid Esters. Telemachos Komnenos (*Monatsh.*, 1911, **32**, 77—88. Compare Abstr., 1910, i, 361, 708).—An extension of the previous investigations. Succinic acid and methyl hydrogen succinate are produced when ethyl succinate is added to a warm solution of sodium methoxide in methyl alcohol. The hydrolysis and subsequent partial esterification are unexpected, since the prolonged heating of ethyl succinate with alcoholic sodium ethoxide does not cause hydrolysis, but the formation of ethyl succinylsuccinate. Consequently ethyl succinate has been heated on the water-bath for forty hours with methyl-alcoholic sodium methoxide, but here, again, hydrolysis occurs, the chief product being sodium succinate; a small amount of a substance, m. p. 155°, probably methyl succinylsuccinate, is formed. When ethyl phenylacetate is heated for two hours on the water-bath with methyl-alcoholic sodium methoxide, methyl phenylacetate, b. p. 215°, D^{15} 1·050, is obtained, together with a little phenylacetic acid. Under similar conditions ethyl benzoate is partly hydrolysed and partly converted into methyl benzoate. This last example is important, in that it shows that the interchange of alkyl groups occurs in the esters of acids which do not contain an active methylene group. C. S.

Theoretical Consideration of the Isomerism of Fumaric and Maleic Acids. Boris Glasmann (*Pharm. Zentr.-h.*, 1911, **52**, 275—281).—The author suggests that the hypothetical ortho-dicarboxylic acid, $C(OH)_3\cdot CH\colon CH\cdot C(OH)_3$, may lose the elements of water in different ways, whereby maleic acid,

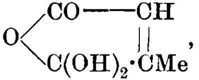


$O{<}\begin{array}{l}\mathrm{CO}\text{——}\mathrm{CH}\\ \qquad\qquad\ \ \|\\ \mathrm{C(OH)_2\cdot CH}\end{array}$, and fumaric acid,

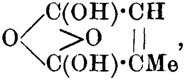


$O{<}\begin{array}{l}\mathrm{C(OH)\cdot CH}\\ \quad {>}O\quad \|\\ \mathrm{C(OH)\cdot CH}\end{array}$, are produced. It is shown that the preceding constitutions serve to account for the chemical behaviour of the two acids, the conversion of the one into the other, and their formation by the oxidation of furan derivatives; also an attempt is made to explain the formation of racemic acid and of mesotartaric acid by the oxidation by potassium permanganate of fumaric acid and maleic acid respectively.

It is remarked that, in addition to maleic and fumaric acids, yet a third acid, having the constitution $CO_2H\cdot CH\colon CH\cdot CO_2H$, may be derived from the hypothetical ortho-dicarboxylic acid; for example, the constitutions



$O{<}\begin{array}{l}\mathrm{CO}\text{——}\mathrm{CH}\\ \qquad\qquad\ \ \|\\ \mathrm{C(OH)_2\cdot CMe}\end{array}$,



$O{<}\begin{array}{l}\mathrm{C(OH)\cdot CH}\\ \quad {>}O\quad \|\\ \mathrm{C(OH)\cdot CMe}\end{array}$, and

$CO_2H\cdot CH\colon CMe\cdot CO_2H$

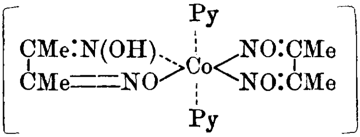
are proposed for citraconic, mesaconic, and itaconic acids respectively. C. S.

Chloral Chloroacetate. Emilio Gabutti (*Gazzetta*, 1911, **41**, i, 111—112).—In the description of this compound previously published (Abstr., 1900, i, 370), the boiling point (224°/760 mm.) of the pure substance was omitted by a printer's error. A direct comparison of the products respectively obtained by the method formerly given and by that of Wegscheider and Späth (Abstr., 1910, i, 155) has demonstrated their identity. R. V. S.

Investigations on Complex Compounds. VII. Complexes of the Dioxime Series. Leo A. Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1466—1487).—[With A. Postnikoff.]—Further investigations have been made on the diammino-base, $[Co2PyD_2H_2]OH$ (where $Py = C_5NH_5$), corresponding with dimethylglyoxime, which separates in the form of sparingly soluble, cinnamon-red crystals when the salts, $[Co2PyD_2H_2]X$, are treated with alkali hydroxide or ammonia. This base loses water, forming the anhydride,

$$[Co2PyD_2H],$$

on precipitation. The fact that its molecular conductivity is only $\mu = 7{\cdot}0$ for a dilution of 1000 litres confirms the co-ordination formula ascribed to it. On solution in acids, it again yields salts of the type $[Co2PyD_2H_2]X$. These transformations recall those occurring in the magenta series and with other colouring matters of similar constitution, and it may be that the loss of water is preceded by the migration of the hydroxyl group of the base from the external sphere to the cobalt atom of the inner sphere, thus creating the conditions for the loss of water and the formation of the anhydrous base. The latter probably has the annexed structure. In accordance with this structure, the free base conducts the electric current only to a slight extent; the conductivity increases very considerably with the dilution, but this is probably due to hydration of the anhydrous base. Aqueous solutions of the base exhibit a distinct alkaline reaction.

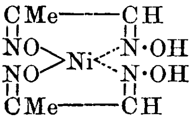


[With I. Kiréeff.]—The chloride and iodide of cobaltidihydroxylaminodimethylglyoxime were prepared. The *chloride*,

$$[Co2NH_2{\cdot}OHD_2H_2]Cl,$$

forms large, yellowish-brown crystals, readily soluble in water. The *iodide*, $[Co2NH_2{\cdot}OHD_2H_2]I$, forms dark yellowish-brown crystals, and, on dissociation, yields two ions. These salts may be kept for a long time, and even recrystallised without appreciable alteration.

[With Iv. Tischtschenko.]—The compound formed by nickel with the dioxime of methylglyoxal exists in a dark red, unstable form and a more stable orange one. These are possibly stereoisomerides, in which the methyl groups of the dioxime occupy either the annexed *syn*-position or the *anti*-position.



Cobaltiamminochloromethylglyoximine,

$$[CoNH_3ClD_2H_2],$$

obtained by the action of methylglyoxime on purpureocobalt chloride, forms a cinnamon-red, crystalline precipitate stable towards acids.

Cobaltidiamminomethylglyoximine chloride, $[Co2NH_3D_2H_2]Cl$, obtained by the action of excess of ammonia on the preceding compound, forms dark cinnamon-red plates. The corresponding *iodide* forms dark yellowish-brown crystals; the ease with which this compound is formed from the chloride by the action of potassium iodide indicates that the iodine is present in an ionisable condition, and this is confirmed by measurements of the electrical conductivity of the salt. The free *base*, $[Co2NH_3D_2H_2]OH$, forms a dark brown solution exhibiting distinct alkaline properties.

[With B. P. Afanaseeff.]—Investigation of the decomposition of

the nickel compounds of glyoxime, methylglyoxime, dimethylglyoxime, and methylethylglyoxime by hydrochloric, hydrobromic, nitric, and acetic acids shows that the stability of these compounds increases with the complexity of the substituent groups of the glyoxime.
T. H. P.

Photochemical Synthesis of Carbohydrates from Carbon Dioxide and Hydrogen in Absence of Chlorophyll. WALTHER LÖB (*Biochem. Zeitsch.*, 1911, **31**, 358—360).—A criticism of the recent work of Stoklasa and Zdobnický (this vol., i, 178). S. B. S.

Investigations of the Phosphorus Compounds of Seeds, Particularly Phytin. WŁAD. VORBRODT (*Bull. Acad. Sci. Cracow*, 1910, *A*, 414—511).—The author obtains from maize meal a solution which contains phytic acid; on evaporation, a yellow, viscous mass is left. When the solution is neutralised with barium hydroxide solution, an acid barium phytate crystallises out; this salt is white when dried in a stream of dry air, but yellow if dried more slowly. On analysis it was found that, for 6 atoms of carbon, only 5·5 of phosphorus were present, hence Posternak's formula is incorrect. Neutralisation of the acid with sodium or barium hydroxides in presence of various indicators showed that more than four hydroxyl groups occurred in the molecule, since more than four salts appeared to be formed.

On heating with water to 155°, phytic acid decomposes with formation of phosphoric acid and inositol.

Evidence was obtained of the presence of enzymes in the seed capable of splitting off phosphoric acid from the organic phosphorus compounds. E. J. R.

Contardi's Polyphosphoric Esters of Mannitol, Quercitol, Inositol, and Dextrose. PAUL CARRÉ (*Bull. Soc. chim.*, 1911, [iv], **9**, 195—199. Compare Abstr., 1905, i, 814, and Contardi, Abstr., 1910, i, 157, 609).—The author has repeated Contardi's experiments, and finds that his supposed polyphosphoric esters of mannitol, quercitol, inositol, and dextrose are in reality mixtures of phosphoric acid, barium dihydrogen phosphate, and the parent substances, or their decomposition products. T. A. H.

Digestive Ferments for Manninotriose and its Derivatives. HENRI BIERRY (*Compt. rend.*, 1911, **152**, 465—467. Compare Tanret, Abstr., 1902, i, 661; 1903, i, 606).—The gastro-intestinal juice of *Helix* readily hydrolyses stachyose, or manninotriose, one of the products of the partial hydrolysis of the sugar. In the latter case the final products are galactose (2 mols.) and dextrose (1 mol.), but an intermediate biose (dextrose-galactose) appears to be produced. The biose has not been isolated; it cannot be lactose, since lactase is without action on it.

The osazone of the trisaccharide undergoes hydrolysis in the same way. This compound has m. p. 122—124°, and not 192—194°, as stated by Neuberg and Lachmann (Abstr., 1910, i, 225): Tanret gives 122° *Manninotriosecarbamide*, $C_{18}H_{32}O_{15}:N \cdot CO \cdot NH_2,H_2O$, $[\alpha]_D^{15}$ +127·4°, is also hydrolysed by the above ferment, with formation of galactose. W. O. W.

Chemical Processes Occurring in the Preparation of Cellulose by the Sulphate Method. PETER KLASON and BROR SEGERFELT (*Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 6, 1—20).—The so-called sulphate method for the preparation of cellulose from wood consists in treatment of the latter with a lye containing chiefly sodium hydroxide and sodium sulphide. The chemical reactions taking place consist, for the most part, in the transformation of the gum-like carbohydrates into saccharinic acids, the latter neutralising the alkali. At the same time the lignin molecules are broken down into simpler ones, which also dissolve in the alkali because they contain hydroxyl groups; about one-fifth of the methoxy-groups in the lignin are also destroyed by saponification, thus increasing the amount soluble in the alkali.

The process of saponification in the boiling solutions give rise also to methyl alcohol, methyl mercaptan, and methyl sulphide, the methyl alcohol being formed in the greater quantity. With insufficient quantity of alkali, the quantity of methyl mercaptan increases; increasing quantity of alkali favours the formation of methyl sulphide. Under the same conditions, fir wood gives about twice as much methyl mercaptan as pine wood. Wheat straw contains fewer methoxy-groups than the woods, and gives less methyl mercaptan.

Both meta- and para-saccharinic acids are found in the liquors, together with a new form of *iso*saccharinic acid, to which the authors give the same sapin-*iso*saccharinic acid (sapin = fir); this latter acid constitutes the greater part of the saccharinic acids. Assuming that Nef's theory of the formation of the saccharinic acids is correct (Abstr., 1908, i, 5; 1910, i, 711), this points to the chief constituent of the gum-like carbohydrates in pine wood, being one of the following ketohexoses: *l*-fructose, *l*-pseudofructose, *l*-tagatose, or *d*-sorbose.

When the process of extraction is complete, about half of the hydrogen sulphide originally present in the lye is chemically combined with the lignin in the black liquors. Because of this, and because of the formation of volatile methyl-sulphur compounds, the sodium sulphide present in the lye is only gradually changed into the active sodium hydroxide. This explains the protecting action of alkali sulphide on the cellulose fibres. T. S. P.

The Nitrogenous Products of Alkaline Hydrolysis of Cellulose Nitrate. ERNST BERL and ANDOR FODOR (*Zeitsch. Schiess. Sprengstoffwesen*, 1910, **5**, 254—256, 269—273).—A discussion of the results obtained by various workers on cellulose during the past ten years. It is shown that by the alkaline hydrolysis and reduction of collodion and cellulose nitrate, aliphatic nitrogenous acids are produced, their decomposition products being demonstrable as hydrogen cyanide, hydroxylamine, ammonia, and nitrous acid.

The formation of a polysaccharide by the condensation of *n* molecules of a hexose is stated to take place according to the formula

$nC_6H_{12}O_6 - (n-1)H_2O$ (compare Kiliani, Abstr., 1908, i, 320), and the expression $(C_6H_{10}O_5)n$ as representing the cellulose molecule is to be considered erroneous. The action of an excess of sodium carbonate on an alcohol-ether solution of collodion wool yielded after two weeks' shaking together, a colourless nitrogenous compound soluble in alkalis with a yellow coloration; after a further period of several weeks two other gelatinous, dextrin-like substances were obtained.

The action of sodium ethoxide on a highly nitrated cellulose in acetone solution resulted in denitration, yielding the hygroscopic, brown sodium salt of a nitrogenous acid, which separated on acidification as an amorphous, flocculent mass.

Cellonic acid nitrate, $C_{24}H_{33}O_{16}(NO_3)_5$, was obtained as a colourless powder by the action of alcoholic potassium hydroxide (1·8 equivalents to each nitric acid residue) on collodion wool, and its formation from glucosidohexonic acid, $C_{24}H_{38}O_{21}$, was probably preceded by the removal of $5H_2O$ (3 by anhydridisation and 2 by lactonisation) from 2 mols. of hexonic acid; it decomposes at 163°; the *phenylhydrazone*, $C_{24}H_{33}O_{13}(NO_3)_5(C_6H_5N_2H)_3$, a brown, amorphous substance, and the p-*bromophenylhydrazone*, $C_{24}H_{33}O_{13}(NO_3)_5(C_6H_4Br{\cdot}N_2H)_3$, a brick-red powder, were also prepared. A molecular mixture of glucosidohexonolactone trinitrite and glucosidodihexonolactone trinitrite was isolated from the alcoholic mother liquors in the form of an orange-yellow, crystalline powder.

The hydrolysis of cellulose nitrate with ammonium sulphide in absolute alcohol yielded a voluminous precipitate, which after elimination of free sulphur was found to consist of hexonolactone (90%) and hydroxypyruvic acid (10%). F. M. G. M.

The Nitrogen-free Products from the Alkaline Hydrolysis of Cellulose Nitrate.

Ernst Berl and Andor Fodor (*Zeitsch. ges. Schiess. und Sprengstoffwesen*, 1910, 5, 296—297, 313—316. Compare *J. Soc. Chem. Ind.*, 1908, 27, 534; Abstr., 1908, i, 504, 505).—A detailed account of experiments on the detection and isolation of the nitrogen-free decomposition products obtained by the alkaline hydrolysis of cellulose nitrate. The relative proportions of the different acids formed were observed to vary according to the concentration of the alkali employed, a dilute solution yielding compounds containing 4—5 carbon atoms, whilst with concentrated alkali, acids with 1—3 carbon atoms predominated. The products detected were hydroxypyruvic acid, which was probably accompanied in the solution by its aldehydo-form, $CHO{\cdot}CH(OH){\cdot}CO_2H$, and the keto-form,

$$CH_2(OH){\cdot}CO{\cdot}CO_2H,$$

with malic, trihydroxyglutaric, malonic, tartronic, oxalic, glycollic, and dihydroxybutyric acids as secondary oxidation products.

The p-*nitrophenylosazone*, $C_{15}H_{12}O_6N_6$, a red, crystalline powder, m. p. 260°, and an *osazone*, m. p. 213—215°, were also prepared.

F. M. G. M.

Iso- and Hetero-poly-acids. III. The Basicity of Some Hetero-poly-acids.

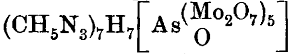
Arthur Rosenheim and Jacob Pinsker (*Zeitsch. anorg. Chem.*, 1911, 70, 73—85. Compare this vol., i, 109; ii, 116).—The extension of Werner's co-ordination theory to poly-acids by Miolati and Pizzighelli (Abstr., 1908, ii, 595) facilitates the correct formulation of these acids. Many hetero-poly-acids have 12 acid anhydride molecules associated with the acid containing the central atom. As it is probable that the dimolybdate and ditungstate radicles, $(Mo_2O_7)''$ and $(W_2O_7)''$, are often present, the formulæ of some "limiting" hetero-poly-acids and salts may be written:

$$\begin{array}{lll} H_5[IO_6] & H_7[PO_6] & H_8[SiO_6] \\ X_5[I(MoO_4)_6] & X_7[P(Mo_2O_7)_6] & X_8[Si(Mo_2O_7)_6] \\ X_5[I(WO_4)_6] & X_7[P(W_2O_7)_6] & X_8[Si(W_2O_7)_6]. \end{array}$$

Actually, molybdo-periodic acid and tungsto-periodic acid are known to be tribasic, and the corresponding hetero-silicic acids octobasic, but only salts of tribasic 12-molybdo- and 12-tungsto-phosphoric acids have hitherto been obtained.

It is now found that these, and the corresponding hetero-arsenic acid, yield heptabasic salts, which are proved by conductivity measurements to be normal, whilst the tribasic salts are acid.

The acid, $H_3PO_4(MoO_3)_{12},30H_2O$, is prepared by extracting an acidified solution of its salts with ether. A solution in water is then gradually mixed with a 10% solution of guanidinium carbonate, when a deep yellow, microcrystalline precipitate is formed, but dissolves on further addition of the carbonate to the warm solution. Crystals of the *heptabasic* salt, $(CH_5N_3)_7H_7[P(Mo_2O_7)_6],8H_2O$, separate on cooling, and have a greenish-yellow colour. The tribasic salt is prepared more conveniently by dissolving 12 mols. of molybdenum trioxide in a boiling solution of guanidinium carbonate (12 mols.), adding 1 mol. of phosphoric acid, and acidifying strongly with hydrochloric acid. This salt has then the composition $(CH_5N_3)_3H_7[P(Mo_2O_7)_6],10H_2O$. The conductivity of the sodium salt (which is more soluble in water) indicates the presence of acid hydrogen, whilst the conductivity of the heptabasic salt is that of a normal salt.

Two tribasic salts of an arsenomolybdic acid containing 12 mols. of molybdenum trioxide are known, but the new heptabasic *salt* contains only 10 mols. It is prepared similarly to the phosphate, and has the composition  $(CH_5N_3)_7H_7\left[As\genfrac{}{}{0pt}{}{(Mo_2O_7)_5}{O}\right],5H_2O$, but decomposes when recrystallised. The conductivity corresponds with its formulation as a normal salt.

It has not been found possible to obtain an octobasic molybdosilicate. The *guanidinium* salt has the composition

$$(CH_5N_3)_4H_8[Si(Mo_2O_7)_6],6H_2O,$$

and crystallises in deep yellow leaflets. When warmed with guanidinium carbonate, silica separates, and the filtrate deposits felted needles of *guanidinium molybdate*, $(CH_5N_3)_2H_2Mo_3O_{10},5H_2O$.

C. H. D.

The Compounds of Hydrated Metallic Salts with Hexamethylenetetramine. (Labile Hydrated Forms Fixed by means of an Organic Base.) II. GIUSEPPE A. BARBIERI and F. CALZOLARI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 119—125. Compare this vol., i, 184).—Compounds of other metallic salts have now been prepared by the method adopted in the case of the halides previously described.

Magnesium thiocyanate yields a compound,

$$Mg(SCN)_2,10H_2O,2C_6H_{12}N_4,$$

whilst the thiocyanates of manganese, iron, cobalt, and nickel give compounds of the type $M''(SCN)_2,4H_2O,2C_6H_{12}N_4$. The magnesium and manganese compounds can be recrystallised from water unchanged, but the others lose a molecule of hexamethylenetetramine, forming substances of the type $M''(SCN)_2,4H_2O,C_6H_{12}N_4$, which are isomorphous.

The nitrates of magnesium, manganese, cobalt, and nickel form isomorphous compounds of the general formula

$$M''(NO_3)_2,10H_2O,2C_6H_{12}N_4.$$

The perchlorates of the same metals form compounds of the type $M''(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, which are isomorphous, and can be recrystallised from water.

The *compound*, $Mg(SCN)_2,10H_2O,2C_6H_{12}N_4$, forms thin, colourless tablets, which show holosymmetry of the triclinic system [$a:b:c=0·9342:1:0·9223$; $\alpha=134°12'$, $\beta=47°4'$, $\gamma=120°56'$]. The *compound*, $Mn(SCN)_2,4H_2O,2C_6H_{12}N_4$, crystallises in colourless tablets, which exhibit holosymmetry of the tetragonal system [$a:c=1:1·0366$]. The *compound*, $Fe(SCN)_2,4H_2O,2C_6H_{12}N_4$, crystallises in colourless scales, which on recrystallisation yield the *compound*,

$$Fe(SCN)_2,4H_2O,C_6H_{12}N_4,$$

in canary-yellow crystals, which exhibit holosymmetry of the triclinic system [$a:b:c=1·4012:1:1·5723$; $\alpha=124°57'$, $\beta=29°54'$, $\gamma=121°36'$]. The *compound*, $Co(SCN)_2,4H_2O,2C_6H_{12}N_4$, forms lustrous, rose-coloured scales. On recrystallisation it yields the *compound*, $Co(SCN)_2,4H_2O,C_6H_{12}N_4$, in dark red, tabular crystals, which show holosymmetry of the triclinic system [$a:b:c=1·4232:1:1·6034$; $\alpha=128°23'$, $\beta=31°6'$, $\gamma=123°33'$]. The *compound*,

$$Ni(SCN)_2,4H_2O,2C_6H_{12}N_4,$$

is a green, crystalline powder. When recrystallised, it gives the *compound*, $Ni(SCN)_2,4H_2O,C_6H_{12}N_4$, in emerald-green, tabular crystals, which show holosymmetry of the triclinic system, and forms mixed crystals with the corresponding cobalt compound in all proportions.

The *compound*, $Mg(NO_3)_2,10H_2O,2C_6H_{12}N_4$, forms colourless, tabular crystals, which exhibit holosymmetry of the rhombic system [$a:b:c=0·8261:1:0·4813$]. The *compound*, $Mn(NO_3)_2,10H_2O,2C_6H_{12}N_4$, crystallises similarly, showing holosymmetry of the trimetric system [$a:b:c=0·8388:1:0·4894$. The *compound*, $Co(NO_3)_2,10H_2O,2C_6H_{12}N_4$, crystallises in rose-coloured scales, and forms solid solutions with the two preceding substances in all proportions. The *compound*,

$$Ni(NO_3)_2,10H_2O,2C_6H_{12}N_4,$$

forms emerald-green scales, and gives solid solutions in all proportions with the three preceding compounds.

The *compound*, $Mg(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, crystallises in small, colourless, lustrous needles. The *compound*, $Mn(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, crystallises similarly. The *compound*, $Co(ClO_4)_2,8H_2O,2C_6H_{12}N_4$, forms rose-coloured needles, and yields solid solutions with the analogous manganese and magnesium compounds.

The *compound*, $Ni(ClO_4),8H_2O,2C_6H_{12}N_4$, crystallises in green needles.

The crystallographic measurements were effected by E. Billows.

R. V. S.

Hydrated Additive Products of Metallic Dichromates. (Labile Hydrated Forms Fixed by means of an Organic Base.) III. GIUSEPPE A. BARBIERI and F. LANZONI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 161—164. Compare Barbieri and Calzolari, this vol., i, 184; also Parravano and Pasta, Abstr., 1907, i, 961).—Hexamethylenetetramine *compounds* of *magnesium*, *zinc*, *manganese*, *cobalt*, and *nickel dichromates* are readily obtained by acting on a concentrated solution of the acetates or sulphates of those metals with a concentrated solution of hexamethylenetetramine in the presence of potassium dichromate. For the most part they crystallise in lustrous scales, but may also be obtained in prisms. They are not very stable; even in the dark the base reduces the chromic acid, and in bright light the orange-red crystals become green superficially in a few minutes. Analysis shows that all the compounds have the composition: $M''Cr_2O_7,7H_2O,2C_6H_{12}N_4$, where M″ represents Mg, Zn, Mn, Co, or Ni, so that there is complete analogy to the mercuric cyanide compounds of Krüss and Unger (Abstr., 1895, ii, 355). R. V. S.

Compounds of Salts of [Metals of] the Rare Earths with Hexamethylenetetramine. GIUSEPPE A. BARBIERI and F. CALZOLARI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 164—169).—By the action of very concentrated solutions of hexamethylenetetramine on concentrated aqueous solutions of *cerium*, *lanthanum*, and *neodymium chlorides*, *compounds* of the type $M'''Cl_3,14H_2O,2C_6H_{12}N_4$ were obtained, whilst the *nitrates* of the same elements yielded substances of the type $M'''(NO_3)_3,8H_2O,2C_6H_{12}N_4$. *Yttrium* and *erbium chlorides* gave compounds of the form $M'''Cl_3,11H_2O,2C_6H_{12}N_4$, and the *nitrates* of these metals yielded products of the composition $M'''(NO_3)_3,10H_2O,2C_6H_{12}N_4$. All these compounds are crystalline, and are more hydrated than the corresponding simple salts of the same metals.

Crystallographic data are given in some cases (by E. Billows). The compound $NdCl_3,14H_2O,2C_6H_{12}N_4$ forms lilac-coloured, silky needles belonging to the triclinic system.

The compound $Nd(NO_3)_3,8H_2O,2C_6H_{12}N_4$ forms minute, lilac-coloured crystals, which show holosymmetry of the monoclinic system [$a:b:c = 0\cdot7336:1:0\cdot4329$; $\beta = 57°29\cdot5'$].

The compound $Er(NO_3)_3,10H_2O,2C_6H_{12}N_4$, like the other erbium and yttrium compounds described, is more exactly represented by a formula, $(Er,Y)(NO_3)_3,10H_2O,2C_6H_{12}N_4$, (Er,Y), having apparent atomic weight 140; it forms pale red crystals, which show holosymmetry of the monoclinic system [$a:b:c = 1\cdot1501:1:1\cdot4892$; $\beta = 57°$]. R. V. S.

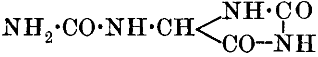
Combination of Amines with Acetylenic Ketones. Preparation of Ethylenic β-Substituted Amino-ketones. ÉMILE ANDRÉ (*Compt. rend.*, 1911, 152, 525—527).—The neighbourhood of a CN or CO_2R group to a triple linking confers on the compound the property of combining additively with primary and secondary amines (Moureu and Lazennec, Abstr., 1906, i, 956). The carbonyl group is effective in the same manner, acetylenic ketones of the type CR⋮C·COR′ (Abstr., 1910, i, 563) uniting readily with amines to form amino-ketones of the types $R\cdot C(NHR'')\colon CH\cdot COR'$ and $R\cdot C(NR''R''')\colon CH\cdot COR'$ respectively. These compounds are hydrolysed by acids with formation of an amine and a β-diketone.

When a primary amine acts on an acetylenic ketone, the principal reaction is one involving elimination of water. The mixtures rapidly blacken, however, and no definite condensation products have been isolated.

The following additive compounds have been prepared: α-cyclo*Hexylamino-α-phenyl-Δ$^{\alpha}$-penten-γ-one*, $C_6H_{11}\cdot NH\cdot CPh\colon CH\cdot COEt$, m. p. 100°. α-cyclo*Hexylamino-α-phenyl-Δ$^{\alpha}$-hexen-δ-one*, m. p. 75°. *Benzylaminostyryl phenyl ketone*, $CH_2Ph\cdot NH\cdot CPh\colon CH\cdot COPh$, m. p. 100°, *α-Diethylamino-α-phenyl-Δ$^{\alpha}$-penten-γ-one*, $NEt_2\cdot CPh\colon CH\cdot COEt$, m. p. 45°. *α-Diethylamino-α-phenyl-Δ$^{\alpha}$-hexen-δ-one*, m. p. 40°. *α-Dipropylamino-α-phenyl-Δ$^{\alpha}$-buten-γ-one*, $NPr_2^{\alpha}\cdot CPh\colon CH\cdot COMe$, m. p. 47°. *Diethylaminostyryl phenyl ketone*, $NEt_2\cdot CPh\colon CH\cdot COPh$, m. p. 63°; the corresponding *piperidyl* compound has m. p. 81°, and the *methylanilino*-compound, m. p. 87°. W. O. W.

Method of Characterising Certain Ureides [Carbamides].

HENRY J. H. FENTON and WILLIAM A. R. WILKS (*Proc. Camb. Phil. Soc.*, 1911, **16**, 64).—Methylfuril, $C_{11}H_8O_4$ (Trans., 1903, **83**, 187; Abstr., 1906, ii, 489), is a very delicate reagent for detecting certain carbamides. Minute quantities of the reagent and of the carbamide are mixed on a filter-paper and treated with a drop of fuming hydrochloric acid; an intense blue coloration is developed after a few seconds. Positive results are given by substances containing the open-chain $\cdot NH\cdot CO\cdot NH_2$ (carbamide, methylcarbamide, benzylcarbamide semicarbazide, oxaluric acid, biuret, and hydantoic acid); cyclic carbamides such as parabanic acid and hydantoin, and also oxamide, succinamide, *s*- and *as*-dimethylcarbamide do not respond to the test.

The positive result of the test given by allantoin is evidence in favour of the Grimaux formula:  $NH_2\cdot CO\cdot NH\cdot CH<\begin{array}{l}NH\cdot CO\\ \qquad\;\; |\\ CO-NH\end{array}$ (compare Biltz, Abstr., 1910, i, 594). C. S.

The Carbonyl Ferrocyanides. Their Extraction, Analysis, and Applications.

ÉMILE LECOCQ (*Bull. Soc. chim. Belg.*, 1911, **25**, 72—80).—In the extraction of ferrocyanides from the spent oxide of the gas purifiers, the filtrate from the insoluble calcium potassium ferrocyanide formed during the process contains any carbonylferrocyanide which may have been present in the spent oxide. Together with this carbonylferrocyanide there is also some calcium potassium ferrocyanide, calcium sulphate, calcium chloride, calcium thiocyanate, and potassium chloride. If this solution is concentrated to a gravity of 30° Bé., a granular mass separates, containing gypsum, the double ferrocyanide of calcium and potassium, and also calcium potassium carbonylferrocyanide. The latter salt deposits, because it is insoluble in the presence of the calcium salts contained in the mother liquor, and it may be dissolved from the the collected precipitate by treatment with warm water. After recrystallisation it has the formula

$$CaKFe(CO)C_6N_6,5H_2O,$$

and forms straw-coloured crystals with a pearly lustre.

In addition to the reactions of this compound described by Muller (Abstr., 1899, ii, 616), the reactions with the following salts are described: Cuprous, zinc, mercurous, mercuric, silver, thallium, vanadium, stannous, and platinum salts. The heat of combustion is 622 Cals. per gram-molecule, and the heat of formation, – 133 Cals.

The method of determining the amount of carbonylferrocyanides in the spent oxide is described in detail. The calcium potassium salt is extracted, essentially according to the method indicated above, the calcium precipitated as carbonate, and the resulting solution of the potassium salt titrated with a standard solution of copper sulphate, the end of the reaction being indicated when the solution no longer gives a violet colour with ferric salts.

Generally speaking, carbonylferrocyanides are only found in the spent oxide when Laming's mixture has been used in the purifying boxes. It is present as the violet-coloured ferric salt to the extent of 0·4—1·1%. This violet salt gives printing inks and paints which are very stable towards the action of light. T. S. P.

Organic Amalgams. Substances with Metallic Properties Composed in part of non-metallic Elements. Herbert N. McCoy and William C. Moore (*J. Amer. Chem. Soc.*, 1911, **33**, 273—292).—Tetramethylammonium amalgam has been prepared by the electrolysis in the cold of solutions of tetramethylammonium chloride in absolute alcohol, using a mercury cathode. The amalgam exhibits certain physical properties of the metals to a high degree, and has a crystalline structure. It is lighter than mercury, but does not expand or become inflated at or below 10°, as does ammonium amalgam. In contact with cold air, it becomes coated with a white alkaline crust, due to oxidation. It reacts violently with water, producing hydrogen, colloidal mercury, and tetramethylammonium hydroxide; the phenomena observed during this reaction point to the existence of more than one active phase in the amalgam.

The amalgam acts on aqueous solutions of ammonium, sodium, potassium, and copper salts, and alcoholic solutions of copper and zinc salts, the alkylammonium group replacing the respective metals. With rubidium and cæsium salts the action is more violent than with potassium salts of equivalent concentration, but there is replacement, even in the case of the cæsium salts. The solution tension of the tetramethylammonium radicle is comparable with that of potassium, but it is much less than that of rubidium or cæsium.

The rate of formation of the tetramethylammonium ion from the amalgam, in contact with absolute alcohol, is about 5% per minute at 0°.

The *E.M.F.* of cells made up of the decinormal calomel electrode and the amalgam in contact with 0·5*N*-alcoholic or aqueous solutions of tetramethylammonium chloride was measured at 0°. With alcoholic solutions, the values obtained were 2·6 and 2·0 volts, whilst with aqueous solutions the values were 2·4 and 1·7 volts. The two values obtained in each case probably correspond with two phases present in the amalgam.

The following salts were studied to see if amalgams could be formed. Methyl-, dimethyl-, trimethyl-, ethyl-, tetraethyl-, propyl- and butylammonium chlorides; iodomethyltrimethylammonium iodide; aniline, dimethylaniline, phenylenediamine, pyridine, hydroxylamine, and hydrazine hydrochlorides; benzenediazonium chloride; tetraethylphosphonium, tetramethylstibium and trimethylsulphinium iodides. Of these, the monomethyl radicle yields an amalgam, and potential measurements show that it is less stable towards alcohol than towards water, in which respect it agrees with ammonium amalgam. The dimethylammonium radicle may possibly form an amalgam, as indicated by potential measurements, and this is also true of the tetraethylammonium radicle, but the amalgams are very unstable. Of all the other substances investigated, a number gave faint indications of amalgam formation, but none gave results as positive as the three substances just mentioned.

The authors consider, therefore, that it is possible to prepare composite metallic substances from non-metallic constituent elements.

T. S. P.

Coal Tar Pitch. Simon Bernus (*Bull. Soc. chim. Belg.*, 1911, 25, 7—40).—A study of coal tar pitch from the point of view of its use in briquetting coal dust.

From ordinary crude coal tar a yield of from 60—80% of residual pitch may be obtained, depending on the point at which distillation is stopped, and the product may be liquid, soft, or hard, according as more or less high boiling coal tar oil is left in it. A large number of high boiling hydrocarbons have been obtained by distilling pitch, but it is very doubtful whether these substances actually occur in it, and are not formed by pyrogenetic decomposition. On treatment with carbon disulphide, pitch dissolves to the extent of 80%. The insoluble matter resembles lampblack, is devoid of plastic properties, and is therefore of no value as an agglomerant. The portion soluble in carbon disulphide forms the plastic matter on which the agglomerating property of pitch depends. By treatment with solvents it can be separated into two fractions. Fraction *A* consists of a brown mass of buttery consistence, which liquefies at 45—60°, forming a black fluid which adheres strongly to any solid substance placed in it. This fraction appears to be largely composed of hydrocarbons.

Fraction *B* forms a solid, black, shining, crystalline powder, which melts at 200°, forming a slightly adherent varnish. It is soluble in carbon disulphide or tetrachloride, but its best solvent is the mixture of hydrocarbons forming fraction *A*. In briquetting coal dust, *A* probably plays the chief part as an agglomerant, whilst *B* solidifies at a comparatively high temperature, and thus assists in the formation of a hard, compact briquette.

The rest of the paper deals with the theory of briquetting, and points out that the formation of a good briquette depends primarily on the adjustment of temperature and pressure, so that each particle of coal is completely enveloped in a layer of pitch, and the latter evenly distributed to fill all interstices between the particles of coal. In valuing pitch for briquetting purposes, the melting point (55—74°) and the total quantity of plastic matter (54—73%) are the chief factors to be considered. T. A. H.

Sabatier's Reduction and its Reversibility. ALADAR SKITA and H. RITTER (*Ber.*, 1911, **44**, 668—676).—The reduction of phenols, cyclic ketones, and alcohols by Sabatier's method is somewhat analagous to that of aliphatic compounds (Abstr., 1908, i, 855). Aromatic and reduced aromatic hydrocarbons are usually formed, especially when a rapid current of hydrogen is used. It is shown that benzene, *cyclo*hexane, and *cyclo*hexene are formed by the reduction of phenol and methyl*cyclo*hexane, and toluene by the reduction of *m*-cresol. *cyclo*Hexanone yields *cyclo*hexane and phenol, but little *cyclo*hexanol; 1-methyl*cyclo*hexan-2-ol yields methyl*cyclo*hexane and *o*-cresol together with unsaturated and aromatic hydrocarbons.

1-Methyl-Δ^1-*cyclo*hexen-3-ol gave methyl*cyclo*hexane and 1-methyl*cyclo*hexan-3-one; *iso*phorone gave a hydrocarbon, C_9H_{18}, b. p. 140—143°, and *d*-pulegone gave *p*-cymene and *d*-*l*-menthane.

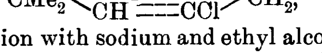
The reduction process consists of a number of equilibria as represented by the scheme:

Phenol $\rightleftarrows$ *cyclo*hexanone $\rightleftarrows$ *cyclo*hexanol $\longrightarrow$
*cyclo*hexene $\rightleftarrows$ *cyclo*hexane $\rightleftarrows$ benzene.

The aromatic hydrocarbons are formed by a process of dehydrogenation, and the amount tends to increase with the temperature, but it appears impossible to work under conditions such that this formation is entirely excluded.

1-*Chloro*-Δ^1-cyclo*hexene*, C_6H_9Cl, obtained by the action of phosphorus pentachloride on an absolute ethereal solution of *cyclo*hexanone, has b. p. 54—56°/20 mm. and D_{18}^{18} 1·0385. When reduced with sodium and methyl alcohol, it yields *cyclo*hexene.

Dihydro*iso*phorone and phosphorus pentachloride yield 5-*chloro*-1 : 1 : 3-*trimethyl*-Δ^5-cyclo*hexene*,



$CMe_2{<}\begin{matrix}CH_2\cdot CHMe\\ CH{=\!=\!=}CCl\end{matrix}{>}CH_2$, b. p. 70—71°/21 mm., and this on reduction with sodium and ethyl alcohol gives 1 : 1 : 3-trimethyl-Δ^5-*cyclo*hexene (β-*cyclo*geraniolene: compare Knoevenagel and Fischer, Abstr., 1897, i, 612), which can also be obtained by the reduction of the chloride of *iso*phorone with sodium and alcohol. The chloride obtained from 1-methyl*cyclo*hexan-2-ol (Gutt, Abstr., 1907, i, 509) has b. p. 156—158° and D_{18}^{18} 0·9676, and when reduced with zinc and an ethereal solution of hydrogen chloride yields the hydrocarbon, methyl*cyclo*hexane, C_7H_{14}, whereas when reduced with sodium and alcohol the chief product is methyl*cyclo*hexene.

The *chloride* obtained from *trans*-dihydro*iso*phorol and phosphorus pentachloride has b. p. 184°/756 or 76—78°/18 mm. and D_{18}^{18} 0·9281, and when reduced with zinc and an ethereal solution of hydrogen chloride yields the hydrocarbon, *trimethyl*cyclo*hexane*, C_9H_{18}, b. p. 137—138° and n_{17} 1·4327.

Sabatier's method of reduction is a convenient one for the preparation of saturated cyclic hydrocarbons; the compounds obtained appear to be identical with the natural naphthenes, and so far the conversion of a 6-membered ring into a derivative of a 5-membered ring has not been observed, although such a molecular rearrangement occurs during reduction with hydriodic acid (Willstätter and Kametaka, Abstr., 1908, i, 401). J. J. S.

Compounds of Antimony Trichloride and Antimony Tribromide with Benzene. Boris N. Menschutkin (*Chem. Zentr.*, 1910, ii, 378; from *Izvista of the St. Petersburg Polytechnic*, **13**, 263).—Among the numerous systems of inorganic salts

$(MgBr_2,MgI_2,AlCl_3,AlBr_3)$

with aromatic hydrocarbons studied by the author, there was not one in which the formation of a molecular compound between the components could be proved. It was also found that the numerous alleged molecular compounds of aromatic hydrocarbons with halogen salts of aluminium could not exist within the temperature ranges studied. As similar additive compounds of antimony trichloride and antimony tribromide with aromatic hydrocarbons have been described, the author subjected these systems to a thorough thermometric study. It was found that these salts form with benzene the additive compounds $2SbCl_3,C_6H_6$ and $2SbBr_3,C_6H_6$. The thermometric analysis of these substances was made by the method of Alexéeff, and the composition of the isolated additive products determined by measuring the volume of benzene liberated by means of 20% hydrochloric acid. The author gives the freezing temperatures and eutectic points obtained for the systems he examined. In the case of the system antimony trichloride and benzene, the freezing diagram shows two eutectic points, at 1°, $SbCl_3,13C_6H_6$, and at 62°, corresponding with $SbCl_3,0{\cdot}12C_6H_6$, and in between a distectic at 79°, the freezing point of the additive compound $2SbCl_3,C_6H_6$, which crystallises in very hygroscopic, rhombic plates. These compounds were erroneously given the formulæ $3SbCl_3,2C_6H_6$ and $3SbCl_3,C_6H_6$ (Smith and Davies, Trans., 1882, **41**, 411; Rosenheim and Stellmann, Abstr., 1902, ii, 68). In the case of the system antimony tribromide and benzene, the freezing diagram shows two eutectic points, at 4·5°, corresponding with $SbBr_3,51{\cdot}6C_6H_6$, and at 85°, corresponding with $SbBr_3,0{\cdot}18C_6H_6$; between the distectic at 92·5°, the freezing point of the additive compound $2SbBr_2,C_6H_6$, which crystallises in liquid, rhombic forms. N. C.

Investigation of Systems of Substituted Benzenes with Antimony Chloride and Antimony Bromide. I. Halogen-substituted Benzene. Boris N. Menschutkin (*Chem. Zentr.*, 1910, ii, 379—380; from *Izvista of the St. Petersburg Polytechnic*, **13**, 277. Compare preceding abstract).—In view of the great chemical differences which benzene derivatives exhibit, the author has determined the behaviour of these derivatives towards the halogen compounds of antimony; thus he examined a number of systems of halogen and nitro-derivatives of benzene with antimony trichloride and tribromide, and gives particulars of their freezing temperatures and eutectic points. The freezing diagram of the system antimony trichloride and chlorobenzene consists of three curves which show a eutectic point at −47°, corresponding with $SbCl_3,44·5C_6H_5Cl$, and a transition point at 0°, corresponding with $SbCl_3,2·56C_6H_5Cl$. Both components of the system form an additive compound, $SbCl_3,C_6H_5Cl$, which crystallises in long needles and decomposes at 0°. The system antimony trichloride and bromobenzene is similar, with a eutectic point at −32·5°, corresponding with $SbCl_3,28·4C_6H_5Br$, and a transition point at 3°, corresponding with $SbCl_3,1·48C_6H_5Br$; the additive compound,

$SbCl_3,C_6H_5Br$,

crystallises in needles, and in the absence of excess of antimony bromide has m. p. 6·5°; the two additive compounds are isomorphous; inoculation with $SbCl_3,C_6H_5Cl$ prevents the crystallisation of $SbCl_3,C_6H_5Br$. The freezing diagram of the system $SbCl_3$ and iodobenzene is similar on the whole to the previous ones. It is distinguished from them by the fact that the additive product, $SbCl_3,C_6H_5I$, only separates exceptionally. Without inoculating with prepared crystals of this additive compound, a freezing diagram is obtained consisting of two curves which cut each other in the eutectic point at −45°, corresponding with $SbCl_5,2·62C_6H_5I$. Inoculation results in a diagram consisting of three curves with a eutectic point at −34·5°, corresponding with $SbCl_3,8·37C_6H_5I$, and a transition point at −4·2°, corresponding with $SbCl_3,1·5C_6H_5I$. The metastable additive compound, $SbCl_3,C_6H_5I$, forms long needles, m. p. −2°. The freezing diagram of the system antimony tribromide and chlorobenzene shows two curves, which cut at the eutectic point at −47°, corresponding with $SbBr_3,58C_6H_5Cl$, and that of the system tribromide and bromobenzene, two curves meeting at the eutectic point at −32°, corresponning with $SbBr_3,37·5C_6H_5Br$. In the case of the system antimony tribromide and iodobenzene, the two curves cut at the eutectic point at −32°, corresponding with $SbBr_3,10·5C_6H_5I$. In all these systems only antimony trichloride showed a tendency to the formation of molecular compounds. Its tendency to combine with halogen-substituted benzene derivatives decreases regularly with the increase in the atomic weight of the substituting halogen atom. Four more systems of disubstituted derivatives of benzene were studied. The freezing diagram of the system antimony trichloride and *p*-dichlorobenzene consists of two curves which cut at the eutectic point at 39·5°, corresponding with $SbCl_3,2·4C_6H_4Cl_2$. In the case of *p*-dibromobenzene the eutectic point is at 49·5°, corresponding with

$SbCl_3,0·54C_6H_4Br_2$.

The diagrams for the systems of antimony tribromide and *p*-dichlorobenzene and *p*-dibromobenzene each show two curves with eutectic points at 48·5°, corresponding with $SbBr_3,6·8C_6H_4Cl_2$, and at 65°, corresponding with $SbBr_3,0·92C_6H_4Br_2$. Disubstituted benzenes do not form molecular compounds with antimony trichloride. N. C.

Examination of Systems of Substituted Benzenes with Antimony Trichloride. II. $SbCl_3,SbBr_3$ and Nitrobenzene. BORIS N. MENSCHUTKIN (*Chem. Zentr.*, 1910, ii, 381—382; from *Izvista of the St. Petersburg Polytechnic*, **13**, 411. Compare preceding abstracts).—The freezing diagram of the system antimony trichloride and nitrobenzene shows three curves, of which the middle one, dividing the area of the solid molecular compound $SbCl_3,C_6H_5\cdot NO_2$ from the liquid, does not always appear. This is because the compound has a very small velocity of crystallisation, and is only separated from the liquid by strong freezing. Apart from that, the diagram has two eutectic points, one at $-16\cdot5°$, corresponding with $SbCl_3,3C_6H_5\cdot NO_2$, the other at $-6\cdot5°$, corresponding with

$$SbCl_3,0\ 9C_6H_5\cdot NO_2.$$

In between lies a very flat distectic at $-6°$, the freezing point of the additive compound $SbCl_3,C_6H_5\cdot NO_2$, which crystallises in long needles.

The results for the system antimony trichloride and *m*-dinitrobenzene are analogous; there is a three-branched curve, but the middle one, corresponding with the compound $SbCl_3,m\text{-}C_6H_4(NO_2)_2$, is only realised exceptionally, as the compound is metastable. As a rule a diagram is obtained consisting of only two curves, which cut at the eutectic point at 1°, corresponding with $SbCl_3,0\cdot66C_6H_4(NO_2)_2$. If the fusion is inoculated with prepared crystals, a three-division freezing diagram is obtained with a eutectic point at 21°, corresponding with

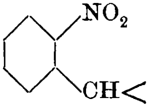
$$SbCl_3,0\cdot53C_6H_4(NO_2)_2,$$

and a transition point at 28·5°, corresponding with

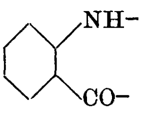
$$SbCl_3,0\cdot94C_6H_4(NO_2)_2.$$

The additive compound, $SbCl_3,C_6H_4(NO_2)_2$, forms rhombic crystals, m. p. 28·5°. The diagram for the system antimony tribromide and nitrobenzene shows two curves, cutting at a eutectic point at $-15°$, corresponding with $SbBr_3,2\cdot34C_6H_5\cdot NO_2$; that for the system with *m*-dinitrobenzene has also two curves, the eutectic point being at 47·5°, corresponding with $SbBr_3,0\cdot84C_6H_4(NO_2)_2$. Of the two halogen compounds with antimony, only the trichloride shows a tendency to the formation of additive compounds, not only with halogen, but also with nitro-derivatives of benzene. N. C.

The Constitution of Anthranil. GUSTAV HELLER [and, in part, ERICH GRÜNTHAL] (*Chem. Zentr.*, 1910, ii, 975; from *Ber. K. Sächs. Ges. Wiss., Math.-phys. Kl.*, 1910, 62, 46. Compare Abstr., 1908, i, 267; 1909 i, 832).—It is first shown that substances containing the group (I) in many reactions have a tendency to form substances of the type (II). In this way the formation of anthranil by the reduction of *o*-nitrobenzaldehyde can be so explained that it is not analogous to the formation of methylanthroxan by the reduction of *o*-nitroacetophenone, and affords no argument as to the formula of anthroxan. Anthranil and methylanthroxan behave differently in nearly all their reactions. With aniline, anthranil condenses to form a *substance*, $C_{20}H_{15}O_3N$ or $C_{20}H_{17}O_3N$; this crystallises in needles, m. p. about 172°. From the solution in concentrated hydrochloric acid there separates a colourless *compound*, which forms needles, m. p. above 280°. By boiling the yellow condensation product for a quarter of an hour with acetic anhydride, the *acetyl* compound, $C_{22}H_{17}O_2N_3$, is obtained as needles, m. p. 186°. A similar condensation product is obtained from anthranil with *p*- and



(I.)



(II.)

o-toluidines; methylanthroxan does not react in a similar way with aniline. There is a slight formation of anthranil on heating anthroxanic acid with water at about 150°. At the same time there is formed an *acid*, m. p. 247°, soluble in sodium hydroxide; this is not identical with the *substance*, m. p. 245°, obtained on heating anthranil with water, which is insoluble in sodium hydroxide. When anthranil is boiled with water at 100°, it remains to a great extent unchanged; at a lower temperature, in addition to the compound, m. p. 245°, a *substance*, m. p. 285°, is formed, which is not basic and seems to be a mixture. That the action of anthranil towards 39% hydrochloric acid and sodium nitrite is analogous to that of methylanthroxan (formation of anthroxan dichloride and *o*-aldehydobenzenediazonium chloride) is probably to be explained by its tendency under the influence of strong mineral acids to suffer intermolecular change and react in the anthroxan form; by the action of concentrated hydrochloric acid a permanent desmotropic form is not produced. Anthroxanaldehyde is readily converted by dilute alkali into isatin; it immediately gives a blue indophenin reaction, but is very resistant towards strong sulphuric acid, separating to a great extent unchanged when water is added after the mixture has been kept for several days. N. C.

Nitrophenol Salts. ANTONI KORCZYNSKI (*Chem. Zentr.*, 1910, ii, 384; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 461).—In continuation of previous work (Abstr., 1908, i, 977; 1909, i, 148, 639) the author notes the analogy between the colour of nitrophenol salts and the tendency of the nitrophenols to form abnormal salts with ammonia, namely, that nitrophenols which form yellow salts tend to form abnormal ammonium salts. The following *ammonium* salts of nitrophenols were prepared: $NO_2 \cdot C_7H_5I \cdot OH,NH_3$, at the ordinary temperature, and $NO_2 \cdot C_7H_5I \cdot OH,2NH_3$, at $-15°$, from 5-iodo-3-nitro-2-cresol; $NO_2 \cdot C_6H_2Br_2 \cdot OH,NH_3,C_4H_8N_2$(?), from 2-4-dibromo-6-nitrophenol at $-15°$; $NO_2 \cdot C_6H_2ClI \cdot OH,2NH_3$, from 4-chloro-6-iodo-2-nitrophenol at $-15°$; $NO_2 \cdot C_6H_2BrI \cdot OH,2NH_3$, from 4-bromo-6-iodo-2-nitrophenol at $-15°$. N. C.

Action of Aluminium Chloride on Benzene. ANNIE HOMER (*Proc. Camb. Phil. Soc.*, 1911, **16**, 65—66).—Benzene containing 25% of its weight of aluminium chloride is heated at 100° under a reflux condenser for ten to fourteen days. After treatment with water and hydrochloric acid, the product yields, in addition to the alkylbenzenes and phenol mentioned by Friedel and Crafts, a fraction, b. p. below 160°/10 mm., containing phenol and naphthalene. The formation of the latter is explained on the assumption that *o*-diethylbenzene is produced and subsequently dehydrogenised by the aluminium chloride. Naphthalene is not obtained when the experiment is performed in sealed tubes at 180° for two days. C. S.

The Action of Light on the Bromination of Tertiary *o*- and *p*-Butyltoluene and the Chlorination of *tert.*-Butylbenzene and *o*-Butyltoluene. JR. SALIBILL (*Bull. Acad. Sci. Cracow*, 1910, *A*, 606—608).—A mixture of bromine and *p*-butyltoluene in molecular proportions was exposed to strong sunlight, when combination rapidly took place, giving a liquid that boiled at 156—159° under 32 mm. pressure. The bromine replaced a hydrogen atom of the side-chain, not in the ring.

o-Butyltoluene reacted with bromine slowly at first, more rapidly afterwards. The bromine did not enter the methyl group, a phenomenon attributed by the author to steric hindrance; instead, it replaced a hydrogen atom of the ring. Chlorine showed a similar behaviour.

tert.-Butylbenzene behaved towards bromine and chlorine like *o*-butyltoluene. E. J. R.

Cyclic Acetylenes. Phenylbutinene. Émile André (*Bull. Soc. chim.*, 1911, [iv], 9, 192—195).—The author proposes to generalise Tiffeneau's method for the preparation of aromatic olefinic hydrocarbons (Abstr., 1904, i, 872), and to prepare from the latter the corresponding acetylenes by bromination and decomposition of the bromides by alcoholic potassium hydroxide.

The application of this process to allylbenzene leads to the formation of phenylmethylacetylene, Ph•C⋮CMe.

Phenylbutylene, $CH_2Ph•CH_2•CH:CH_2$, prepared by the action of allyl iodide on magnesium benzyl chloride, contrary to Aronheim's statement (this Journ., 1874, 689), is readily converted by bromination in chloroform and the subsequent action of potassium hydroxide in alcohol into *phenylbutinene*, $CH_2Ph•CH_2•C⋮CH$, D^0 0·9391, b. p. 189—191°/758 mm., which is best purified through the sodium derivative, and then forms a colourless, highly refractive liquid.

T. A. H.

A Convenient Method for the Reduction of Alcohols of the Diphenyl- and Triphenyl-methane Series. Alexei E. Tschitschibabin (*Ber.*, 1911, 44, 441—443).—The methods at present available for the reduction of the above-mentioned alcohols often yield poor results. The author finds that the reduction with hydriodic acid in acetic acid solution proceeds very readily, and gives almost quantitative yields.

The reduction is carried out by dissolving the alcohol in the smallest possible quantity of glacial acetic acid and adding an excess of a saturated solution of hydriodic acid in the same solvent; the mixture is heated to boiling, and the reduction product precipitated by pouring the solution into water containing sodium hydrogen sulphite, which removes the iodine formed in the reaction. Ethers and halogen derivatives may be reduced in the same manner.

The method has been applied for the preparation of triphenylmethane, diphenylmethane, and diphenylacetic acid from triphenylcarbinol, diphenylcarbinol, and benzilic acid respectively. F. B.

Dinaphthylmethanes and Some of their Derivatives. Alexei E. Tschitschibabin (*Ber.*, 1911, 44, 443—450).—The paper deals with the application of the author's method of reduction (preceding abstract) to the preparation of the three isomeric dinaphthylmethanes.

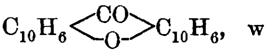
αα-Dinaphthylcarbinol, prepared by a modification of the method described by Schmidlin and Massini (Abstr., 1909, i, 561), is readily reduced to *αα*-dinaphthylmethane, m. p. 109° (compare Schmidlin and Huber, Abstr., 1910, i, 832); the latter compound is also produced, together with *αα*-dinaphthyl ketone, by distilling *αα*-dinaphthylcarbinol under diminished pressure: $2CH(C_{10}H_7)_2{\cdot}OH = CH_2(C_{10}H_7)_2 + CO(C_{10}H_7)_2$. The hydrocarbon is separated from the mixture by taking advantage of its insolubility in concentrated sulphuric acid. *αα*-Dinaphthylmethyl bromide is obtained by the action of hydrogen bromide on the carbinol in glacial acetic acid solution (compare Wheeler and Jamieson, Abstr., 1902, i, 763).

The interaction of magnesium *α*-naphthyl bromide and *β*-naphthaldehyde yields *αβ-dinaphthylcarbinol*, which crystallises in soft needles, m. p. 108—109°, dissolves in sulphuric acid with a blue colour, and, on reduction, yields *αβ-dinaphthylmethane*, crystallising in glistening, flat prisms, m. p. 96°. The carbinol forms with benzene a crystalline *compound*, $2CH(C_{10}H_7)_2{\cdot}OH,C_6H_6$, which decomposes at 78° into its constituents.

αβ-Dinaphthylmethyl bromide, $CH(C_{10}H_7)_2Br$, prepared from the carbinol and hydrogen bromide in glacial acetic acid solution, crystallises in needles, m. p. 123—123·5°.

By the interaction of magnesium *β*-naphthyl bromide and ethyl formate, *ββ*-dinaphthylcarbinol is obtained as an oil, which crystallises when left over sulphuric acid (compare Schmidlin and Huber, *loc. cit.*); on treatment with hydrogen bromide in acetic acid solution, it yields *ββ-dinaphthylmethyl bromide*, which forms a crystalline powder, m. p. 168—169°, gives a violet coloration with sulphuric acid, and yields *ββ*-dinaphthylmethane when reduced with hydriodic acid.

The *ββ*-dinaphthylmethane thus obtained has m. p. 93°, and is identical with the hydrocarbon prepared by Richter (Abstr., 1881, 281) by the reduction of the corresponding ketone.

By reducing di-*β*-naphthaxanthone,  $C_{10}H_6<\overset{CO}{\underset{O}{}}>C_{10}H_6$, with hydriodic acid, Claus and Ruppel (Abstr., 1890, 511) obtained a hydrocarbon to which they assigned the formula of *αα*-dinaphthylmethane; Schmidlin and Huber consider it to be the *αβ*-compound. The hydrocarbon differs, however, in properties from the three isomeric dinaphthylmethanes described above, so that its constitution remains undetermined. F. B.

Halogen Derivatives of Triphenylmethane. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1911, 44, 450—459).—A further application of the author's method of reduction (preceding abstracts) to the preparation of the halogen derivatives of triphenylmethane.

p-Chlorotriphenylcarbinol, previously obtained by Gomberg and Cone (Abstr., 1906, i, 822), crystallises from light petroleum in large cubes, m. p. 85°. On reduction it yields p-*chlorotriphenylmethane*, which crystallises in two forms, glistening needles, m. p. 59·5°, and large, transparent crystals, m. p. 54°. The latter form is unstable, and is transformed, when kept, into the less fusible modification.

o-*Chlorotriphenylcarbinol*, prepared by the action of magnesium phenyl bromide on methyl *o*-chlorobenzoate, forms a crystalline powder, m. p. 91—92°, gives an orange-yellow coloration with concentrated sulphuric acid, and yields o-*chlorotriphenylmethyl bromide*, m. p. 118—121°. The bromide gives, on reduction, o-*chlorotriphenylmethane*, which crystallises in short prisms, m. p. 77°, and forms a crystalline *compound* with benzene; this decomposes at 40° into its constituents.

p-*Bromotriphenylmethyl bromide*, prepared from the corresponding carbinol (Cone and Long, Abstr., 1906, i, 424), has m. p. 132—134°, and is readily reduced to p-*bromotriphenylmethane*, which resembles the *p*-chloro-compound in being dimorphous. The stable modification, obtained by inoculating a solution of *p*-bromotriphenylmethane in light petroleum with the stable form of the *p*-chloro-compound, crystallises in glistening needles, m. p. 82·5°. The second modification has m. p. 68°, and is more soluble than the stable form. *p*-Bromotriphenylmethane differs from the ortho- and meta-isomerides in not forming a crystalline compound with benzene.

o-*Bromotriphenylcarbinol*, obtained by the interaction of magnesium phenyl bromide and methyl *o*-bromobenzoate, crystallises from hot glacial acetic acid in soft leaflets, m. p. 158°, and gives an orange-yellow coloration with sulphuric acid.

o-*Bromotriphenylmethyl bromide* forms a coarsely crystalline powder, m. p. 120—125° (decomp.), and yields, on reduction, o-*bromotriphenylmethane*; the latter crystallises in short, glistening prisms, m. p. 81°, and forms a crystalline *compound* with benzene, m. p. 45° (decomp.).

m-*Bromotriphenylmethyl bromide*, obtained by the action of hydrobromic acid on *m*-bromotriphenylcarbinol (Cone and Long, *loc. cit.*), separates from light petroleum in glistening crystals, m. p. 145—146°; it is deposited from its solutions in glacial acetic acid in the form of white granules, m. p. 75°, which apparently contain acetic acid.

m-*Bromotriphenylmethane*, prepared from the corresponding bromide by reduction, separates from benzene in large, crystalline granules of the composition $C_{19}H_{15}Br,C_6H_6$; these have m. p. 55°, and, on keeping, are slowly transformed into a viscid oil; when heated to 80° the benzene of crystallisation is lost, *p*-bromotriphenylmethane separates as an oil which could not be obtained in a crystalline form.

p-Iodotriphenylcarbinol, prepared by the interaction of magnesium phenyl bromide and methyl *p*-iodobenzoate, is converted by the action of acetyl chloride into the carbinyl chloride, m. p. 123°: Gomberg and Cone (*loc. cit.*) give 125°.

p-*Iodotriphenylmethane* crystallises in yellow needles, m. p. 81·5°.

Tri-*p*-bromotriphenylmethane, prepared by reducing tri-*p*-bromotriphenylmethyl ethyl ether, has m. p. 115° (compare Fischer and Hess, Abstr., 1905, i, 205). F. B.

α-Methylanthracene. OTTO FISCHER and A. SAPPER (*J. pr. Chem.*, 1911, [ii], **83**, 201—208).—α-Methylanthracene and its β-isomeride, which both crystallise in white leaflets, are stated to have approximately the same m. p., and yield methylanthraquinones also having nearly the same m. p. Since the two hydrocarbons are produced by the distillation of very different natural substances with zinc dust, it is desirable to have a certain method of distinguishing between them. The authors obtain a very poor yield of impure α-methylanthracene by Birukoff's method of distilling 4-hydroxy-1-methylanthraquinone with zinc dust, the main product being anthracene. α-Methylanthracene is conveniently obtained by distilling 4-chloro-1-methylanthraquinone (Heller and Schülke, Abstr., 1908, i, 994) with zinc dust at a very low red heat; it has m. p. 85—86°, crystallises in long, white needles, is much more soluble in most solvents than anthracene or β-methylanthracene, forms a blue fluorescent solution in alcohol, and yields a *picrate*, red needles, m. p. 113—115°. α-Methylanthraquinone, m. p. 170—171°, does not lose its methyl group by distillation with zinc dust, and differs from β-methylanthraquinone by rapidly reddening on exposure to light. It is oxidised by dilute nitric acid at 160° to anthraquinone-1-carboxylic acid, which develops a rose coloration when heated with soda-lime; anthraquinone-2-carboxylic acid turns blue under similar conditions. 4-*Chloro*-1-*methylanthracene*, $C_{15}H_{11}Cl$, m. p. 112°, obtained by boiling 4-chloro-1-methylanthraquinone with zinc dust and aqueous ammonia, does not lose its halogen by distillation with zinc dust. 4-*Methoxy*-1-*methylanthraquinone*, m. p. 128°, yellow needles, obtained from 4-chloro-1-methylanthraquinone and methyl-alcoholic potassium hydroxide at 100° under pressure, reddens in light, and is converted into 4-hydroxy-1-methylanthraquinone by glacial acetic and concentrated hydrochloric acids at 100° under pressure. C. S.

Aliphatic Nitro-compounds. IX. Action of Phenylcarbimide on Sodium Nitromethane and Nitroethane.

Wilhelm Steinkopf and H. M. Daege (*Ber.*, 1911, **44**, 497—502. Compare this vol., i, 4).—When sodium nitromethane and phenylcarbimide in benzene solution are set aside for some weeks, nitroacetanilide and a little malonanilide are formed (Michael, Abstr., 1905, i, 195). Reaction is quicker when the components are warmed for an hour on the water-bath; in both cases a further investigation has proved that *s*-diphenylcarbamide and triphenylbiuret are also formed. The last is converted on boiling with potassium hydroxide into diphenylcarbamide, and its formation is obviously due to the action of excess of phenylcarbimide on diphenylcarbamide. The constitution of nitroacetanilide was confirmed by its conversion into nitroacetic acid by boiling with strong aqueous potassium hydroxide.

Sodium nitroethane and phenylcarbimide only yield traces of the sodium salt of α-nitropropionanilide, the main products here being *s*-diphenylcarbamide and triphenylbiuret. In other experiments, particularly those made with fresh phenylcarbimide, triphenyl*iso*cyanurate, $C_3N_3O_3Ph_3$, together with nitrogen and some diphenylcarbamide are formed. This reaction is in opposition to Michael's theory (*loc. cit.*) that the course of change followed is that in which a maximum of chemical neutrality is attained. E. F. A.

Action of Nitrous Acid on Dinitrodialkylanilines. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 820—822).—The substance, m. p. 175—176°, obtained by Hantzsch by the action of nitric acid, D 1·3, on dimethylaniline, and described as 3 : 4-dinitrodimethylaniline (Abstr., 1910, i, 475), is proved to be 2 : 4-dinitromethylaniline; its mixture with the true 3 : 4-dinitrodimethylaniline, m. p. 176°, causes a large depression of the m. p. The production of the dinitromethylaniline is due to the elimination of one methyl group by the nitrous acid formed during the nitration; in fact, 2 : 4-dinitrophenylmethylnitrosoamine is produced when a solution of dimethylaniline in ten volumes of nitric acid, D 1·3, is kept overnight. When, however, carbamide is added to the nitric acid to decompose the nitrous acid formed, the main product of the nitration of dimethylaniline is 2 : 4-dinitrodimethylaniline, m. p. 87°. By treating a solution of this substance in five times its weight of nitric acid, D 1·3, with sodium nitrite, 2 : 4-dinitrophenylmethylnitrosoamine is obtained, from which 2 : 4-dinitromethylaniline is produced by boiling with acetic acid. Precisely similar reactions are exhibited by 2 : 4-dinitrodiethylaniline and 2 : 4-dinitrodipropylaniline.

The action of nitrous acid on 3 : 4-dinitrodialkylanilines in dilute sulphuric acid also results in the elimination of one alkyl group and the formation of a nitrosoamine; thus, 3 : 4-dinitrodiethylaniline yields a pale yellow *nitroso*-compound, m. p. 79—80°. Also, the same behaviour is shown by 3 : 6-dinitrodiethylaniline, which is converted by nitrous acid into a yellow *nitroso*-compound, m. p. 69°, from which 3 : 6-dinitroethylaniline is produced almost instantly by boiling acetic acid. 3 : 6-Dinitrodimethylaniline behaves in a similar manner.

C. S.

A New Preparation of Diphenylmethylamine (Benzhydrylamine). HEINRICH BILTZ and KARL SEYDEL (*Ber.*, 1911, **44**, 411—413).—Diphenylmethylamine is readily prepared by heating 5 : 5-diphenylhydantoin (Biltz and Rimpel, Abstr., 1908, i, 462) at 230—300° with an excess of potassium hydroxide and a small quantity of water; it has b. p. 303·6° (corr.). The *picrate*, $C_{19}H_{16}O_7N_2$, crystallises in deep yellow needles, m. p. 205—206° (decomp.).

5 : 5-Diphenylthiohydantoin, when fused with potassium hydroxide at 300°, is quantitatively converted into diphenylmethylamine; at 260°, 5 : 5-diphenylhydantoin is produced simultaneously.

An improved method for the preparation of the last-mentioned compound is described.

F. B.

Doubly Linked Carbon Atoms and the Carbon–Nitrogen Linking. V. Fission of Quaternary Ammonium Salts by Nascent Hydrogen. VI. Formation of Mixed Tertiary Amines. VII. Relative Mobility of Allyl-, Benzyl-, and Cinnamyl- in the Fission of Quaternary Ammonium Salts by Reduction. HERMANN EMDE [with HANS SCHELLBACH in VI and VII] (*Arch. Pharm.*, 1911, **249**, 106—111, 111—117, 118—122. Compare Abstr., 1909, i, 565, 708, 709).—Phenylbenzyldimethylammonium chloride (*aurichloride*, m. p. 97—98°, decomp.; *platinichloride*, m. p. 181°, decomp.) reduces normally (*loc. cit.*) with sodium amalgam in water, giving dimethylaniline and toluene, but when the reduction is effected in alcohol, toluene is in part replaced by benzyl ethyl ether. It is probable that in presence of alcohol the substituted ammonium chloride breaks up, first, into dimethylaniline and benzyl chloride, and that the latter then reacts with sodium ethoxide. The general method of carrying out the reaction and isolating the products is described.

The fission by reduction method may be applied to the preparation of mixed tertiary amines in the following way (compare Emmert, Abstr., 1909, i, 376).

Tribenzylmethylammonium iodide, m. p. 184°, gives a *cadmi-iodide*, m. p. 238°, and with silver chloride the corresponding *chloride*, m. p. 202°; the *platinichloride* has m. p. 209°, and the *aurichloride*, m. p. 188° (decomp.). The iodide itself on reduction with sodium amalgam in aqueous alcohol gives benzyl ethyl ether and dibenzylmethylamine (Abstr., 1909, i, 709); the latter reacts with allyl iodide to form *dibenzylmethylallylammonium iodide*, m. p. 149°, which on reduction gives *benzylmethylallylamine*, b. p. 255—256°/760 mm. (*platinichloride*, m. p. 139°). From this amine, *benzylmethylallylpropylammonium chloride*, m. p. 279°, was prepared, and this on reduction furnished *methylallylpropylamine*, b. p. 171—172°/765 mm., which gives a *platinichloride*, m. p. 144° (decomp.), and an oily *aurichloride*.

The foregoing work shows that in the fission of a quaternary ammonium compound containing both allyl- and benzyl- the latter is perferably removed from the *N*-atom, and the following results show that cinnamyl-, like benzyl-, is more mobile than allyl- in this connexion (compare von Braun, Abstr., 1907, i, 899; Wedekind and Paschke, Abstr., 1910, i, 372). *Dicinnamyldiethylammonium chloride*, on reduction with sodium amalgam in water, furnishes phenylpropylene and *cinnamyldiethylamine*, b. p. 263—265°/765 mm. (*platinichloride*, m. p. 208°, decomp.), which combines with allyl iodide to give *cinnamyldiethylallylammonium iodide*, m. p. 106° (*platinichloride*, m. p. 157°), and this on reduction with sodium amalgam in water yields diethylallylamine (platinichloride, m. p. 166°, not 128—130°, as stated by Liebermann and Paal, Abstr., 1883, 908). T. A. H.

Tetracinnamyl- and Tetrabenzyl-ammonium. HERMANN EMDE (*Arch. Pharm.*, 1911, **249**, 93—106. Compare Abstr., 1909, i, 708).—It is now well-established that there is a difference in function between the first three and the fifth valencies of a nitrogen atom, but it is not yet certain whether the fourth valency is of the same type as the first three, or has some special function. With a view to throwing light on this point, the author is investigating the formation and stability of substituted ammonium compounds containing four similar organic radicles. Tetracinnamylammonium salts are now described, but tetrabenzylammonium compounds could not be obtained.

[With HANS SCHELLBACH.]—Tetracinnamylammonium chloride, m. p. 199°, may be obtained by melting together tricinnamylamine and cinnamyl chloride and washing the product with ether. A process for its isolation from the mixed amines formed by the action of ammonia on cinnamyl chloride is also described. It is almost insoluble in water, but readily soluble in acetone or alcohol. It is stable towards alkalis, but is decomposed by silver hydroxide, suspended in alcohol, giving *tetracinnamylammonium hydroxide*, which crystallises in colourless, compact rods, sinters at 146°, solidifies again at 165°, and re-melts at 170°; the hydroxide absorbs carbon dioxide from the atmosphere, and on heating decomposes at 150—175°/20—30 mm., yielding a thick, yellow distillate, b. p. 184°, which rapidly resinifies.

Cinnamyltrimethylammonium chloride, m. p. 156°, was obtained crystalline; it does not give the corresponding hydroxide by the action of silver hydroxide, as decomposition ensues with the formation of trimethylamine.

Attempts to prepare tetrabenzylammonium chloride by various methods, including Brunner's, confirmed Marquardt's experience that this substance cannot be obtained. Its non-formation is probably a special case of "steric hindrance." T. A. H.

Red and White Silver Salts of 2:4:6-Tribromophenol.

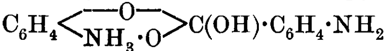
HENRY A. TORREY and WILLIAM H. HUNTER (*J. Amer. Chem. Soc.*, 1911, 33, 194—205).—In an earlier paper (Abstr., 1907, i, 1030) the authors described red and white isomeric silver salts of 2 : 4 : 6-tribromophenol. This observation was confirmed by Hantzsch and Scholtze (Abstr., 1908, i, 17), who also described similar derivatives of 2 : 6-dibromo-*p*-cresol.

It has now been found that 2 : 4 : 6-tribromoresorcinol methyl ether and 3 : 4 : 6-tribromoguaiacol also yield red and white silver salts, but in these cases the red salts undergo transformation into the white isomerides too rapidly to permit of their isolation.

When solid potassium hydroxide is added to a solution of 3 : 4 : 6-tribromoguaiacol in dry acetone, a yellow *potassium* derivative is produced, which is immediately decolorised on addition of water. On adding a solution of silver nitrate in acetone to the acetone solution of the salt, a red precipitate is produced, which rapidly turns black.

The two silver salts of 2 : 4 : 6-tribromophenol do not show any difference in their behaviour towards acids, alkali hydroxides, alkyl iodides, or other reagents. It is considered probable that the change of the red salt into the white modification is due to tautomerism, the white salt being the stable form with the ordinary benzenoid formula, and the red salt the labile form with the ortho-quinonoid constitution, $O:C_6H_2Br_2:BrAg$. Hantzsch, however, has raised objections to the latter formula, and has stated that if silver could behave in this way, mercury ought to show even greater tendency to form such compounds, and should, therefore, give coloured salts, whereas the mercuric salts of tribromophenol and other phenols obtained by Hantzsch and Auld (Abstr., 1906, i, 471) were white. It is pointed out, however, that mercuric salts do not resemble silver salts so closely as do mercurous salts, and, as the result of experiments, it has been found that 2 : 4 : 6-tribromophenol and 2 : 4 : 6-tribromoresorcinol both yield yellow *mercurous* salts, and tri-iodophenol, an orange *mercurous* salt. Yellow precipitates were also obtained on the addition of mercurous nitrate to alcoholic solutions of tribromoresorcinol methyl ether and tetrabromoguaiacol.

2 : 4 : 6-*Tribromoresorcinol dimethyl ether,* m. p. 68—69°, forms a crystalline powder. E. G.

Salt Formation by Aminophenols. WILHELM SUIDA (*J. pr. Chem.*, 1911, [ii], **83**, 233—242).—The problem of the formation of salts by amphoteric organic substances has been approached by dissolving equivalent quantities of an aminophenol and of an aromatic amino-acid in just sufficient hot water, heating the solution rapidly to boiling, filtering, cooling, and examining the crystals obtained. The unexpected result has been obtained, that of the three aminophenols only the ortho-compound forms salts with anthranilic acid (orange-red prisms, decomp. below 100°), *m*-aminobenzoic acid (stout, red prisms, decomp. 100°), and *p*-aminobenzoic acid (brownish-red prisms, m. p. 139°). The explanation suggested, namely, that salts of the type  $C_6H_4{<}\overset{\text{——O——}}{\underset{NH_3\cdot O}{}}{>}C(OH)\cdot C_6H_4\cdot NH_2$ are formed, is supported by the fact that again only *o*-aminophenol forms salts with benzoic acid (yellowish-brown or brownish-red prisms which lose benzoic acid at 100°), phenylacetic acid (colourless leaflets, m. p. 130—131°), and sulphanilic acid (brownish-red prisms, nearly unchanged at 250°). o-*Aminophenyl formate* has m. p. 119—120°; all of these salts can be recrystallised from boiling water; when animal charcoal is added, however, the substance separates in two distinctly different crystalline forms. The salts lose weight continuously at 100—105°, owing partly to the volatilisation of the salt itself, partly to the escape of the more volatile constituent; oxazoles are not formed. *o*-Aminophenol does not form additive compounds of the above type with other substances containing a carbonyl group. It condenses, under the conditions mentioned, with methyl oxlate to form o-*aminophenol* o-*hydroxyphenyloxamate,* $C_{14}H_{14}O_5N_2$, and with acetylacetone to form a *substance,* m. p. 186—187°, which is probably $OH\cdot C_6H_4\cdot N\colon CMe\cdot CH_2\cdot COMe$.

C. S.

Phenyl Ether and Some of its Derivatives. ALFRED N. COOK (*J. Amer. Chem. Soc.*, 1911, **33**, 254—255).—An addendum to the earlier paper (Abstr., 1910, i, 731).

*Tetrabromo-*p*-tolyl ether,* $O(C_6H_2MeBr_2)_2$, b. p. 310—330°/40 mm., is obtained by the action of bromine in direct sunlight on a warm solution of *p*-tolyl ether as a light yellow, viscous substance which crystallises on cooling. A more highly brominated derivative could not be obtained. Dibromo-*p*-tolyl ether was obtained in small yield by adding bromine gradually to *p*-tolyl ether heated at 150°.

The results of experiments on the action of bromine on *o*-tolyl ether were not satisfactory, but were sufficient to show that the bromine enters the nucleus and not the side-chain. E. G.

Attempts to Prepare Optically Active Phosphorus Compounds. FRITZ EPHRAIM (*Ber.*, 1911, **44**, 631—637. Compare Caven, Trans., 1902, **81**, 1362; Luff and Kipping, *ibid.*, 1909, **95**, 1993; Meisenheimer and Lichtenstadt, this vol., i, 344).—Attempts to resolve compounds of the types $NH_2\cdot PO(ONa)\cdot OPh$ and $NH_2\cdot PS(ONa)\cdot OPh$ into optically active components were unsuccessful. A better yield of Stokes' diphenyl aminophosphate (Abstr., 1893, i, 315) is formed when an excess of phosphoryl chloride is used. The ester reacts with a hot boiling solution of barium hydroxide (equal weights of ester and crystallised hydroxide in 100 c.c. of water), yielding the *barium* salt of phenyl aminophosphoric acid, $[NH_2\cdot PO(OPh)\cdot O]_2Ba,H_2O$, which crystallises in microscopic needles readily soluble in water. The corresponding *cinchonine* salt, $NH_2\cdot PO(OPh)\cdot OH,C_{19}H_{22}ON_2$, crystallises in minute needles, m. p. 194°, and then in flat prisms, but both fractions had the same value for $[\alpha]_D$, namely, $+11\cdot5°$

The *chloride*, $PSCl(OPh)_2$, prepared by the addition of sulphur to the chloride of diphenyl phosphite at 200—300°, crystallises from alcohol in brilliant, colourless, glistening needles, m. p. 68°. It is decomposed when boiled with water, and its alcoholic solution reacts with concentrated aqueous ammonium hydroxide, yielding the *diphenyl aminothiophosphate*, $NH_2\cdot PS(OPh)_2$, which crystallises in thin, rhombic leaflets, m. p. 112°. This ester is hydrolysed by alcoholic sodium hydroxide solution, yielding the *sodium* salt,

$$OPh\cdot PS(NH_2)\cdot ONa,2H_2O,$$

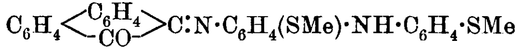
which dissolves readily in both alcohol and water; its aqueous solution yields precipitates with silver nitrate, lead acetate, and copper sulphate. The corresponding *cinchonine* salt, $C_{25}H_{30}O_3N_3SP$, obtained by the action of the sulphate of the base on the sodium salt in absolute alcoholic solution, forms a syrupy mass, and has $[\alpha]_D$ $+11\cdot06°$.

J. J. S.

p-Aminothiophenol [*p*-Aminophenyl Mercaptan]. III.

THEODOR ZINCKE and P. JÖRG (*Ber.*, 1911, **44**, 614—626. Compare Abstr., 1909, i, 789; this vol., i, 39).—A *dye*, $C_{14}H_{15}N_2S_2Cl$, which crystallises in violet-black, lustrous plates and yields deep blue alcoholic solutions, is formed by the oxidation of an alcoholic solution of *p*-methylthiolaniline (*p*-aminophenyl methyl sulphide) with a $1\cdot5N$-aqueous solution of ferric chloride. The free *base*, prepared by the action of dilute ammonia on the hydrochloride, forms a heavy, brownish-red, flocculent mass, which readily undergoes decomposition when in solution or when dried. The dye is decomposed when left in contact with dilute hydrochloric acid for some time, and yields *p*-methylthiolaniline and reacts with a methyl-alcoholic solution of *p*-toluidine, yielding a compound, $SMe\cdot C_6H_4\cdot N\colon C_6H_2(NH\cdot C_7H_7)_2\colon N\cdot C_7H_7$, which crystallises from toluene in dark reddish-brown, glistening plates, m. p. 238°. The *leuco*-compound, $C_{14}H_{16}N_2S_2$, obtained by reducing the dye with stannous chloride, crystallises from dilute alcohol in slender, colourless needles resembling asbestos, and has m. p. 105°. The *hydrochloride* crystallises from alcohol in colourless plates, and both base and hydrochloride are readily oxidised to the dye by means of ferric chloride or nitrous acid. The *acetyl* derivative, $C_{16}H_{18}ON_2S_2$, crystallises from dilute acetic acid in glistening prisms, m. p. 155°, and the *trimethylammonium iodide*, $C_{17}H_{23}N_2S_8I$, forms a colourless, crystalline powder, m. p. 186—190° (decomp.). The leuco-base is regarded as a derivative of *p*-phenylenediamine, and is given the formula: $\overset{4}{N}H_2\cdot C_6H_3(\overset{2}{S}Me)\cdot \overset{1}{N}H\cdot C_6H_4\cdot \overset{4'}{S}Me$, and the corresponding dye the structural formula: $HCl,NH:C_6H_3(SMe):N\cdot C_6H_4\cdot SMe$. The para-formula is preferred, as the leuco-compound does not give the reactions characteristic of an orthodiamine, for example, it does not yield an azimino-derivative with nitrous acid, but this formula necessitates the assumption of the wandering of a ·SMe-group during the oxidation of the methylthiolaniline to the dye (compare Bamberger, Abstr., 1901, i, 140; Zincke, 1901, i, 330; Kumazai and Wolffenstein, 1908, i, 159). When oxidised with hydrogen peroxide, the acetyl derivative yields the *disulphone*, $NHAc\cdot C_6H_3(SO_2Me)\cdot NH\cdot C_6H_4\cdot SO_2Me$, which crystallises from nitrobenzene in yellow needles, m. p. 273—275° (decomp.).

The leuco-compound reacts with a glacial acetic acid solution of phenanthraquinone, yielding

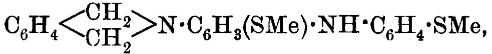


$$C_6H_4<\begin{smallmatrix}C_6H_4\\CO\end{smallmatrix}>C:N\cdot C_6H_4(SMe)\cdot NH\cdot C_6H_4\cdot SMe$$

in the form of a dark carmine-red, crystalline powder, m. p. 281°. It has feebly basic properties, and its salts have an intense deep-blue colour. The leuco-base also reacts with carbon disulphide in the presence of alcohol at 100°, yielding a thiocarbamide derivative,

$$CS[NH\cdot C_6H_3(SMe)\cdot NH\cdot C_6H_4\cdot SMe]_2,$$

which crystallises from glacial acetic acid in small, colourless needles, m. p. 160°. The compound,



$$C_6H_4<\begin{smallmatrix}CH_2\\CH_2\end{smallmatrix}>N\cdot C_6H_3(SMe)\cdot NH\cdot C_6H_4\cdot SMe,$$

obtained by shaking the leuco-base with a chloroform solution of *o*-xylylene bromide for two days, crystallises from alcohol in colourless needles, m. p. 139°.

Azoxyphenyl methyl sulphone, $ON_2(C_6H_4\cdot SO_2Me)_2$, prepared by oxidising *p*-methylthiolaniline with hydrogen peroxide, crystallises from glacial acetic acid in yellow prisms, m. p. 264°.

The dye formed by the oxidation of *p*-anisidine with ferric chloride has not been obtained in a pure state. *p*-Aminothiophenol is not readily oxidised, and does not yield a dye analogous to that obtained from *p*-aminophenol (Willstätter and Piccard, Abstr., 1909, i, 517). It is suggested that the leuco-compound derived from the dye from *p*-aminophenol is 4-amino-3 : 4′-dihydroxydiphenylamine.

J. J. S.

Action of Thionyl Chloride and of Sulphur Dioxide on Magnesium Alkyl Halides. BERNARDO ODDO (*Gazzetta*, 1911, **41**, i, 11—16. Compare Strecker, also Grignard and Zorn, Abstr., 1910, i, 532).—Thionyl chloride reacts with magnesium ethyl iodide, forming ethyl sulphide, and with magnesium phenyl bromide it yields phenyl sulphide, in addition to small quantities of phenylsulphoxide and diphenyl.

Sulphur dioxide and magnesium phenyl bromide react, producing phenyl sulphide as well as small quantities of phenylsulphoxide and diphenyl.

R. V. S.

Sulphur Derivatives of *p*-Cresol. THEODOR ZINCKE and J. KEMPF (*Ber.*, 1911, **44**, 413—424).—*Potassium 5-bromo*-p-*cresol*-3-*sulphonate*, $HO\cdot C_6H_2MeBr\cdot SO_3K$, prepared by the addition of a mixture of bromine and glacial acetic acid to an aqueous solution of potassium *p*-cresol-3-sulphonate, forms lustrous, white leaflets; the *methyl* ester crystallises in long, prismatic needles, m. p. 79—80°; the *ethyl* ester in stout prisms, m. p. 54—55°.

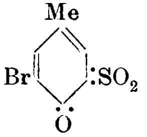
5-*Bromo*-p-*cresol*-3-*sulphonyl chloride*, $OH\cdot C_6H_2MeBr\cdot SO_2Cl$, obtained by treating the corresponding potassium salt with chlorosulphonic acid, crystallises in needles, m. p. 94—95°. The action of phosphorus pentachloride or phosphoryl chloride on the potassium salt yields, besides the sulphonyl chloride, an *ester* having the formula

$$SO_2Cl\cdot C_6H_2MeBr\cdot O\cdot POCl_2,$$

and crystallising in colourless prisms, m. p. 147°.

The *acetyl* derivative of 5-bromo-*p*-cresol-3-sulphonyl chloride forms lustrous, apparently monoclinic prisms, m. p. 84—85°.

When anhydrous potassium acetate is added to solutions of the sulphonyl chloride in acetone or ether, a yellow coloration is produced, due to the removal of hydrogen chloride and the formation of 5-*bromo*-o-*toluosulphonoquinone* (annexed formula).



A similar action takes place on the addition of ammonia to an alcoholic solution of the sulphonyl chloride, but the sulphonoquinone thus produced unites with the alcohol to form an ester of the sulphonic acid. By evaporating the yellow acetone or ethereal solutions, a white, crystalline powder, consisting of the polymeric form of the sulphonoquinone, is obtained; the same substance is also produced by the action of chlorosulphonic acid on 5-bromo-*p*-cresol-3-sulphonyl chloride.

On reduction with zinc dust and hydrochloric acid in alcoholic solution, the sulphonyl chloride yields 5-*bromo*-p-*cresol* 3-*mercaptan*, $OH\cdot C_6H_2MeBr\cdot SH$, crystallising in long, lustrous, silky needles, m. p. 32—33°; the *diacetyl* derivative is a liquid; the *dibenzoyl* derivative forms colourless needles, m. p. 93—94°.

5-*Bromo*-p-*cresol* 3-*disulphide*, $S_2(C_6H_2MeBr\cdot OH)_2$, prepared by oxidising the mercaptan with ferric chloride, crystallises in lustrous, pale yellow needles, m. p. 76—77°; the *dibenzoyl* derivative forms colourless needles, m. p. 130—131°.

On methylation with methyl iodide and sodium methoxide in methyl-alcoholic solution, the mercaptan is converted into 5-*bromo*-3-*methylthiol*-p-*cresol*, $OH\cdot C_6H_2MeBr\cdot SMe$, which forms a colourless, strongly refractive oil, b. p. 162—163°/13—14 mm., yields an *acetyl* derivative, crystallising in colourless needles, m. p. 51—52°, and, when treated with bromine in chloroform solution, gives 2 : 5-*dibromo*-3-*methylthiol*-p-*cresol dibromide*, $HO\cdot C_6HMeBr_2\cdot SMeBr_2$. The latter compound crystallises in stout, almost black needles and prisms, strongly resembling iodine in appearance; it sinters at 100°, and melts at 128—130°, with the evolution of bromine and hydrobromic acid. It loses bromine on exposure to air, and when treated with bromine in chloroform solution yields 2 : 3 : 5-tribromocresol.

2 : 5-*Dibromo*-3-*methylthiol*-p-*cresol*, $OH\cdot C_6HMeBr_2\cdot SMe$, prepared

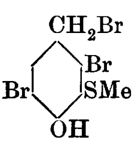
from the dibromide by shaking with aqueous sodium hydrogen sulphite, or by boiling with glacial acetic acid, forms small, compact, colourless crystals, m. p. 53—54°; from hot glacial acetic acid, it separates in colourless prisms containing acetic acid; it unites with bromine to form the original dibromide. On treatment with nitric acid in glacial acetic acid solution, it yields 2 : 5-dibromo-3-nitro-*p*-cresol.

The *acetyl* derivative of 2 : 5-dibromo-3-methylthiol-*p*-cresol crystallises in short, colourless prisms, m. p. 88—89°.

2 : 5-*Dibromo*-p-*cresol*-3-*methylsulphoxide*, $OH\cdot C_6HMeBr_2\cdot SOMe$, obtained together with the pseudo-bromide described below by shaking an ethereal solution of 2 : 5-dibromo-3-methylthiol-*p*-cresol dibromide with water, forms small, lustrous prisms, which sinter at 185°, and melt at 188—190° (decomp.); on treatment with saturated aqueous hydrobromic acid, it is reconverted into the dibromide.

2 : 5-*Dibromo*-p-*cresol*-3-*methylsulphone*, $HO\cdot C_6HMeBr_2\cdot SO_2Me$, prepared by oxidising 2 : 5-dibromo-3-methylthiol-*p*-cresol with hydrogen peroxide in glacial acetic acid solution, crystallises in lustrous needles, m. p. 160—161°.

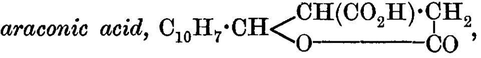
2 : 5-*Dibromo*-3-*methylthiol*-p-*cresol* ψ-*bromide* (annexed formula) is obtained from the above-mentioned dibromide either by shaking with water in ethereal solution or by the action of glacial acetic acid and anhydrous potassium acetate; it crystallises in long, colourless needles, m. p. 130—131°, yields an orange-red *additive* product with bromine, and in contact with alkali slowly acquires a greenish colour, finally becoming almost black. On treatment with aqueous sodium acetate and ether, it is converted into an intensely black *quinone*, probably belonging to the stilbene series. F. B.



Synthesis of 4-Hydroxyphenanthrene. ROBERT BEHREND and WILHELM LUDEWIG [and, in part, THEODOR KLINCKHARD] (*Annalen*, 1911, **379**, 351—362).—4-Hydroxyphenanthrene has been synthesised by a method analogous to that for the synthesis of a 4-naphthol from phenyl*iso*crotonic acid.

Full details are given of the best method for preparing β-naphthaldehyde from calcium α-naphthoate and calcium formate, the yield being about 65% of the theoretical.

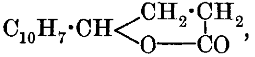
β-*Naphthylparaconic acid*,



$C_{10}H_7\cdot CH{<}\begin{array}{l}CH(CO_2H)\cdot CH_2\\ O\text{————}CO\end{array}$, obtained by heating the aldehyde with anhydrous sodium succinate (1·2 mols.) and freshly distilled acetic anhydride (1·3 mols.) at 108—114° for six to eight hours after keeping overnight in a closed vessel at the ordinary temperature, is extracted with hot carbon disulphide to remove colouring matter, dissolved in sodium hydrogen carbonate solution, precipitated with hydrochloric acid, and crystallised from hot water.

It has m. p. 169—170° (decomp.) when the bath is previously heated to 160°. When dissolved in the theoretical amount of *N*/3-potassium hydroxide solution, then well cooled, and acidified with the theoretical amount of sulphuric acid and extracted with ether, β-*naphthylitamalic acid*, $C_{10}H_7\cdot CH(OH)\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, is obtained. It has m. p. 124—125° (decomp.), and is transformed readily into the paraconic acid.

*β-Naphthyl*iso*crotonic acid*, $C_{10}H_7\cdot CH{:}CH\cdot CH_2\cdot CO_2H$, is formed together with 4-hydroxyphenanthrene (Pschorr and Jackel, Abstr., 1900, i, 488) and naphthylbutyrolactone when the paraconic acid is heated at 200—275°, or when it is distilled slowly. The acid dissolves in dilute sodium carbonate solution, crystallises from carbon disulphide in glistening rods, or from toluene in glistening plates, m. p. 163—164°, and when heated for some time at 100° yields 4-hydroxyphenanthrene.

β-Naphthylbutyrolactone,  $C_{10}H_7\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ O\text{——}CO\end{matrix}$, crystallises from water in small, glistening, colourless plates, m. p. 120—121°, after sintering at 115—116°. J. J. S.

Reactions which lead to the Formation of Iodine Derivatives. G. Gérard (*Chem. Zentr.*, 1910, ii, 1050; from *Bull. Sci. Pharmacol.*, 1910, **17**, 381—382).—When a solution of 2 grams of resorcinol and 1 gram of iodine in 10 grams of alcohol and 20 grams of water is mixed with a solution of 2 grams of borax and 1 gram of iodine in 10 grams of alcohol and 20 grams of water, a colourless solution is obtained which does not yield a blue coloration with starch paste; on boiling the solution, or exposing it to light, an intense red coloration is produced, and the mixture gives a reaction with starch paste. When the solution is concentrated, violet, hexagonal plates are deposited, which are soluble in water, alcohol, and ether (tri-iodoresorcinol?). Another colourless solution, in which free iodine cannot be detected, is obtained by mixing a solution containing resorcinol, iodine, and sodium benzoate with a solution containing resorcinol, iodine, and sodium salicylate. If the resorcinol is replaced by tannin, brown solutions are obtained; these show no reactions for free iodine, and, when dried at a temperature of 50°, yield brown scales having a sweet, and not an astringent, taste. W. P. S.

Basic Properties of Oxygen: Compounds of the Halogen Acids with Benzene Derivatives Containing Oxygen. O. Maass and Douglas McIntosh (*J. Amer. Chem. Soc.*, 1911, **33**, 70—71).—Baeyer and Villiger (Abstr., 1901, i, 658) have stated that the substitution of positive groups, such as alkyl groups, for the hydrogen in water renders the oxygen basic, whilst negative groups, like phenyl, do not have this effect, and that such compounds as phenol and benzophenone do not yield salts with acids. It is now shown that this generalisation is not correct, since many substances containing the phenyl group dissolve in liquid hydrogen bromide or chloride with formation of compounds.

The following compounds have been obtained in the crystalline state: resorcinol *hydrobromide*, $C_6H_4(OH)_2,4HBr$, m. p. −71°; benzoic acid *hydrobromide*, $C_7H_6O_2,2HBr$, m. p. −44°; benzophenone *hydrobromide*, $COPh_2,6HBr$, m. p. −42°; and resorcinol *hydrochloride*, $C_6H_4(OH)_2,3(\text{or }4)HCl$, and benzophenone *hydrochloride*,

$$(C_6H_5)_2CO,7HCl,$$

both with m. p. below −85°. The benzophenone compounds contain more acid than would unite with the oxygen if it were quadri- or even sexa-valent, and it is therefore suggested that they should at present be regarded merely as substances with acid of crystallisation.

E. G.

Derivatives of Butyl*cyclo*hexane.

Georges Darzens and **H. Rost** (*Compt. rend.*, 1911, **152**, 607—609).—p-*tert.*-Butylphenol is readily hydrogenated by Sabatier and Senderens' method if the nickel is prepared by reduction below 260°; the yield is practically theoretical if hydrogenation is effected below 160°. tert.-*Butyl*cyclo*hexan*-4-*ol*, $C_{10}H_{20}O$, m. p. 83°, b. p. 110—115°/15 mm., has a camphoraceous odour; on oxidation with chromic acid it yields tert.-*butyl*cyclo*hexan*-4-*one*, b. p. 106—109°/18 mm., 65—67°/3 mm.; the *semicarbazone* has m. p. 215—216°.

1-*Methyl*-3-tert.-*butyl*cyclo*hexan*-6-*one*, b. p. 118—122°/31 mm., has a fruity odour.

5-tert.-*Butyl*-m-*xylen*-2-*ol*, prepared by sulphonating butylxylene and heating the product with potassium hydroxide, has m. p. 75°, b. p. 107°/6 mm. On hydrogenation it yields 1 : 3-*dimethyl*-5-tert.-*butyl*cyclo*hexan*-2-*ol*, a viscous liquid, b. p. 123—124°/22 mm. 1 : 3-*Dimethyl*-5-tert.-*butyl*cyclo*hexan*-2-*one* has b. p. 120—121°/21 mm., and, like the foregoing ketone, does not form a semicarbazone.

W. O. W.

Crystallography of Some Organic Additive Compounds.

Giovanni Boeris (*Zeitsch. Kryst. Min.*, 1911, **49**, 72—73; from *Mem. R. Accad. Sci. Ist. Bologna*, 1907-1908, [vi], **5**, 303—308).—The additive compound of *iso*apiole and picryl chloride,

$$C_{12}H_{14}O_4,C_6H_2Cl(NO_2)_3,$$

forms dark garnet-red, triclinic crystals [$a : b : c = 0·5453 : 1 : 0·4847$; $\alpha = 86°6'$, $\beta = 111°58'$, $\gamma = 106°57'$].

The compound of *iso*apiole with *s*-trinitrotoluene,

$$C_{12}H_{14}O_4,C_6H_2Me(NO_2)_3,$$

forms scarlet, triclinic crystals [$a : b : c = 0·5495 : 1 : 0·4907$; $\alpha = 87°36'$, $\beta = 112°34'$, $\gamma = 105°16'$].

This and other examples not quoted confirms the author's view that the groups Cl and Me replace one another isogonically.

L. J. S.

Oxidation of Tertiary Alcohols of the Tolylallyl Series.

E. Grishkewitsch-Trochimowsky (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1543—1552).—The author has studied the products of oxidation of some of the alcohols previously described (Abstr., 1909, i, 151; 1910, i, 108) by means of potassium permanganate.

p-Tolylmethylallylcarbinol yields: (1) β-*p*-tolylpentane-$\beta\delta\epsilon$-triol, $C_6H_4Me·CMe(OH)·CH_2·CH(OH)·CH_2·OH$, needles, m. p. 101—103°, and (2) the unstable β-*p*-tolyl-β-methylhydracrylic acid, m. p. 103—106°; on dry distillation this acid yields β-*p*-tolylpropylene (compare Matschurevitsch, Abstr., 1909, i, 304).

p-Tolylethylallylcarbinol yields: (1) γ-p-*tolylhexane*-$\gamma\epsilon\zeta$-*triol*,

$$C_6H_4Me·CEt(OH)·CH_2·CH(OH)·CH_2·OH,$$

colourless needles, m. p. 89—90·5°, and (2) β-p-*tolyl*-β-*ethylhydracrylic acid*, $C_6H_4Me·CEt(OH)·CH_2·CO_2H$, short prisms and plates, m. p.

109—111°, decomposing at 125°; the *silver* and *barium* salts were prepared. On dry distillation, the acid yields β-p-*tolyl*-Δ^{a}-*butylene*, $C_6H_4Me\cdot CEt\colon CH_2$, b. p. 206—209°/750 mm., $D_4^{22\cdot5}$ 0·8926, $n_D^{22\cdot5}$ 1·52735.

p-Tolylpropylallylcarbinol gives: (1) δ-p-*tolylheptane*-αβδ-*triol*, $C_6H_4Me\cdot CPr^{a}(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, a very viscous, yellow liquid, and (2) β-p-*tolyl*-β-*propylhydracrylic acid*,

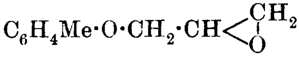
$$C_6H_4Me\cdot CPr^{a}(OH)\cdot CH_2\cdot CO_2H,$$

thin needles, m. p. 99—101°, of which the *barium* and *sodium* salts were prepared. On dry distillation, the acid yields β-p-*tolyl*-Δ^{a}-*amylene*, $C_6H_4Me\cdot CPr^{a}\colon CH_2$, as a colourless liquid, b. p. 221—224°/760 mm.

p-Tolyl*iso*propylallylcarbinol yields: (1) β-*methyl*-γ-p-*tolylhexane*-γεζ-*triol*, $CHMe_2\cdot C(C_6H_4Me)(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH$, as a viscous, pale yellow liquid, and (2) β-p-*tolyl*-β-iso*propylhydracrylic acid*, $C_6H_4Me\cdot CPr^{\beta}(OH)\cdot CH_2\cdot CO_2H$, thin, colourless needles, m. p. 106—108°; the *potassium*, *sodium*, and *silver* salts were prepared. On dry distillation, the acid gives β-p-*tolyl*-γ-*methyl*-Δ^{a}-*butylene*, $C_6H_4Me\cdot CPr^{\beta}\colon CH_2$, as a colourless liquid, b. p. 210—212°, D_4^{27} 0·8838, n_D^{27} 1·52543.

T. H. P.

Preparation of Secondary Amino-alcohols. LES ETABLISSEMENTS POULENC FRÈRES and ERNEST FOURNEAU (D.R.-P. 228205).—The preparation of numerous secondary amino-alcohols of the general formula $OR\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NR_1R_2$ (where R is an aryl or substituted aryl residue; R_1 an hydrogen, alkyl, aryl, or substituted aryl or alkylaryl group; R_2 an alkyl, aryl, or substituted aryl or alkylaryl residue) by the interaction of glycerol ethers on primary or secondary aliphatic or aromatic amines, or on amino-phenols or -naphthols, has previously been described (compare Fourneau, Abstr., 1910, i, 246, 822).

p-*Tolyl glycide ether*,  $C_6H_4Me\cdot O\cdot CH_2\cdot CH<\begin{matrix}CH_2\\|\\O\end{matrix}$, a liquid, b. p. 165—166°/20 mm., is obtained by heating together *p*-cresol, dichlorohydrin, and sodium hydroxide (2 mols.); this when boiled during several days with dimethylamine (in petroleum solution) yields *dimethylamino*-p-*tolyloxypropanol*,

$$C_6H_4Me\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2,$$

a colourless oil, b. p. 175—176°/10 mm., and strongly alkaline to litmus; the *hydrochloride* of the *benzoyl* derivative has m. p. 155°.

The glycide ether, prepared from thymol and epichlorohydrin or dichlorohydrin, is stated to have m. p. 61° and b. p. 176°/20 mm. (Abstr., 1910, i, 246 gives 88° and 180° respectively).

Dimethylamino-β-*phenoxy*-α-*methoxypropanol*,

$$OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot NMe_2,$$

crystals, m. p. 60—61°, is prepared by the action of dimethylamine on the corresponding glycide ether (b. p. 166—168°/12 mm.); the *methiodide* has m. p. 114°.

The *glycide ether*, prepared from β-naphthol and dichlorohydrin, has b. p. 212—213°/12 mm., and γ-dimethylamino-β-naphthoxypropanol, b. p. 217°/16 mm. (*loc. cit.* gives 217°/11 mm.). The action of dichlorohydrin on sodium *p*-nitrophenoxide yields the glycide ether, b. p.

250—255°/15 mm., m. p. 69°, accompanied by glycerol di-*p*-nitrophenyl ether.

γ-Dimethylamino-α-phenoxypropanol has a fish-like odour, and b. p. 162°/11 mm. (*loc. cit.* gives 161°/13 mm.); its ethobromide has m. p. 110° (*loc. cit.* 112°).

γ-Anilinophenoxypropanol yields with gold chloride a violet-red precipitate, which rapidly changes to green; and with potassium mercury iodide an oily, green precipitate; the *picrate* separates as an oil, which after crystalisation from alcohol forms needles, m. p. 121—122°. F. M. G. M.

Two New Methods for Synthesising Nitriles. VICTOR GRIGNARD (*Compt. rend.*, 1911, **152**, 388—390).—Cyanogen chloride, preferably prepared by Held's method, is dried over calcium chloride and passed into dry ether at 0°. An ethereal solution of an organo-magnesium halide is now allowed to flow in drop by drop. After some hours the liquid is treated in the usual way, and a good yield (55—80%) of a pure nitrile is thus obtained. The reaction is represented as: $RMgX + CNCl = MgXCl + R{\cdot}CN$. The other halogen derivative of cyanogen are not suitable for this preparation; thus, with cyanogen iodide the reaction proceeds entirely according to the equation: $RMgBr + CNI = RI + MgBr{\cdot}CN$. In the case of cyanogen bromide, both reactions occur, the latter predominating. Benzonitrile, 1-naphthonitrile, anisonitrile, and phenylpropionitrile have been prepared by this process.

The second method consists of substituting cyanogen itself for the halogen derivative. It has been used to prepare benzonitrile, *iso*hexonitrile, and phenylbutyronitrile, but the yields are inferior to those obtained with the chloride. If the order of mixing the organo-magnesium compound with the cyanogen or its chloride is reversed, ketones are produced in the usual way. W. O. W.

3:5-Dibromoanthranilic Acid. FRITZ ULLMANN and EDUARD KOPETSCHNI (*Ber.*, 1911, **44**, 425—431).—3:5-Dibromo-2-aminobenzoic acid (Wheeler and Oates, Abstr., 1910, i, 481) is readily obtained by passing bromine vapour into a dilute solution of anthranilic acid in aqueous hydrochloric acid; it is converted by bromine water into tribromoaniline, and yields diazonium salts which are very stable in aqueous solution.

3 : 5-*Dibromophthalic acid*, prepared from the preceding acid by the Sandmeyer reaction, crystallises in colourless needles; when rapidly heated, it melts at 198°, and is simultaneously converted into the *anhydride*, m. p. 121·5°.

2 : 3 : 5-Tribromobenzoic acid has been obtained in colourless needles, m. p. 190° (compare Rosanoff and Prager, Abstr., 1909, ii, 32); the *methyl* ester crystallises in long, silky needles, m. p. 77°.

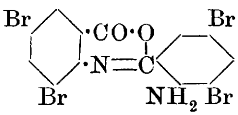
When boiled with aqueous potassium carbonate and copper, 2 : 3 : 5-tribromobenzoic acid is converted into 3 : 5-dibromosalicylic acid, m. p. 228° (Lellmann and Grothmann, Abstr., 1885, 265, give 223°).

The dibromosalicylic acid obtained by Lassar-Cohn and Schultze (Abstr., 1905, i, 893), by the action of potassium hypobromite on potassium salicylate, and considered by them to be the 5 : 6-derivative, is identical with the above-mentioned 3 : 5-dibromosalicylic acid.

4 : 6-Dibromophenylglycine-2-carboxylic acid is produced in small quantities by the interaction of 2 : 3 : 5-tribromobenzoic acid and glycine in the presence of copper. It is best prepared by brominating phenylglycine-*o*-carboxylic acid in sulphuric acid solution; it crystallises in pale yellow, microscopic needles, m. p. 248° (decomp.); the *methyl* ester has m. p. 88°.

When boiled with anhydrous potassium acetate and acetic anhydride, 4 : 6-dibromophenylglycine-2-carboxylic acid yields 5 : 7 : 5′ : 7′-tetrabromoindigotin (Grandmougin, Abstr, 1910, i, 259).

The interaction of *p*-toluenesulphonyl chloride and 3 : 5-dibromo-2-aminobenzoic acid, either in aqueous potassium carbonate or pyridine solution, leads to the formation of *dibromoanthranoyl-dibromoanthranilic acid O-anhydride* (annexed formula), which crystallises in citron-yellow needles, m. p. 342° (corr.) F. B.

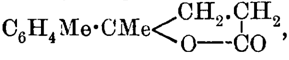


Action of Nitrous Acid on Methyl Dimethylanthranilate.

JOSEF HOUBEN (*Ber.*, 1911, **44**, 547).—In consequence of an error in the estimation of the nitrogen, the azomethine compound obtained from methyl dimethylanthranilate has been stated to be a monomethyl derivative (this vol., i, 128). This is incorrect; the percentage of nitrogen found corresponds with the formula of a dimethyl derivative, and the condensation follows a normal course. C. S.

Turmeric Oil. III. Synthesis of γ-*p*-Tolylvaleric Acid.

HANS RUPE and A. STEINBACH (*Ber.*, 1911, **44**, 584—588. Compare this vol., i, 69).—Since it has been shown that curcumic acid is possibly γ-*p*-tolylvaleric acid, the synthesis of this acid has been effected; the product, however, is not curcumic acid, although very similar to it.

γ-p-*Tolyl-γ-methyl*iso*crotonic acid*, $C_6H_4Me \cdot CMe{:}CH \cdot CH_2 \cdot CO_2H$, m. p. 86—87°, is obtained by adding ethereal magnesium methyl iodide to ethyl β-*p*-toluoylpropionate in ether (when the order of addition is reversed hardly any reaction occurs), and decomposing the product with water and dilute sulphuric acid at 0°. When boiled for four hours with 10% sulphuric acid, it is converted into γ-p-*tolyl-γ-valerolactone*,  $C_6H_4Me \cdot CMe<\begin{matrix} CH_2.CH_2 \\ O \text{---} CO \end{matrix}$, m. p. 52°, which is reduced by boiling hydriodic acid, D 1·702, and red phosphorus to γ-p-*tolylvaleric* acid, $C_6H_4Me \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot CO_2H$, m. p. 32°, b. p. 173—174°/9 mm. Like curcumic acid (m. p. 33—34°, b. p. 168—170°/12 mm.), this acid is extremely soluble in the usual solvents; also, its calcium salt melts in boiling water. The two acids, however, liquefy when mixed, and yield different p-*toluidides*, that from curcumic acid having m. p. 126—127°, whilst the toluidide of the synthetic acid has m. p. 77—79°; also, the two acids yield different products by oxidation. When *p*-tolylvaleric acid is treated with 4% potassium permanganate and sodium carbonate at 0°, the chief product is the lactone mentioned above; a small amount of *p*-tolylmethyl ketone (identified as the semicarbazide) and a *substance*, m. p. 150—151° (not identical with the acid, m. p. 150—151°, obtained amongst the products of oxidation of curcumic acid) are also formed. This result is important, since it proves that curcumic acid must have a constitution which does not admit of the formation of a lactone when the acid is oxidised. C. S.

Condensation of β-Naphthaldehyde with Methylsuccinic Acid. ROBERT BEHREND and THEODOR KLINCKHARD (*Annalen*, 1911, **379**, 362—376).—According to Fittig and Liebmann (Abstr., 1890, 775), two structurally isomeric phenyl-α-methylparaconic acids are obtained by the condensation of benzaldehyde with sodium methylsuccinate and acetic anhydride, and the two acids yield α-methylphenyl*iso*crotonic acid and the isomeric β-methyl derivative when distilled. Heptaldehyde (Fittig and Riechelmann, Abstr., 1890, 593) and valeraldehyde (Fittig and Feist, *ibid.*, 591) each yield two structurally isomeric paraconic acids when condensed with methylsuccinic acid. When β-naphthaldehyde is used, it is shown that two isomeric β-naphthylmethylparaconic acids are formed, but these are stereoisomeric, as they yield the same naphthyl-β-methyl*iso*crotonic acid when distilled. The constitution of the condensation products follows from the fact that the hydroxymethylphenanthrene obtained by the removal of water from the *iso*crotonic acid yields on distillation with zinc dust a methylphenanthrene which is not identical with Pschorr and Quade's 3-methylphenanthrene (Abstr., 1906, i, 848).

The separation of the two naphthylmethylparaconic acids can be effected by fractional crystallisation from dilute alcohol. The one acid, $C_6H_{14}O_4,H_2O$, separates from 60% alcohol in transparent, monoclinic crystals, and when slowly heated has m. p. 199—200° (decomp.), after sintering at 198—199°. The anhydrous compound has the same m. p. The *stereoisomeride*, $C_{16}H_{14}O_4$ crystallises from 50% alcohol in nodular masses of minute plates, or in well developed prisms, m. p. 174—175° (decomp.). When distilled slowly under reduced pressure, the two acids yield *naphthyl-β-methyl*iso*crotonic acid*, together with 4-hydroxy-2-methylphenanthrene, naphthyl*iso*butylene, and unaltered acid. The unsaturated acid can be separated from unaltered paraconic acids by extraction with cold carbon disulphide, and crystallises from the solvent in rectangular plates, m. p. 137—138°.

4-*Hydroxy*-2-*methylphenanthrene*, $C_{15}H_{12}O$, crystallises from dilute alcohol, and its alcoholic solution gives an orange-red coloration with ferric chloride and a lemon-yellow with bleaching powder solution. Its *acetyl* derivative, $C_{17}H_{14}O_2$, crystallises from dilute alcohol in slender needles or glistening plates, m. p. 110·5—111·5°. 2-*Methylphenanthrene*, $C_{15}H_{12}$, has m. p. 52—53°, and when mixed with the isomeric 3-methyl derivative has m. p. 40—42°.

*β-Naphthyl*iso*butylene*, $C_{10}H_7{\cdot}CH{:}CMe_2$, is a colourless oil, with b. p. 287—288°. J. J. S.

Chemical Investigation of Resin from the Pine (Picea excelsa). II. Lævo-pimaric Acid. JOHN KÖHLER (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 5, 1—29. Compare Abstr., 1906, i, 92, 100; 1907, i, 213).—Hitherto, the only source of pimaric acid has been galipot resin; it has now been found to occur universally in pines from Rottanne (*Picea excelsa*), usually accompanied by weaker lævo-rotatory, more easily soluble, and easily oxidisable acids, probably sapinic acids [?]. A very pure specimen was found in the winter-resin from the upper half of the trunk of one of the pines, and after recrystallisation from methyl alcohol it gave $[\alpha]_D^{20} = -280{\cdot}5°$, which is a higher rotation than has hitherto been found. Analysis and determination of the molecular weight by titration with alkali confirm the formula $C_{20}H_{80}O_2$. It does not possess a definite melting point, since at the melting-point temperature it undergoes a partial change into colophonic acids, the amount of change depending on the rapidity of heating. The crystals have the axial ratio:

$$[a:b:c = 0{\cdot}80975:1:0{\cdot}6102].$$

On being heated, *l*-pimaric acid changes into a mixture of an inactive colophonic acid and lævo-rotatory colophonic acids, which are identical with the α-colophonic acids prepared from sapinic acids [?].

The active colophonic acids crystallise in the monoclinic system, and are completely isomorphous with each other, so that it is not possible, with certainty, to isolate any given acid by fractional crystallisation. Inactive colophonic acid, like *l*-pimaric acid, crystallises in the rhombic system, although it is not isomorphous with it $[a:b:c = 0{\cdot}47698:1:\infty c]$.

Analysis of a colophonic acid with $[\alpha]_D^{20} = -83{\cdot}3°$, and determination of the molecular weight by titration with alkali, gave results agreeing with the formula $C_{20}H_{30}O_2$.

The colophonic acids possess the general property of forming a gel when their solutions in alcohol and ammonia are diluted with water; in this way, they may be distinguished from the naturally occurring resin acids. They are a general transformation product of the action of heat on the naturally occurring acids, such as *l*-pimaric acid and the sapinic acids.

The following classification is given:

A. Natural Resin Acids.—(1) Acids which do not oxidise in the air, and are relatively stable on heating. (2) Acids which readily oxidise in the air, and are very sensitive towards heat. Class (1) includes the pimaric acids, and class (2) the sapinic acids. On heating, both classes change into:

B. Colophonic Acids.—(1) α-Colophonic acids, lævorotatory. (2) β-Colophonic acids, dextrorotatory. Both the α- and β-acids are readily oxidised in the air, and, on heating, change into acids in the same group. (3) Inactive colophonic acids. T. S. P.

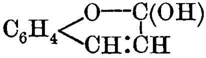
Conversion of Stable Stereoisomerides into Labile Modifications by Ultra-violet Light. II. RICHARD STOERMER [with EGON FRIDERICI, BRÄUTIGAM, and W. NECKEL] (*Ber.*, 1911, **44**, 637—668. Compare Abstr., 1910, i, 114).—The stable, less fusible forms of the following compounds are transformed into the labile, more fusible stereoisomerides when their benzene or alcoholic solutions are exposed to the action of the ultra-violet rays from a uviol lamp for several days: coumaric acid, 75; methylcoumaric acid, 75; ethylcoumaric acid, over 90; propylcoumaric acid, 85; methylcoumaramide, 50; ethylcoumaramide, 100; propylcoumaramide, 95; methyl coumarate ⟶ coumarin; acetylcoumaric acid, over 90; methyl benzoylcoumarate; methyl a-*o*-nitro-*o*′-methoxycinnamate, 80; a-*o*-nitro-*o*′-methoxycoumaric acid, 40; *p*-methoxycinnamic acid, 25; sodium *o*-chlorocinnamate, 10; piperonylacrylic acid, 17; maleic acid; bromofumaric acid, 50; *o*-anisylcinnamic acid, 35—40; *o*-anisylcinnamide, 70; *o*-anisylcinnam-methylamide, 36, and corresponding ethylamide, 40; b-*o*-anisyl-α-methylcinnamic acid, 5, and the corresponding amide, 5; cinnamic ⟶ *iso*cinnamic acid, m. p. 42°, 30—40; phenyl tolyl ketoxime, 40; phenyl anisyl ketoxime. In most cases the reaction is a balanced one, and the number given for each compound represents the percentage of the less fusible compound which has been transformed when equilibrium is established. Crotonic acid is not transformed to any appreciable extent.

The method is recommended as a suitable one for the preparation of *allo*-stereoisomerides in several cases, and also for the detection of spatial isomerism between a pair of compounds. In a few instances the addition of methyl or ethyl alcohol to the unsaturated compound occurs during the exposure to the ultra-violet light, but the amounts of such products are usually small. It is suggested that the transformation and the percentage amount transformed depends on the energy differences between the stereoisomerides. Sodium fumarate is not transformed, although the corresponding acid yields 30% of maleic acid.

The following new compounds are described: *propylcoumaric* [a-o-*propoxycinnamic*] *acid*, $OPr{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$, obtained by hydrolysing the corresponding methyl ester, crystallises from dilute alcohol in glistening needles, m. p. 104—105°, and the stereoisomeric *propylcoumarinic* [b-o-*propoxycinnamic*] *acid* has m. p. 83—84°. The solubilities of the two acids in light petroleum at 18° are 0·106 and 0·301% respectively. Both compounds with sodium amalgam yield b-*propoxyphenylpropionic acid*, $OPr{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, m. p. 63°.

b-o-*Methoxycinnamamide* can be obtained by the action of phosphorus pentachloride on a dry ethereal solution of b-*o*-methoxycinnamic acid (compare Perkin, Trans., 1877, **31**, 422) and treating the product with ice-cold ammonium hydroxide solution; it crystallises from carbon disulphide in needles, m. p. 62·5—63·5°. a-o-*Ethoxycinnamamide*, $C_{11}H_{13}O_2N$, has m. p. 161°, and the stereoisomeric b-o-*ethoxycinnamamide*, m. p. 115—116°.

a-o-*Propoxycinnamamide*, $C_{12}H_{15}O_2N$, has m. p. 145°, and β-o-*propoxycinnamamide*, m. p. 104°. b-o-*Acetoxycinnamamic acid*, $OAc{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CO_2H$, prepared by the action of acetic anhydride on dry sodium β-coumarate at 0°, crystallises from carbon disulphide, has m. p. 85°, and when boiled with water for some time yields coumarin. b-o-*Benzoyloxycinnamic acid*, $C_{16}H_{12}O_4$, forms compact crystals from carbon disulphide, and has m. p. 96—97°. *Methyl* a-o-*benzoyloxycinnamate*, $C_{17}H_{14}O_4$, obtained by benzoylating methyl coumarate, crystallises from alcohol in slender needles, m. p. 87°, and on hydrolysis yields benzoic and coumaric acids.

Methyl b-o-*benzoyloxycinnamate*, prepared from the silver salt of the corresponding acid, has m. p. 46°. *Ethyl* b-o-*methyloxycinnamate*, obtained from the sodium salt and ethyl sulphate, has b. p. 291—292·5°, and the isomeric *methyl* b-o-*ethyloxycinnamate*, b. p. 288·5—289·5°; each ester gives the corresponding acid on hydrolysis, and this points to the conclusion that β-coumaric acid cannot have the dihydroxylic structure,  $C_6H_4<\begin{array}{l}O—C(OH)_2\\ CH:CH\end{array}$, as the two esters should then be identical. p-*Methoxy*allo*cinnamic acid*, $C_{10}H_{10}O_3$, separates from light petroleum in triclinic crystals, m. p. 64—65°. Its solubility in benzene at 18° is 34%, and in light petroleum, 0·28%. It does not show the properties of a crystalline liquid, and is readily transformed into the less fusible stereoisomeride when its carbon disulphide solution is mixed with a little bromine and exposed to sunlight. The *aniline* salt, $C_{26}H_{27}O_6N$, crystallises from benzene in slender needles, m. p. 68°; the *amide*, prepared by the action of phosphorus pentachloride on the acid in presence of ether and treatment of the product with ammonium hydroxide, has m. p. 129°; in the absence of ether the amide of *p*-methoxycinnamic acid (m. p. 186°) is formed.

o-*Chloro*allo*cinnamic acid*, $C_9H_7O_2Cl$, crystallises from water, and has m. p. 127°. Its solubility in benzene at 18° is 1·88%. *o*-Chlorocinnamic acid has m. p. 205° (Gabriel and Herzberg, Abstr., 1883, 1123, give 200°), and its solubility in benzene is 0·04%. When this acid or its sodium salt is exposed to ultra-violet light, it is partly transformed into the *allo*-acid, but when glacial acetic acid solutions are used, part of the acid combines with acetic acid, giving a product, $C_{11}H_{11}O_4Cl$, m. p. 212—213°. The *aniline* salt of the *allo*-acid forms slender needles, m. p. 136°; the *amide*, C_9H_8ONCl, which crystallises from dilute alcohol in blue, fluorescent needles, has m. p. 112°, and the isomeric *amide* has m. p. 163—163·5°. allo-*Piperonylacrylic acid*, $C_{10}H_8O_4$, crystallises from water, and has m. p. 96—97°. Its solubility in benzene at 18° is 5·9%. Its *aniline* salt has m. p. 83·5—84°; the *amide*, $C_{10}H_9O_3N$, crystallises from ether in glistening plates, m. p. 131°, and the isomeric *amide* from alcohol in slender needles, m. p. 180°.

The piperidine salt of *o*-anisylcinnamic acid has m. p. 145°, not 54—55°, and the silver salts of both isomeric acids are soluble in benzene. o-*Anisylcinnamamide*, $C_{16}H_{15}O_2N$, has m. p. 137°, and its solubility in benzene is 0·8%; the *stereoisomeride* has m. p. 115—116°, and its solubility in benzene is 1·7%. o-*Anisylcinnam-methylamide*, $C_{17}H_{17}O_2N$, has m. p. 121°; the corresponding *ethylamide*, $C_{18}H_{19}O_2N$, m. p. 101°, and the respective stereoisomerides, m. p.'s 104—105° and 74—80°. o-*Anisylcinnambenzylamide* has m. p. 144—145°; the *amylamide*, m. p. 102—103°, and the *anilide*, m. p. 138°.

The β-anisyl-α-methylcinnamic acids are most readily prepared from *o*-methoxybenzophenone and methyl α-bromopropionate; the condensation product, *methyl* β-*phenyl*-β-*anisyl*-α-*methylhydracrylate*, $C_{18}H_{20}O_4$, crystallises from alcohol in brilliant, rhombic crystals, m. p. 82—83°, and when treated with dry hydrogen chloride in methyl-alcoholic solution containing sodium sulphate yields methyl β-anisyl-α-methylcinnamate, m. p. 60—61°, together with the *allo*-ester.

The solubilities of the two acids in benzene are 11·6 and 20·2%, and the *amides*, $C_{17}H_{17}O_2N$, of the two acids melt at 137—138° and 115—118° respectively.

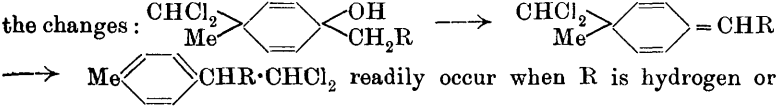
The conversion of b-*o*-ethoxycinnamic acid in carbon disulphide solution by means of iodine (compare Michael and Lamb, Abstr., 1907, i, 134) depends on the concentration of the iodine solution.

It is shown that the methoxy-groups in the methyl ether of *o*-nitrosalicylic acid and in *m*-nitro-*o*-methoxybenzaldehyde are readily hydrolysed when boiled with sodium carbonate solution. *m*-Nitro-*o*-methoxybenzoic acid has m. p. 194° (compare Keller, Abstr., 1908, i, 285).

When a solution of mesaconic acid is subjected to the action of ultra-violet light, water or methyl alcohol appears to combine with the acid. J. J. S.

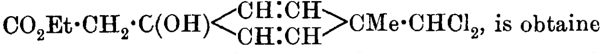
Hydroaromatic Compounds. Carboxylic Acid of the "Semibenzene" Group. Karl Auwers (*Ber.*, 1911, 44, 588—601. Compare Abstr., 1907, i, 399, 400, 401).—

It has been shown that the changes :

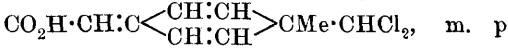


readily occur when R is hydrogen or an alkyl group. The present communication shows that R may also be a carboxyl group.

Ethyl 4-*hydroxy*-1-*methyl*-1-*dichloromethyl*cyclo*hexadiene*-4-*acetate* (I)



$CO_2Et\cdot CH_2\cdot C(OH)<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CMe\cdot CHCl_2$, is obtained in an impure state as a viscous, yellow oil by heating a benzene solution of 4-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene with ethyl bromoacetate and zinc, and decomposing the product with dilute sulphuric acid. The ester cannot be purified, owing to its tendency to lose the elements of water, but by the careful hydrolysis of its concentrated alcoholic solution by potassium hydroxide at 0° it yields the corresponding *acid*, $C_{10}H_{12}O_3Cl_2$, m. p. 119° (which cannot be kept long), and the dehydrated derivative thereof, 1-*methyl*-1-*dichloromethyl*cyclo*hexadiene*-Δ^4-*acetic acid* (II),



$CO_2H\cdot CH{:}C<\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}>CMe\cdot CHCl_2$, m. p. 107—108°, the two acids being separated by the greater solubility of the latter in benzene. The *ethyl* ester of the latter acid can be obtained by treating the preceding ester (I) with 98% formic acid, or in a pure state from the silver salt of the acid (II) and ethyl iodide. It has $D_4^{21\cdot 9}$ 1·2151, n_D 1·56911, and the presence of three conjugated double linkings is denoted by the exaltations of the specific and molecular refractions and the dispersion. By treatment with concentrated sulphuric acid at 0° for eighteen hours, the ester is converted into *ethyl* 4-*aldehydo*-2 (or 3)-*methylphenylacetate*, $CHO\cdot C_6H_3Me\cdot CH_2\cdot CO_2Et$, b. p. 160—172°/13 mm., which is isolated as the *semicarbazone*, $C_{13}H_{17}O_3N_3$,

m. p. 191—192° (compare Abstr., 1907, i, 399); the *semicarbazone* of the free acid has m. p. 234—235°.

1-Methyl-1-dichloromethyl*cyclo*hexadiene-Δ^4-acetic acid (II) can also be obtained by the hydrolysis of its ester by 50% alcoholic potassium hydroxide in the cold, or by treating 4-hydroxy-1-methyl-1-dichloromethyl*cyclo*hexadiene-4-acetic acid with 98% formic acid; in the latter method 1-methyl-4-$\beta\beta$-dichloroethylbenzene (IV) (Abstr., 1907, i, 400) is obtained as a by-product by the elimination of carbon dioxide and simultaneous intramolecular change of the "semibenzene" acid (II).

Ethyl $\beta\beta$-*dichloro*-α-p-*tolylpropionate*, $C_6H_4Me\cdot CH(CHCl_2)\cdot CO_2Et$, b. p. 162—164°/15 mm., $D_4^{19\cdot 4}$ 1·2011, n_D 1·52137, is obtained by heating the ester (I) or, in a purer state, the ester of II; its aromatic character is proved by the very small exaltations of its molecular refraction and dispersion. By hydrolysis with alkalis, the ester yields either a mixture of the acid and β-chloro-α-p-tolylacrylic acid or the latter alone. $\beta\beta$-*Dichloro*-α-p-*tolylpropionic acid*, $C_{10}H_{10}O_2Cl_2$, m. p. 156°, therefore, is best obtained by heating the "semibenzene" acid (II) on the water-bath; when heated over a naked flame, the acid II yields a considerable quantity of 1-methyl-4-$\beta\beta$-dichloroethylbenzene (IV). $\beta\beta$-Dichloro-α-p-tolylpropionic acid can be titrated with sodium hydroxide, but is much more sensitive to the attack of an excess of the alkali than the isomeric acid (II); for whilst the latter can be warmed with 10% sodium hydroxide without decomposition, the former is converted into β-*chloro*-α-*p*-*tolylacrylic acid*, $CHCl:C(C_6H_4Me)\cdot CO_2H$, m. p. 112°. This acid is obtained from each of the preceding compounds—most conveniently from the ester (I)—by heating with aqueous or alcoholic alkalis. It forms an *ethyl* ester, $C_{12}H_{13}O_2Cl$, b. p. 155—156°/15 mm., $D_4^{20\cdot 9}$ 1·1353, n_D 1·53579, which is oxidised in aqueous acetone by potassium permanganate, yielding ethyl p-tolylglyoxylate.

Unsuccessful attempts have been made to obtain compounds similar to the preceding from 2-keto-1-methyl-1-dichloromethyl*cyclo*hexadiene and 2-keto-1:5-dimethyl-1-dichloromethyl*cyclo*hexadiene. C. S.

Action of Ethyl Chlorocarbonate on Sodium Derivatives of Ketones Prepared by means of Sodamide

ALBIN HALLER and ÉDOUARD BAUER (*Compt. rend.*, 1911, **152**, 551—558).—The sodium derivatives of aliphatic or mixed aromatic-aliphatic ketones of the type $R\cdot CO\cdot CHR'R''$, on treatment with ethyl chlorocarbonate in benzene solution, form carbonates of the type $CR'R'':CR\cdot O\cdot CO_2Et$. Under the same conditions, however, ketones of the type

$$CPh\cdot CO\cdot CH_2R$$

yield compounds having the constitution $CO_2Et\cdot CR:CPh\cdot O\cdot CO_2Et$. On hydrolysis with alcoholic sodium hydroxide these form sodium ethyl carbonate and monoalkyl derivatives of ethyl benzoylacetate; the latter are thus obtained in a purer condition than when prepared by direct alkylation of the ester.

The sodium derivative of phenyl *iso*propyl ketone reacts vigorously with ethyl chlorocarbonate, giving a 70% yield of α-*ethylcarbonato*-α-*phenyl*-Δ^{α}-iso*butylene*, $CMe_2:CPh\cdot O\cdot CO_2Et$, m. p. 41—42°. The constitution of this compound follows from its conversion into sodium ethyl carbonate and phenyl *iso*propyl ketone when treated with the calculated amount of water and sodium ethoxide. It is the enolic form of *ethyl benzoyl*iso*butyrate*, $COPh\cdot CMe_2\cdot CO_2Et$, a liquid of b. p. 145—146°/13 mm.: also obtained by the action of methyl iodide and sodium ethoxide on Perkin and Colman's ethyl methylbenzoylacetate (Trans., 1886, **49**, 156); the *oxime* has m. p. 135—136°.

Propiophenone gives rise to *a-ethylcarbonato-a-phenyl-*Δ^{a}*-propylene*, $CHMe\!:\!CPh\cdot O\cdot CO_2Et$, b. p. 140—145°/11—12 mm., together with *ethyl β-ethylcarbonato-a-methylcinnamate*, $CO_2Et\cdot O\cdot CPh\!:\!CMe\cdot CO_2Et$, b. p. 182—185°/11—12 mm.

Butyrophenone gives *a-ethylcarbonato-a-phenyl-*Δ^{a}*-butylene*,
$CHEt\!:\!CPh\cdot O\cdot CO_2Et$,
b. p. 143°/10 mm., and *ethyl β-ethylcarbonato-a-ethylcinnamate*,
$CO_2Et\cdot O\cdot CPh\!:\!CEt\cdot CO_2Et$,
m. p. about 35°, b. p. 183—184°/10 mm.

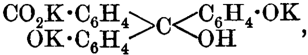
Acetophenone in the same way gives diethyl benzoylmalonate, together with an oil containing (1) a *compound*, $C_{11}H_{14}O_4$, b. p. 128—129°/11 mm.; it forms an unstable *bromo*-derivative, m. p. 78°; (2) ethyl β-carbethoxycinnamate.

Pentamethylacetone forms *γ-ethylcarbonato-βδδ-trimethyl-*Δ^{β}*-pentene*, $CMe_2\!:\!C(O\cdot CO_2Et)\cdot CMe_3$, b. p. 89—90°/13·5 mm.

*cyclo*Hexanone yields an oil containing (1) a substance, b. p. 108—110°/20 mm., having the composition of ethyl *cyclo*hexanonecarboxylate; (2) Wallach's di*cyclo*hexanone, characterised by the oxime, m. p. 155°, and the *semicarbazone*, m. p. 210—212°; (3) *ethylcarbonato-*Δ^1-cyclo*hexene*, $C_6H_9\cdot O\cdot CO_2Et$, b. p. 108—110°/20 mm., an enolic form of the ester of Gardner, Perkin, and Watson's *cyclo*hexanone-2-carboxylic acid (Trans., 1910, **97**, 1796). W. O. W.

Phenolphthalein and its Colourless Salts. PHILIP A. KOBER and J. THEODORE MARSHALL (*J. Amer. Chem. Soc.*, 1911, **33**, 59—70).—During the course of certain work on tests for blood (Kober, Lyle, and Marshall, Abstr., 1910, ii, 910) it was observed that the colour of a standard solution of phenolphthalein gradually faded. Although this phenomenon has been observed by others, it has not hitherto been fully investigated, and the present work was therefore undertaken.

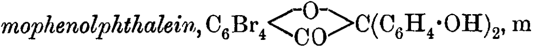
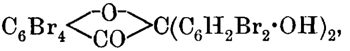
The rate of fading has been determined colorimetrically, and a curve has been obtained which resembles that of an irreversible unimolecular reaction. It has been shown by conductivity measurements that the change of colour is due to a chemical reaction in which alkali hydroxide takes part. From a study of concentrations at equilibrium, it has been found that the intensity of the colour depends on two factors: (1) dissociation or hydrolysis of the coloured dibasic salt, and (2) hydration with the formation of a colourless tribasic salt (compare Meyer and Hantzsch, Abstr., 1907, i, 932). If follows therefore that phenolphthalein is not an accurate colorimetric standard.

The *tripotassium* salt,  $\begin{matrix}CO_2K\cdot C_6H_4\\ OK\cdot C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_4\cdot OK\\ OH\end{matrix}$, $5H_2O$, has been isolated; it forms colourless, microscopic plates, and is fairly stable; when, however, an aqueous solution is boiled or left for a considerable time, it develops an intense red colour. The corresponding *trisodium* salt crystallises in cubes.

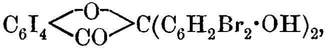
When the tripotassium salt is administered hypodermically to dogs, it produces a purgative effect. E. G.

Phenolphthalein Derivatives and their Behaviour as Indicators.

ERWIN RUPP (*Arch. Pharm.*, 1911, **249**, 56—68).—The behaviour of phenolphthalein derivatives containing negative substituents towards ammonia and alkaloids indicates that this is better explained by the chromophore theory of indicators than by the dissociation theory.

Tetrabromophenolphthalein,  $C_6Br_4<\substack{-O-\\CO}>C(C_6H_4\cdot OH)_2$, m.p. 280—285° (decomp.), prepared by heating tetrabromophthalic anhydride with phenol in sulphuric acid, crystallises from warm alcohol or acetic acid, and gives a violet colour with alkalis, which is discharged by acids. When heated with bromine in acetic acid, it gives *octabromophenolphthalein,*  $C_6Br_4<\substack{-O-\\CO}>C(C_6H_2Br_2\cdot OH)_2$, which crystallises in colourless needles, and gives a blue colour with alkalis.

Tetraiodophenolphthalein was not obtained crystalline; it gives a violet coloration, with alkalis and on heating with bromine in acetic acid gives *tetrabromotetraiodophenolphthalein,*



$$C_6I_4<\substack{-O-\\CO}>C(C_6H_2Br_2\cdot OH)_2,$$

which crystallises from dilute alcohol and gives a bluish-green coloration with alkalis.

These and other halogenated phenolphthaleins, as well as nitrophenolphthalein and dibromodinitrophenolphthalein, were tried as indicators with ammonia and morphine, and the results are tabulated in detail in the original. They show that the mere acidification of the phenolphthalein molecule by the introduction of negative groups does not effect any marked improvement in the values of the phthaleins as indicators for weak bases. The introduction of negative substituents in the phenol nucleus leads to a diffuse, gradual colour change, whilst their introduction into the phthalein nucleus gives rise to a rapid colour change with bases. This is best explained on the assumption that the free phenolphthaleins exist in the *pseudo*-form and their salts in the *quinonoid* form. The value of any phthalein as an indicator depends on the rapidity with which this change may occur, and this is influenced by the position of the substituents. This view is supported by the fact that acylated phenolphthaleins are unsuitable for use as indicators. T. A. H.

Acylated Salicylosalicylic [*o*-2-Acyloxybenzoyloxybenzoic] Acids.

ALFRED EINHORN [with GUSTAV HAAS, ALEXANDER VON BAGH, CARL LADISCH, and LEO ROTHLAUF] (*Ber.*, 1911, **44**, 431—439).—In the preparation of *o*-ethylcarbonatobenzoic acid by the interaction of ethyl chlorocarbonate and salicylic acid in pyridine solution, *o*-2-ethylcarbonatobenzoyloxybenzoic acid is produced simultaneously. The relative proportions of the two acids depend on the time the reaction is allowed to proceed, the last-mentioned acid being produced in larger quantity the longer the reaction mixture is kept.

o-2-*Ethylcarbonatobenzoyloxybenzoic acid*,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

crystallises from benzene in small, white needles, m. p. 119°. It dissolves in strong aqueous ammonia with a yellow colour, and at the same time is converted into salicylic acid and salicylamide. When hydrolysed with dilute ammonia according to Fischer's method, or when heated with aluminium bromide in benzene solution, it yields *o*-salicyloxybenzoic acid, $OH\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$ (Abstr., 1909, i, 803). It has also been obtained (1) by the action of ethyl chlorocarbonate on salicylic acid in benzene solution in the presence of dimethylaniline, (2) by the action of ethyl *o*-ethylcarbonatobenzoylcarbonate, $CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot CO_2Et$, on salicylic acid in dimethylaniline or pyridine solution, and (3) by the interaction of ethyl chlorocarbonate ($\frac{3}{4}$ mol.) and sodium salicylate (1 mol.) in acetone solution. When excess of ethyl chlorocarbonate is employed in the latter reaction, the main product is *o*-ethylcarbonatobenzoic acid, which forms leafy crystals, m. p. 95°; from carbon tetrachloride it separates in pearly leaflets of the composition $2CO_2Et\cdot O\cdot C_6H_4\cdot CO_2H,CCl_4$; these rapidly lose carbon tetrachloride on being exposed to the air.

o-2-*Methylcarbonatobenzoyloxybenzoic acid*,

$$CO_2Me\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

prepared by the action of methyl chlorocarbonate on salicylic acid in pyridine solution, crystallises in clusters of tapering needles, m. p. 112°.

o-2-*Acetoxybenzoyloxybenzoic* (*acetylsalicylosalicylic*) *acid*,

$$OAc\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

prepared by the prolonged action of pyridine on ethyl *o*-acetoxybenzoylcarbonate, crystallises in leaflets, m. p. 161—162° (compare Einhorn and Seuffert, this vol., i, 53). It has also been obtained (1) by the action of ethyl *o*-acetoxybenzoylcarbonate on salicylic acid in the presence of dimethylaniline, and on sodium salicylate in dilute alcoholic or acetone solution, (2) by the interaction of pyridine and *o*-acetoxybenzoic anhydride, and (3) by the action of *o*-acetoxybenzoic anhydride on salicylic acid in the presence of pyridine, or on sodium salicylate in acetone solution. F. B.

Ketones Derived from Phenylpropionic Acid. JEAN B. SENDERENS (*Compt. rend.*, 1911, **152**, 384—386. Compare Abstr., 1909, i, 286, 627; 1910, i, 11, 179, 318, 489; this vol., i, 134).—When a mixture of phenylpropionic acid (1 mol.) and an aliphatic acid (3 mols.) are passed over thorium oxide at about 460°, the product consists almost exclusively of the mixed aromatic ketone and the symmetrical aliphatic ketone. The following compounds, prepared by this method, are liquids with an agreeable odour; except in the first case their oximes are oily.

α-Phenylbutan-γ-one, b. p. 228·5°/750 mm. (corr.), D_4^0 0·9877; the *oxime*, m. p. 80°; the *semicarbazone*, m. p. 136°. *α-Phenylpentan-γ-one*, $CH_2Ph\cdot CH_2\cdot COEt$, b. p. 244°/750 mm. (corr.), D_4^0 0·9793; the *semicarbazone*, m. p. 82°. *α-Phenylhexan-γ-one*, $C_{12}H_{16}O$, b. p. 263°/

760 mm. (corr.), D_4^0 0·9719. *α-Phenyl-δ-methylpentan-γ-one*, $C_{12}H_{16}O$, b. p. 256°/760 mm. (corr.), D_4^0 0·9755; the *semicarbazone*, m. p. 86°. *α-Phenyl-ε-methylhexan-γ-one*, $C_{13}H_{18}O$, b. p. 268·5°/760 mm. (corr.), D_4^0 0·9619.

αε-Diphenylpentan-γ-one, $CH_2Ph\cdot CH_2\cdot CO\cdot CH_2\cdot CH_2Ph$, produced in small quantity during the preparation of the foregoing ketones, is best prepared by passing phenylpropionic acid over thorium oxide at about 440°. It has b. p. 347·5°/760 mm. (corr.), D_4^0 1·0356; the *semicarbazone* has m. p. 105°.

Attempts to prepare unsaturated ketones by the catalytic method have not been successful. Cinnamic acid, for example, yields metastyrene as the chief product, whilst crotonic acid furnishes only decomposition products. W. O. W.

Desmotropism of Formyldeoxybenzoin. WILHELM WISLICENUS and ALEXANDER RUTHING (*Annalen*, 1911, **379**, 229—261).—It is shown that Claisen and Meyerowitz's formyldeoxybenzoin (Abstr., 1890, 359) exists in two isomeric modifications, which are represented by the two formulæ: $\alpha = COPh\cdot CPh\colon CH\cdot OH$, and

$\beta = CHO\cdot CPh\colon CPh\cdot OH$.

A 60—70% yield of the formyl derivative can be obtained by the action of deoxybenzoin on a mixture of sodium ethoxide and ethyl formate under specific conditions. The crude product obtained by the addition of dilute sulphuric acid to the alkaline solution is partly molten at 75°, but resolidifies, and then has m. p. 110°. α-Formyldeoxybenzoin (hydroxymethylenedeoxybenzoin) crystallises from light petroleum (b. p. 100—120°) in sulphur-yellow needles or prisms; it is partly molten at 76—80°, but is quickly transformed into the β-isomeride. It has b. p. 183°/14 mm. It can be kept for a few days at the ordinary temperature, but is stable at temperatures above 110°. The α-compound is more soluble than the β-isomeride in most solvents, and the solutions have a yellow colour. In benzene solutions a portion of the β-compound is transformed into the α, so that an equilibrium mixture is formed, whereas alcohol readily transforms the α- into the β-isomeride, even when the greater portion of the compound is not dissolved. The α-compound is partly transformed into the β- by dissolving in benzene and alcohol, and an equilibrium mixture is obtained.

β-Formyldeoxybenzoin crystallises from alcohol in colourless, microscopic plates, m. p. 112—113°, and the fused mass, when cooled rapidly, yields crystals of the α-isomeride. Both compounds give colorations with ferric chloride; in the case of the α-compound this is best shown by using benzene solutions of the compound and of ferric chloride.

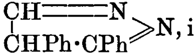
The enol-ketonic structure is ascribed to the α-compound, on account of its yellow colour and similarity to benzoin; the aldo-enolic formula is given to the β-isomeride, as it gives a coloration with Schiff's reagent (decolorised magenta). Both compounds form salts, but it is probable that during salt formation the β-compound undergoes molecular rearrangement, and all the salts obtained appear to belong to the α-series, although the product obtained by acidifying the solution of the salts may be the α- or β-compound, according to the conditions of the experiment. The β-compound can be transformed into the α- by dissolving in alcohol containing the theoretical amount of sodium ethoxide, keeping for twelve hours, and then diluting with water and precipitating by adding sulphuric acid (dil.) drop by drop. The *copper* derivative, $(C_{15}H_{11}O_2)_2Cu$, crystallises in green plates, and has m. p. 220—221°.

When a dilute alcoholic solution of the β-compound is kept for some time, a slow change takes place; at the end of two days the solution no longer yields a copper derivative, and gives only a faint coloration with ferric chloride. This is probably due to the formation of a third isomeric form, namely, a γ-form, which is regarded as the aldo-keto-compound, $O\!:\!CH\cdot CHPh\cdot COPh$. The transformation of the β- into the γ-compound takes place more readily in methyl-alcoholic solution. The γ-compound does not form a copper derivative, and does not give colorations with ferric chloride, but reacts readily with Schiff's reagent. It has not been found possible to isolate the solid γ-compound, as on concentrating its solutions it passes over into the β- and possibly α-compounds.

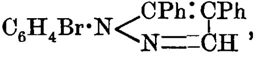
The α- and β-forms yield identical derivatives, although the rates at which they react are different. Both yield an additive *compound* with ammonia, $C_{15}H_{15}ON_2$, in the form of a colourless solid, m. p. 161°, after sintering at 154°. The compound with aniline,

$$COPh\cdot CPh\!:\!CH\cdot NHPh,$$

crystallises from alcohol, has m. p. 92—93°, does not give a coloration with ferric chloride, but forms a yellowish-brown *copper* derivative, $(C_{21}H_{16}ON)_2Cu$, m. p. 213—214°.

Hydrazine hydrate reacts with the α-compound, yielding Curtius and Blumer's bisphenylbenzylazimethylene (Abstr., 1895, i, 608). When an alcoholic solution of hydrazine hydrate is used, the product is 3 : 4-*diphenylpyrazole*,  $\begin{matrix} CH{=\!=\!=}N \\ | \\ CHPh\cdot CPh \end{matrix}\!\!>\!N$, in the form of yellow needles, m. p. 154—155°. The corresponding 1 : 4 : 5-*triphenylpyrazole*,

$$C_{21}H_{16}N,$$

m. p. 210—211°, is formed when phenylhydrazine is used. 4 : 5-*Diphenyl*-1-p-*bromophenylpyrazole*,  $C_6H_4Br\cdot N\!\!<\!\begin{matrix} CPh\!:\!CPh \\ \quad\;\, | \\ N{=\!=\!=}CH \end{matrix}$, crystallises in colourless, felted needles, m. p. 182—183°.

Formyldeoxybenzoin reacts with an aqueous alcoholic solution of benzenediazonium chloride and sodium acetate, yielding benzil monophenylhydrazone, and with phenylcarbimide both forms yield the additive *compound*, $COPh\cdot CPh\!:\!CH\cdot O\cdot CO\cdot NHPh$, in the form of colourless plates, m. p. 129—130°.

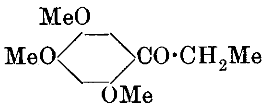
The *benzoyl* derivative, $C_{22}H_{16}O_3$, prepared from either the α- or β-compound, crystallises from benzene in colourless prisms, m. p. 105—106°, and the p-*nitrobenzoyl* derivative, $C_{22}H_{15}O_5N$, forms pale yellow needles, m. p. 118—119°. *Bromoformyldeoxybenzoin*,

$$COPh\cdot CBrPh\cdot CHO,$$

crystallises from light petroleum, and has m. p. 60—61°.

J. J. S.

Some Derivatives of Hydroxyquinol. GUIDO BARGELLINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 22—26. Compare this vol., i, 68).—The present paper deals with 2 : 4 : 5-trimethoxypropiophenone (annexed formula) and some of its derivatives. The substance is obtained by the action of propionyl chloride on hydroxyquinol trimethyl ether in carbon disulphide solution in the presence of aluminium chloride. It crystallises in small, white needles, m. p. 106—108°, and is identical with the ketoasarone of Paolini (Abstr., 1910, i, 394). It gives a yellowish-green coloration with concentrated sulphuric acid, no coloration with ferric chloride, and with sodium nitroprusside and potassium hydroxide an intense red coloration which quickly becomes pale yellow. The *semicarbazone*, $C_{13}H_{19}O_4N_3$, forms colourless, hexagonal crystals, m. p. 166—167°. The semicarbazone obtained by the author from a sample of Paolini's ketoasarone also had this m. p., so that the semicarbazone of m. p. 182—183° described by the latter may be a stereoisomeride. *Trimethoxypropiophenoneoxime*, $C_{12}H_{17}O_4N$, forms colourless laminæ, m. p. 106—108°.



In the preparation of trimethoxypropiophenone a substance is also formed which crystallises in small, colourless needles, m. p. 110—112° (softening at 108—109°), and is probably 2 : 4 : 5-*trihydroxypropiophenone* 4 : 5-*dimethyl ether*. It dissolves in alkali with production of a yellow coloration, and yields a green coloration with ferric chloride.

R. V. S.

Relation between Chemical Constitution and Fastness to Light and Other Agencies of Polyhydroxybenzophenone Dyes. EDWIN R. WATSON and JATINDRA M. DUTTA (*J. Soc. Chem. Ind.*, 1911, **30**, 196—197).—The following values have been obtained for the fastness of polyhydroxybenzophenones and xanthones to light. (*a*) Polyhydroxybenzophenones : 2 : 3 : 4-trihydroxy-III, 2 : 3 : 4 : 4′-tetrahydroxy-IV—V, 2 : 3 : 4 : 3′-tetrahydroxy-III—IV, 2 : 3 : 4 : 2′-tetrahydroxy-III, 2 : 4 : 3′ : 4′-tetrahydroxy-III, 2 : 3 : 4 : 2′ : 4′-pentahydroxy-II, 2 : 3 : 4 : 3′ : 4′ : 5′-hexahydroxy-I—II ; (*b*) Polyhydroxyxanthones : 1 : 2-dihydroxy-II, 1 : 2 : 7-trihydroxy-II. The roman numerals indicate the fastness of each compound as recorded according to the British Association Committee's scale. It is evident that an increase in the number of hydroxyl groups tends to diminish the fastness to light, with the exception of the 2 : 3 : 4-trihydroxy-compound.

2 : 4 : 3′ : 4′-Tetrahydroxybenzophenone is the only dye appreciably faded by alkali, and those dyes which do not contain two hydroxyl groups in the ortho-position to one another and adjacent to the carbonyl group are most affected by acids. Most of the dyes are brightened and deepened by treatment with alkali, and the xanthones are not so fast to acid or light as the polyhydroxybenzophenones.

1 : 2 : 7-Trihydroxyxanthone is formed when the pentahydroxybenzophenone is heated with water in sealed tubes at 180—220° for

two and a-half hours. It crystallises from dilute alcohol in needles, is not molten at 285°, and its alkaline solutions are highly fluorescent.

J. J. S.

Ketens. XVI. Formation and Fission of Four-membered Rings. HERMANN STAUDINGER (*Ber.*, 1911, **44**, 521—533).—The extreme ease with which the conversion of ethyl ethylketencarboxylate into ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate and the reverse change occur (Abstr., 1910, i, 89) suggests that the two simple molecules may be united in the bimolecular substance by some kind of valency other than that operating between the ring carbon atoms of true *cyclo*butane derivatives. However, the decompositions described below show that the facile fission of ethyl diethyl*cyclo*butandionedicarboxylate is different in degree, not in kind, from the disruption of other *cyclo*butandiones obtained by the polymerisation of ketens, such as dimethylketen and diphenylketen. Attention is called to the polymerisation of phenylcarbimide, nitroso-compounds, and other substances, also to the additive compounds obtained from ketens and carbonyl compounds or anils, whereby β-lactones or β-lactams are produced (Abstr., 1909, i, 410; this vol., i, 215). In all of these cases four-membered heterocyclic substances are obtained which can be converted by comparatively simple means either into their generators or into a pair of new substances. A general connexion cannot be traced between the stability of the rings and their ease of formation; thus, for example, the β-lactams are easily obtained, and yet are very stable in comparison with the β-lactones, which are produced only with difficulty.

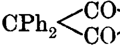
[With ST. BEREZA and MODRZEJEWSKI.]—Ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate suffers rupture when shaken with water, yielding ethyl diethylacetonedicarboxylate and carbon dioxide. The molecule is also ruptured by the following reagents: boiling dilute barium hydroxide produces impure butyrone, cold alcoholic potassium hydroxide yields ethylmalonic acid (2 mols.), and alcoholic semicarbazide hydrochloride and potassium acetate cause the formation of *diethyl heptane-δ-one-γεε-tricarboxylatesemicarbazide*,

$$CO_2Et\cdot CHEt\cdot CO\cdot CEt(CO_2Et)\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2,$$

m. p. 140°, which develops a deep violet coloration with ferric chloride.

[With J. MAYER.]—2 : 2 : 4 : 4-Tetramethyl*cyclo*butan-1 : 3-dione (Abstr., 1906, i, 234) undergoes fission, aniline at 200° under pressure producing the anilide of *iso*butyric acid, and water at 160—180° or boiling dilute sodium hydroxide producing *iso*butyrone.

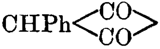
[With H. GÖLLER.]—2 : 2 : 4 : 4-*Tetraphenyl*cyclo*butan*-1 : 3-*dione*,

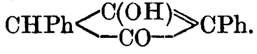


$CPh_2{<}^{CO}_{CO}{>}CPh_2$, m. p. 244—245°, is best obtained by heating diphenylketen-quinoline in benzene at 170° for eighty hours; amongst other substances, two polymerides are formed, one, m. p. 176° (as yet unexamined), in large amount, and the other, tetraphenyl*cyclo*butandione, in poor yield. It is very stable, but suffers depolymerisation when strongly heated. It is ruptured by 50% potassium hydroxide and methyl alcohol on the water-bath, yielding *tetraphenylacetone*, $CO(CHPh_2)_2$, m. p. 135°, and a little diphenylacetic acid.

The additive compound of diphenylketen and *cyclo*pentadiene is converted, with considerable loss, into its generators by distillation at 160—180°/15 mm. in carbon dioxide.

The β-lactam of β-anilino-$\alpha\alpha\beta$-triphenylpropionic acid is very stable, and can be distilled without appreciable decomposition. When, however, it is heated under a reflux condenser in a current of carbon dioxide, phenylcarbimide is removed, leaving triphenylethylene in the residue. The β-lactam of β-anilino-$\alpha\alpha\beta\beta$-tetraphenylpropionic acid (*loc. cit.*), by slow distillation in carbon dioxide, decomposes partly into tetraphenylethylene and phenylcarbimide, and partly into its generators, diphenylketen and benzophenoneanil. The β-lactam of β-*p*-dimethylaminoanilino-$\alpha\alpha\beta\beta$-tetraphenylpropionic acid (*loc. cit.*), however, decomposes at its m. p., or, better still, by distillation at 200—250°/15 mm., yielding diphenylketen; tetraphenylethylene is not formed, and *p*-dimethylaminophenylcarbimide cannot be detected with certainty. C. S.

Ketens. XVII. Phenylketen and Methylketen. HERMANN STAUDINGER (*Ber.*, 1911, **44**, 533—543).—[With ST. BEREZA.]—Since ethyl ethylketencarboxylate is obtained so easily by heating its polymeride, ethyl 1 : 3-diethyl*cyclo*butan-2 : 4-dione-1 : 3-dicarboxylate (Abstr., 1910, i, 89), attempts have been made to prepare the very unstable phenylketen (Abstr., 1905, i, 444) in a similar manner. When an ethereal solution of phenylchloroacetyl chloride (which can be obtained in 66% yield by heating mandelic acid and phosphorus pentachloride [2 mols.] at 120—140° for about four hours, whereby the phosphoryl chloride is mainly removed as it is formed) is treated with zinc and kept for two hours after the addition of petroleum, the initially formed phenylketen polymerises completely. In addition to other substances, two polymerides are obtained, 1 : 3-*diphenyl*cyclo*butan*-2 : 4-*dione*,  $\mathrm{CHPh}{<}\substack{\mathrm{CO}\\ \mathrm{CO}}{>}\mathrm{CHPh}$, m. p. 73°, and its enolic modification, 1 : 3-*diphenyl*-Δ^1-cyclo*buten*-2-*ol*-4-*one*,



$$\mathrm{CHPh}{<}\substack{\mathrm{C(OH)}\\ \mathrm{CO}}{>}\mathrm{CPh}.$$

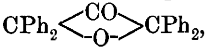
The former does not react with ferric chloride, phenylcarbimide, or a solution of bromine, and yields a *disemicarbazone* (?), m. p. 220—230° (decomp.). It distils undecomposed at about 133° in a high vacuum, and does not yield phenylketen when more strongly heated. In other respects, however, it suffers fission like other polymeric ketens (compare preceding abstract); thus, with sodium hydroxide it yields dibenzyl ketone, and with methyl-alcoholic ammonia, diphenylacetoacetamide.

*Diphenyl*cyclo*butenolone*, which is also obtained by treating diphenyl*cyclo*butandione with 5% sodium hydroxide, separates from a mixture of benzene and ethyl acetate in crystals, m. p. 160°, containing 1 mol. of benzene. It develops a deep violet coloration with ferric chloride, decolorises a solution of bromine and of potassium permanganate, and is rapidly decomposed by warm water or dilute acids; its solution in sodium hydroxide, however, can be boiled for some time without decomposition.

[With H. W. Klever and J. Mayer.]—Attempts to prepare methylketen give results similar to the preceding. A 0·4—0·5% ethereal solution can be obtained in 6—8% yield by treating α-bromopropionyl bromide in ethereal solution with zinc, and removing the methylketen and the solvent by distillation. From this solution, by fractional distillation in a high vacuum, fairly pure methylketen is obtained as a white, crystalline mass in a receiver cooled by liquid air; at higher temperatures the substance polymerises rapidly, yielding a small amount of a volatile substance with an unpleasant odour (*dimethyl*cyclo*butandione*?), together with 1 : 3-dimethyl-Δ^1-*cyclo*buten-2-ol-4-one (m. p. 140°, decomp. when pure). The latter polymeride is obtained better by keeping a dilute ethereal solution of methylketen for two days; it does not yield methylketen when heated, gives a deep-reddish violet coloration with alcoholic ferric chloride, and dissolves unchanged in warm sodium hydroxide.

C. S.

Ketens. XVIII. Decomposition of Benzilic Acid. Hermann Staudinger (*Ber.*, 1911, **44**, 543—547).—Nef has shown that the decomposition of benzilic acid by heating yields benzophenone, diphenylacetic acid, and a red resin, and explains the formation of these substances by assuming the initial production of diphenylmethylene, CPh_2:. This explanation is incorrect.

[With M. R. Schöller.]—When benzilic acid is heated at 155—165°/15 mm., it is partly converted into benzilide; this at a higher temperature decomposes into carbon dioxide and a ketone (unisolated),  $CPh_2<\begin{smallmatrix}CO\\-O-\end{smallmatrix}>CPh_2$, which suffers the typical fission of *cyclo*butanones (compare preceding abstracts), yielding diphenylketen and benzophenone, together with a red resin. In the decomposition of benzilic acid by heat, therefore, the diphenylacetic acid is produced by the interaction of the diphenylketen and the water formed during the decomposition.

[With H. Göller.]—Benzilide is decomposed by water and benzene at 200°, yielding diphenylacetic acid, benzophenone, and other products. Benzilide must be boiled with 50% potassium hydroxide in order to reconvert it into benzilic acid. When benzilide is heated at 200° for two days with aniline (2 mols.) and benzene, it yields benzophenone and the anilide of diphenylacetic acid. When boiled with aniline under a reflux condenser for sixty hours, benzilide yields the anilide of anilinodiphenylacetic acid and a *substance*, m. p. about 200°.

C. S.

Isomerism of Naphthaquinone Derivatives. I. Oswald Miller (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1418—1446).—The author has studied the transformations undergone by amino-α-naphthaquinoneimide (di-iminonaphthol) and its hydrochloride in aqueous solutions. This base acts as a mixture of isomerides, the action of water resulting in the simultaneous formation of 2-amino-α-naphthaquinone and 4-amino-β-naphthaquinone, in addition to ammonia.

According to Martius and Griess (*Annalen*, 1865, **134**, 377), and Graebe, and Ludwig (*Annalen*, 1870, **154**, 312), amino-α-naphthaquinoneimide hydrochloride forms anhydrous crystals, but the author finds that it crystallises from water or 95% alcohol as the dihydrate; it also forms crystals with $\frac{1}{2}H_2O$. In order to effect the separation of the base, the action of water on the hydrochloride was carried out in presence of excess of ammonia.

The results show that the yield of 2-amino-α-naphthaquinone (or 4-amino-β-naphthaquinone) increases in arithmetical progression as the concentration of the amino-α-naphthaquinoneimide hydrochloride diminishes (or increases) in geometrical progression. T. H. P.

Chrysophanic Acid. OTTO FISCHER, FERDINAND FALCO, and HANS GROSS (*J. pr. Chem.*, 1911, [ii], **83**, 208—214).—Chrysarobin and the chrysophanic acid derived from it have frequently been regarded as derivatives of α-methylanthracene. By demethylating chrysarobin by hydriodic acid under pressure and distilling the chrysophanhydranthrone obtained, after purification, with zinc dust, the authors have obtained β-methylanthracene, which is identified by its m. p., 203—204°, and by its conversion into β-methylanthraquinone and dibromomethylanthraquinone (Abstr., 1909, i, 563).

The oxidation of crude chrysophanhydranthrone by acetic and chromic acids on the water-bath yields chrysophanic acid containing as much as 10% of frangula-emodin; when the chrysophanhydranthrone has been purified, however, the amount of frangula-emodin in its products of oxidation is only 2—3% (compare Oesterle and Johann, Abstr., 1910, i, 860).

A solution of diacetylchrysophanic acid in acetic acid and acetic anhydride is oxidised by chromic acid to the diacetyl derivative (m. p. 246° [decomp.]) of rhein.

It only remains now to discover some means of smoothly eliminating carbon dioxide from rhein (which is most probably 1:8-dihydroxyanthraquinone-3-carboxylic acid) in order to settle definitely the constitutions of chrysophanic acid, aloe-emodin, and barbaloin. C. S.

Preparation of a Nitrogenous Oxidation Product of Acenaphthene. KALLE & Co. (D.R.-P. 228698. Compare Abstr., 1903, i, 500).—The oxidation of acenaphthene with potassium dichromate and acetic acid gives an unsatisfactory yield of acenaphthenequinone, which is not improved by substituting manganese dioxide and sulphuric acid or nitric acid as the oxidising agent. It is now found that by the action of nitrous acid esters in the presence of condensing agents (such as concentrated mineral acids, zinc chloride, or sodium ethoxide) on acenaphthene a yellow compound, m. p. about 220° and having the composition of acenaphthenequinoneoxime, is obtained; this on hydrolysis yields acenaphthenequinone. F. M. G. M.

***o*-Menthene-5-one.** ARTHUR KÖTZ and ERWIN ANGER (*Ber.*, 1911, **44**, 466—467).—A number of new derivatives of the menthenone (1-methyl-2-*iso*propyl*cyclo*-Δ^6-hexene-5-one; compare Rabe and Rahm, Abstr., 1904, i, 747; 1905, i, 348; Merling, Abstr., 1905, i, 349;

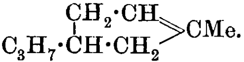
Wallach, 1908, i, 813) obtained by Callenbach from Hagemann's ester have been prepared.

The *semicarbazone* occurs in two forms, melting at 138° and 152° respectively. The oxime has m. p. 90—91°, and the *hydrochloride* of this, m. p. 135—136°.

The corresponding *methyl*iso*propyl*cyclo*hexanone*, b. p. 95°/25 mm. or 204°/760 mm., furnishes an *oxime*, m. p. 75°, and a *benzylidene* derivative, m. p. 162°. T. A. H.

Terpenes and Ethereal Oils. CIII. Studies in the Fenchone Series. OTTO WALLACH (*Annalen*, 1911, **379**, 182—215).—The hydrocarbon C_9H_{16}, previously described (Abstr., 1909, i, 812; compare Bouveault and Levallois, *ibid.*, 1910, i, 572, 627, 686, 863), is now shown to be an equlibrium mixture. The proof is based on an examination of the products of oxidation with dilute permanganate at 0°, and on an examination of the nitroso-chlorides and their derivatives.

When oxidised with 2% permanganate solution at 0°, using 3 gram-atoms of oxygen for each gram-molecule of hydrocarbon, the chief products are unaltered hydrocarbon, a small amount of a glycol, and a mixture of two ketonic acids. One of the acids yields a *semicarbazone*, which crystallises from methyl alcohol in sparingly soluble needles, m. p. 173—175°, and an *oxime*, $C_9H_{17}O_3N$, in the form of plates, m. p. 118—119°. The acid has m. p. 19° and $[\alpha]_D^{18}$ +0·61°, and when oxidised with hypobromite yields Bouveault and Levallois' *β-iso*propylglutaric acid. The ketonic acid is therefore regarded as *β-iso*propyl-γ-acetylbutyric acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CHPr^{\beta}{\cdot}CH_2{\cdot}CO_2H$, although not identical with the acid described by Crossley (Trans., 1902, **81**, 676), and the hydrocarbon from which it is formed as 1-*methyl*-3-iso*propyl*-Δ⁵-*cyclopentene*,



$\begin{matrix} CH_2{\cdot}CH \\ | \\ C_3H_7{\cdot}CH{\cdot}CH_2 \end{matrix}\!\!>\!CMe$.

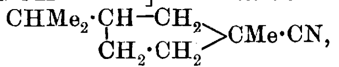
The second ketonic acid yields a semicarbazone, which is amorphous, and has m. p. 138—140° or 150—152°, according to the method of heating. The corresponding oxime is an oil, and the acid itself has b. p. 175—180°/19 mm. and $[\alpha]_D$ −6·18°. On oxidation with hypobromite the ketonic acid yields a dibasic acid, which, after purification by conversion into its anhydride, has m. p. 92—93°; the anhydride crystallises from light petroleum, has m. p. 64—66°, and $[\alpha]_D^{17}$ +3·6°. The dibasic acid is regarded as *l-α-iso*propylglutaric acid (compare Abstr., 1903, i, 568), although the corresponding anilic acid has a lower m. p. than that previously given.

[With FRIEDRICH RITTER.]—The nitroso-chloride prepared by the action of concentrated hydrochloric acid at 0° to −10° on a mixture of the hydrocarbon, C_9H_{16}, glacial acetic acid, methyl alcohol, and freshly-prepared ethyl nitrite is not homogeneous; it consists of 40% of solid together with oily compounds. The solid appears to consist of a mixture of two nitroso-chlorides, but it has not been found possible to isolate both of these, as one is excessively unstable in solution. The nitroso-chloride, m. p. 115° (compare Abstr., 1909, i, 812), has $[\alpha]_D^{15}$ −272°, and yields a nitrolpiperidide, m. p. 160—161°. By decomposing the oxime (*loc. cit.*) with dilute sulphuric acid and distilling in steam, a considerable amount of resin is formed, and comparatively small amounts of volatile products. These contain in addition to the ketone, $C_9H_{14}O$, a saturated nitrogen derivative, $C_9H_{15}ON$, b. p. 250—252°, which yields a *semicarbazone*, $C_{10}H_{18}ON_4$, in the form of colourless plates, m. p. 171—172°. The ketone reacts but slowly with an aqueous semicarbazide solution, but in methyl-alcoholic solution yields a *semicarbazone*, $C_9H_{14}\text{:N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, in the form of colourless needles, m. p. 210—212°. The ketone regenerated from this semicarbazone has b. p. 191—192°, and an odour of thujone. If the nitroso-chloride is not purified by repeated crystallisation, the ketone prepared from it yields a mixture of two semicarbazones, namely, the one with m. p. 210—212°, and the one with m. p. 149—150° (Abstr., 1909, i, 813).

When reduced with zinc dust and glacial acetic acid, the crystalline nitroso-chloride yields an appreciable amount of a saturated ketone, together with a saturated primary amine and unsaturated ketone. The formation of the saturated ketone is represented by the following scheme: $>\text{CCl}\cdot\underset{|}{\text{C}}\text{:N}\cdot\text{OH} \longrightarrow >\text{CH}\cdot\underset{|}{\text{C}}\text{:NH} \longrightarrow >\text{CH}\cdot\underset{|}{\text{C}}\text{:O}$.

The saturated *ketone*, $C_9H_{16}O$, freed from the unsaturated compound by oxidation with 1% cold permanganate solution, has b. p. 184°, D^{20} 0·887, and n_D^{20} 1·4402. The ketone is, however, non-homogeneous, as it yields two semicarbazones. The one has m. p. 197—198°, and when hydrolised yields a ketone identical in all respects with dihydropulegenone (dihydrocamphorphorone) (Abstr., 1903, i, 568, 569). The formation of this ketone leads to the conclusion that the original hydrocarbon contains 1-methyl-3-*iso*propyl-Δ^1-*cyclo*pentene.

[With LUDWIG OLDENBERG.]—The *nitrile* of fencholic acid,



$$\begin{array}{l}\text{CHMe}_2\cdot\text{CH}-\text{CH}_2\\ \qquad\quad\;|\qquad\qquad\;\;>\text{CMe}\cdot\text{CN},\\ \qquad\quad\;\text{CH}_2\cdot\text{CH}_2\end{array}$$

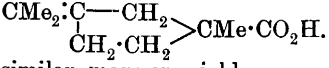
prepared by the action of phosphoric oxide on the amide, is a colourless oil, b. p. 217—218°, has D^{19} 0·8660, n_D^{19} 1·4433, and $\alpha_D + 5°45'$ in a 1 dcm. tube. When reduced with sodium and alcohol, it yields 1-*methyl*-3-iso*propyl*cyclo*pentylmethylamine*, $C_{10}H_{19}\cdot NH_2$, with b. p. 204°, D^{20} 0·8500, and n_D^{20} 1·4545. The *hydrochloride* has m. p. 172—173°, the *benzoyl* derivative, m. p. 81—82°, and the *phenylcarbamide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot C_{10}H_{19}$, m. p. 104—105°. The base readily absorbs carbon dioxide and combines with fenchylcarbimide, yielding the mixed *carbamide*, $C_9H_{17}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot C_{10}H_{19}$, m. p. 127—128°. The amine reacts with nitrous acid, yielding a mixture of an alcohol and a hydrocarbon. The alcohol, $C_{10}H_{20}O$, is tertiary, has b. p. 212—214°, D^{18} 0·903, and n_D^{18} 1·4603, and is probably either *p*-menthanol or a mixture of the meta- and para-compounds. The hydrocarbon, $C_{10}H_{18}$, has b. p. 175—176°, D^{20} 0·824, n_D^{20} 1·4571, and α_D + 32°13′ in a 1-dcm. tube, and is somewhat similar to carvomenthene. It is highly probable that by the action of nitrous acid on the base, the 5-membered has been transformed into a 6-membered ring (compare Abstr., 1907, i, 602). Fenchylamine (1-amino-1-methyl-3-*iso*propyl*cyclo*pentane) (*loc. cit.*, 812) reacts with nitrous acid, yielding the corresponding tertiary alcohol and hydrocarbon. 1-*Methyl*-3-iso*propyl*cyclo*pentan*-1-*ol*, $C_9H_{18}O$, has b. p.

185—187°, m. p. 76°, and the corresponding hydrocarbon, C_9H_{16}, which is probably a mixture of Δ^1- and Δ^5-derivatives, has b. p. 142—143°.

[With H. WIENHAUS.]—Different specimens of fenchonitrile differ somewhat in properties, as they are mostly mixtures. The α-compound forms a crystalline *nitrosochloride*, $C_{10}H_{15}N,NOCl$; this crystallises from acetone, has m. p. 123—124°, and is strongly lævorotatory. It reacts with alkalis or organic bases, regenerating the nitrile, which has D^{18} 0·749 and $[\alpha]_D^{18}$ +43°19′.

The nitrile prepared from the amide of fencholic acid, and also specimens prepared from fenchoneoxime, yield *dihydroxydihydrofenchonitrile*, $CN{\cdot}C_9H_{15}(OH)_2$, when oxidised with 1% permanganate at 0°. The hydroxynitrile forms a viscid, brown oil, b. p. 168—220°/12—14 mm., and crystallises from ethyl acetate in colourless, tabular prisms, m. p. 86°. The nitrile is readily hydrolysed by sodium hydroxide solution to *dihydroxydihydrofencholenic acid*, $CO_2H{\cdot}C_9H_{15}(OH)_2$, which crystallises from ethyl acetate in short, slender prisms, m. p. 111°. When boiled with dilute sulphuric acid, the hydroxynitrile yields a *ketonitrile*, m. p. 62—63°, the *semicarbazone* of which has m. p. 204—206°. When further oxidised with permanganate, the hydroxynitrile yields a *ketonitrile-carboxylic acid*, $C_{10}H_{15}O_3N$, the *oxime* of which has m. p. 260—262°, and the *semicarbazone*, m. p. 190—192°.

β-Fencholenic acid, when reduced with hydrogen and colloidal palladium, yields fencholic acid, and is, therefore, presumably



$$\begin{array}{l}\mathrm{CMe_2{:}C{-}CH_2}\\ \qquad\;|\qquad\qquad>\mathrm{CMe{\cdot}CO_2H.}\\ \qquad\mathrm{CH_2{\cdot}CH_2}\end{array}$$

α-Fencholenic acid, when reduced in a similar manner, yields a product which appears to be identical with Mahla's dihydrofencholenic acid (Abstr., 1902, i, 107). The amide has m. p. 133—134°.

The amides of α- and β-fencholenic acids are reduced more readily than the acids themselves. J. J. S.

Terpenes and Ethereal Oils. CIV. OTTO WALLACH (*Annalen*, 1911, **379**, 215—228).—[With PAUL VIRCK.]—The author confirms Angeli and Rimini's statement (Abstr., 1897, i, 88; compare Rimini, 1900, i, 554; Tiemann and Mahla, *ibid.*, 1897, i, 85) that the isomeric nitro-imines, $C_{10}H_{16}O_2N_2$, from fonchoneoxime and camphoroxime yield the same unsaturated ketone, 1-methyl-5-*iso*propyl-Δ^6-*cyclo*hexen-2-one*iso*camphor, when treated with concentrated sulphuric acid and then poured into water. It is shown that the ketone is not formed by the acid, but by the subsequent treatment with water. The compound, $C_{10}H_{16}O_2N_2$, from fenchoneoxime crystallises from dilute methyl alcohol, has m. p. 59—60° (Rimini, 66—67°; Tiemann and Mahla, 58°), and $[\alpha]_D$ +25·83°. The ketone, although optically active, on oxidation yields *dl-α-iso*propylglutaric acid (compare Angeli and Rimini). The ketone is extremely unstable; it has D^{20} 0·9260, n_D^{20} 1·4758, and b. p. 216°. The b. p. is somewhat lower than that of the isomeride of the para-series, namely, carvotanacetone, b. p. 228°. The b. p. of 1-methyl-3-*iso*propyl-Δ^6-hexene-5-one, namely, 244—245° (Knoevenagel, Abstr., 1893, i, 419), is too high.

1-Methyl-5-*iso*propyl-Δ^6-*cyclo*hexene-2-one forms an oily, additive compound with hydrogen sulphide, and also yields a solid condensation product with benzaldehyde. When reduced with sodium and moist ether, the ketone yields the saturated alcohol, 1-*methyl*-5-iso*propyl*cyclo*hexane*-2-*ol*, $CHMe_2\cdot CH<\begin{matrix}CH_2\cdot CHMe\\ CH_2—CH_2\end{matrix}>CH\cdot OH$, and this on oxidation yields 1-*methyl*-5-iso*propyl*cyclo*hexan*-2-*one*, $C_{10}H_{18}O$, b. p. 211—212°, D^{21} 0·8885, n_D^{20} 1·4466. The *semicarbazone* has m. p. 162—163°. The alcohol has b. p. 215—216°, D^{21} 0·889, and n_D^{20} 1·4563 (compare Spica, Abstr., 1902, i, 43).

[With FRIEDRICH HENJES.]—It is pointed out that various unsaturated nitriles of the camphor series combine readily with nitrosyl chloride. *Menthonitrile nitrosochloride*, $C_{10}H_{17}N,NOCl$, crystallises from methyl alcohol, and has m. p. 96—97°; the corresponding *nitrolpiperidide*, $C_{10}H_{17}N\cdot NO\cdot C_5NH_{10}$, has m. p. 83—85°. The nitrosochloride when treated with alkalis or reducing agent regenerates the nitrile. *Citronellalnitrile nitrosochloride*, $C_{10}H_{17}N\cdot NOCl$, has m. p. 106°; the *nitrolpiperidide*, m. p. 88—90°; and the *nitrol*-p-*toluidide*, m. p. 107—108°. Camphonitrile and pulegenonitrile yield bluish-green oils when treated with nitrosyl chloride. J. J. S.

Action of Piperidine on *d*-Pinene Chloro-oxime. L. V. BUSCHUEFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1447—1448).—In Schimmel's Bericht (Oct., 1910, 171) it is stated that the results of the author's investigations on the action of piperidine on *d*-pinene chloro-oxime (Abstr., 1910, i, 122) confirm those of Wallach (Abstr., 1888, 1098). The author points out, however, that he obtained nitrosopinene and pinene nitrolpiperidine as the products of this reaction (compare Golubeff, Abstr., 1908, i, 902), whilst Wallach obtained pinene nitrolpiperidine only. T. H. P.

New Constituent of Angelica Root Oil. E. BÖCKER and ALFRED HAHN (*J. pr. Chem.*, 1911, [ii], **83**, 243—248).—The least volatile fraction of angelica root oil deposits, after long keeping, a small amount of a crystalline substance, m. p. 84° (compare Ciamician and Silber, Abstr., 1896, i, 595), which exhibits the properties of an unsaturated γ-lactone. It has the formula $C_{15}H_{16}O_3$, is not changed by hot or cold aqueous alkalis or cold alcoholic potassium hydroxide, but is hydrolysed by boiling *N*/2-alcoholic potassium hydroxide (saponification number 238), the product regenerating the lactone by acidification. It forms a *dibromide*, $C_{15}H_{16}O_3Br_2$, m. p. 143—145°, and an additive *compound*, $C_{15}H_{17}O_3Cl$, m. p. 101°, with ethereal hydrogen chloride. C. S.

Constituents of Essential Oils. Identity of the Alcohol, $C_{10}H_{16}O$, of Gingergrass Oil with Perilla Alcohol. Tricyclenecarboxylic Acid. FRIEDRICH W. SEMMLER and B. ZAAR (*Ber.*, 1911, **44**, 460—463).—The supposed dihydrocuminol obtained by Schimmel & Co. from gingergrass oil (Abstr., 1905, i, 536) and examined by Wahlbaum and Hüthig (*loc. cit.*, p. 53) has been re-investigated, and proved to be identical with the alcohol obtained by reducing Perilla-aldehyde (Semmler and Zaar, this vol., i, 218). The alcohol, purified as far as possible from geraniol, has the following constants: b. p.

107—110°/12·5 mm., D^{20} 0·946, n_D 1·4968, a_D − 7° (100 mm.). The low optical activity is doubtless due to partial racemisation. With phosphorus pentachloride it gives a *chloride*, $C_{10}H_{15}Cl$, b. p. 97—102°/14 mm., D^{20} 0·9848, n_D 1·50058, a_D − 16° (100 mm.), and this, on reduction with sodium in alcohol, furnishes limonene, identified by means of its tetrabromide. These data, and the fact that the alcohol yields Perilla-aldehyde on oxidation, prove that it is identical with Perilla alcohol.

Comparison of tricyclenecarboxylic acid (Bredt and May, Abstr., 1910, i, 32) with teresantalic acid proves that the two are not identical (compare Semmler, *Äther. Öle*, 1906, ii, 90, and Abstr., 1907, i, 703, 1062). T. A. H.

Action of Chromyl Chloride on India-rubber. David Spence and J. C. Galletly (*J. Amer. Chem. Soc.*, 1911, **33**, 190—194).—Although the action of chromyl chloride on terpenes has been extensively studied, its action on caoutchouc has not hitherto been investigated.

When chromyl chloride is added to a solution of caoutchouc in carbon disulphide, the *compound*, $C_{10}H_{16},2CrO_2Cl_2$, rapidly separates as a voluminous, dark brown precipitate, which is insoluble in organic solvents; on exposure to the air it absorbs moisture, and rapidly undergoes decomposition. The same product was obtained from several caoutchoucs of different botanical origin. When the compound is treated with water, it is immediately decomposed with formation of a dark green solution, from which, on heating, a brown, gummy mass separates. By extracting the latter product with ether or chloroform, a *substance* is obtained in an impure state which gives the reactions of an aldehyde, and when treated with phenylhydrazine yields a crystalline compound, m. p. about 92°. If the solution obtained by the action of water on the chromyl chloride compound is submitted to dialysis, an opalescent, colloidal solution is produced, from which an insoluble *substance* has been isolated containing definite proportions of chromium and chlorine. The investigation is being continued. E. G.

Vulcanisation of Caoutchouc. B. V. Bysoff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1358—1362. Compare Abstr., 1910, i, 865).—The author finds that, given constant conditions of vulcanisation, the ratio between the proportions of total and free sulphur (extractable by acetone) is approximately constant. In preparations containing small amounts of sulphur, this ratio increases as the total proportion diminishes.

When caoutchouc is vulcanised with steam under three atmospheres pressure, the curve showing the relation of the proportion of free sulphur to the time is asymptotic to the time axis. Hence, in order to compare the proportions of free sulphur in different vulcanised caoutchoucs, it is necessary to vulcanise until the amount of free sulphur becomes practically constant; under the above conditions this requires two hours.

A series of mixtures of caoutchouc and sulphur containing 1·0, 1·2, 1·4, 1·6, 1·8, and 2% of sulphur respectively were vulcanised with steam as above. Examination of the various samples showed that (total sulphur)^n/(free sulphur) = a constant. The value of n was 3·1, and that of the constant, 26·692, but these values may vary with the kind of caoutchouc and with the method of vulcanisation.

T. H. P.

Bixin. ALFR. HEIDUSCHKA and H. RIFFART (*Arch. Pharm.*, 1911, **249**, 43—48).—The results of an investigation of the action of halogens on bixin are given, and the old formula, $C_{28}H_{34}O_5$, is adopted for this dye in preference to $C_{29}H_{34}O_5$ suggested recently by van Hasselt (Abstr., 1909, i, 598).

On adding bromine to bixin, dissolved in chloroform, a colourless, amorphous compound, $C_{28}H_{34}O_5Br_{10},4HBr$, m. p. 143°, is obtained. This on heating at 100° decomposes, yielding a yellow *decabromide*, which can be crystallised from alcohol, but decomposes when heated or when kept (compare van Hasselt, *loc. cit.*). The analogous *substances*, $C_{28}H_{34}O_5Cl_{10},4HCl$, m. p. 91°, and $C_{27}H_{32}O_5Cl_{10},4HCl$, m. p. 102°, the latter obtained from *nor*bixin, are similarly prepared by the action of chlorine and are amorphous.

Bixin and *nor*bixin each combine with 11 mols. of hydrogen chloride to form amorphous, pale yellow *additive products*; the one has m. p. 74°, and the other, m. p. 108°.

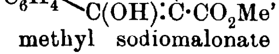
T. A. H.

The Benzotetronic Acid Group. II. Ketonic Hydrolysis of Benzotetronic Acid [4-Hydroxycoumarin] and its Homologues. RICHARD ANSCHÜTZ and MAX EUGEN SCHOLL (*Annalen*, 1911, **379**, 333—350. Compare Abstr., 1909, i, 660).—*o*-Hydroxyacetophenone and its three methyl derivatives can be obtained by hydrolysing benzotetronic acid and its methyl derivatives with potassium hydroxide solution at relatively high temperatures. When the ethyl ether of benzotetronic acid [4-ethoxycoumarin] is hydrolysed, the first product is the free acid, and finally *o*-hydroxyacetophenone; the intermediate product, *o*-hydroxybenzoylacetic acid,

$$OH\cdot C_6H_4\cdot CO\cdot CH_2\cdot CO_2H,$$

cannot be isolated. For the preparation of the hydroxyacetophenones it is not necessary to prepare the benzotetronic acids, but to start with the condensation products of acetylated salicylic acid chlorides and ethyl sodiomalonate.

Methyl 4-hydroxycoumarin-3-carboxylate,



$$C_6H_4<\begin{array}{l}O\text{——}CO\\C(OH){:}C\cdot CO_2Me\end{array},$$

prepared from acetylsalicyl chloride and methyl sodiomalonate crystallises from alcohol in colourless needles, m. p. 136°; when hydrolysed with 33% potassium hydroxide solution at 115° for ten hours, it yields potassium benzotetronate, but at 180° gives an 80% yield of *o*-hydroxyacetophenone, b. p. 96—97°/10 mm. (compare Friedländer and Neudörfer, Abstr., 1897, i, 424); the oxime has m. p. 117°, not 112° (Dunstan and Henry, Trans., 1899, **75**, 66), and the phenylhydrazone is only sparingly soluble in sodium hydroxide solution. The *benzoyl* derivative, $COPh\cdot O\cdot C_6H_4\cdot COMe$, crystallises from alcohol in colourless needles, m. p. 88°; the *semicarbazone*,

$$OH\cdot C_6H_4\cdot CMe{:}N\cdot NH\cdot CO\cdot NH_2,$$

also crystallises in colourless needles, and when heated at 225° is rapidly transformed into o-*hydroxyacetophenoneazine*,

$N_2(:CMe\cdot C_6H_4\cdot OH)_2$,

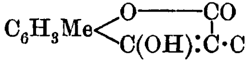
which is also formed when the hydroxyacetophenone is shaken for several days with an aqueous solution of hydrazine sulphate. The azine crystallises from alcohol in glistening, pale yellow needles, m. p. 197—198°.

Acetyl-*o*-cresotic [2-acetoxy-*m*-toluic] acid,

$OAc\cdot C_6H_3Me\cdot CO_2H$ [$CO_2H : OAc : Me = 3 : 2 : 1$],

crystallises from benzene in colourless needles, m. p. 113°, and reacts with phosphorus pentachloride in the presence of light petroleum, yielding the *chloride*, $OAc\cdot C_6H_3Me\cdot COCl$, which can be distilled under extremely low pressures.

Methyl 4-*hydroxy*-8-*methylcoumarin*-3-*carboxylate*,



$$C_6H_3Me<\begin{matrix}O\text{———}CO\\ C(OH):C\cdot CO_2Me\end{matrix}$$

crystallises from alcohol in colourless plates, m. p. 109°, and with aqueous potassium hydroxide solution at 100° yields 4-*hydroxy*-8-*methylcoumarin* (3-*methylbenzotetronic acid*), $C_{10}H_8O_3$, which crystallises from water in colourless, glistening needles, m. p. 228° (decomp.). 2-*Hydroxy*-3-*methylacetophenone*, $OH\cdot C_6H_3Me\cdot COMe$, has b. p. 106—107°/10·5 mm.; the *phenylhydrazone*, $C_{15}H_{16}ON_2$, crystallises from alcohol in yellow needles, m. p. 122°; the *semicarbazone*, $C_{10}H_{13}O_2N_3$, in colourless needles, m. p. 228°, and the *azine*,

$C_{18}H_{20}O_2N_2$,

in slender, orange-yellow needles, m. p. 237°.

Methyl 4-*hydroxy*-7-*methylcoumarin*-3-*carboxylate*, $C_{10}H_{12}O_2$, crystallises from alcohol in colourless needles, m. p. 208° (decomp.), and on hydrolysis with potassium hydroxide solution at 200° yields 2-hydroxy-4-methylacetophenone, which has b. p. 105—106°/9 mm. (compare Eykman, Abstr., 1904, i, 664). The *phenylhydrazone* of the latter crystallises from alcohol in yellow, glistening plates, m. p. 105°; the *semicarbazone* in colourless needles, m. p. 214°, and the *azine*, in slender, yellow needles, m. p. 219°.

Methyl 4-*hydroxy*-6-*methylcoumarin*-3-*carboxylate*, $C_{10}H_{12}O_2$, obtained from acetyl *p*-cresotyl chloride, crystallises from alcohol in soft, felted needles, m. p. 210° (decomp.), and on hydrolysis yields 2-hydroxy-5-methylacetophenone (compare Auwers and Müller, Abstr., 1909, i, 223). The *benzoyl* derivative of the latter, $C_{16}H_{14}O_3$, crystallises from alcohol in stout, colourless prisms, m. p. 65°. The *oxime*,

$OH\cdot C_6H_3Me\cdot CMe:N\cdot OH$,

forms small, colourless needles, m. p. 145°; the *semicarbazone*,

$C_{10}H_{13}O_2N_3$,

in colourless, rhombic crystals, m. p. 212°, and the *azine*, $C_{18}H_{20}O_2N_2$, in orange-yellow needles, m. p. 223°. J. J. S.

The Grignard Reaction. Syntheses of Fluoran. ENOS FERRARIO [and, in part, M. NEUMANN] *Gazzetta*, 1911, **41**, i, 1—11).—By the series of reactions described below, the author has effected the synthesis of fluoran. Another method by which this was attempted yielded only phenolphthalein diphenyl ether.

Magnesium *o*-methoxyphenyl iodide (in ethereal solution) reacts with phthalic anhydride (in benzene solution), yielding 2 : 2′-*dimethoxyphthalophenone*, $C_{22}H_{18}O_4$, which crystallises in colourless needles or in small cubes, m. p. 145—146°, and dissolves in concentrated sulphuric acid, producing a bluish-violet coloration. On reducing it with zinc and glacial acetic acid, 2 : 2′-*dimethoxytriphenylmethane*-2″-*carboxylic acid*, $(OMe\cdot C_6H_4)_2CH\cdot C_6H_4\cdot CO_2H$, is obtained ; it forms colourless needles, m. p. 249—250° (on rapid heating ; if the m. p. is taken slowly, the substance begins to melt at 235°, is almost melted at 240°, and completely so at 245°). The acid forms *potassium* and *sodium* salts, which crystallise in laminæ ; amorphous *barium* and *calcium* salts, and a *silver* salt, which blackens quickly. The *methyl* ester has m. p. 149—150°. When the acid is demethylated, preferably by heating it with hydrochloric acid (D 1·4) for two hours in a sealed tube at 130—140°, it yields fluoran. This synthetic fluoran crystallises with two molecules of alcohol, part of which it retains for a time even when fused.

Phenolphthalein diphenyl ether is obtained by heating together phthalic anhydride, phenyl ether, and zinc chloride for six hours at 180—190°, and also (but not so well) by the action of phthalyl chloride on phenyl ether. It has m. p. 105—106°, and dissolves in concentrated sulphuric acid, producing a cherry-red coloration.

R. V. S.

Thalleioquinine. EZIO COMANDUCCI (Pamphlet, 1910, 7 pp. Compare Abstr., 1910, i, 581).—The author gives a more detailed account of the properties of this substance, and of its behaviour with a number of reagents. It has m. p. 148—149° (corr., sintering at 130°). Analysis gave C 59·00%, H 8·47%, N 7·53—8·52%, Cl 3·88—4·13%. In alcoholic solution the compound has $[\alpha]_D^{21}$ − 187·5°. The molecular weight determined ebullioscopically in various solvents varies from 300—450. The *hydrochloride* is an amorphous residue, m. p. 120—122° (sintering at 100°), and has $[\alpha]_D^{21}$ − 255·1°. The *platinichloride* is a greenish-white precipitate, which becomes brown at 230°, sinters at 240°, and melts at 263°. The *picrate* is an amorphous, yellowish-green powder, m. p. 135° (sintering at 130°). An account is given of the absorption spectrum of the substance and also of that of quinine. R. V. S.

Volatility of Cocaine. H. C. FULLER (*J. Ind. Engin. Chem.*, 1910, 2, 426).—Attention is drawn to the fact that cocaine is appreciably volatile at temperatures of, and exceeding, 98°, a fact which is of importance in the method usually employed in the assay of coca leaves. Experiments showed that cocaine can be heated at 60°, 80°, and 90° without loss of weight, and the conclusion is drawn that these residues should be dried at a temperature not exceeding 90°, or, preferably, desiccated, without heating, over sulphuric acid.

F. M. G. M.

Alkaloids of the Perennial Papaveraceæ. Papaver orientale and P. lateritium. JOHANNES GADAMER (*Arch. Pharm.*, 1911, 249, 39—42).—With a view to obtaining data bearing on the function and method of formation of alkaloids in plants, the author proposes to examine a number of the perennial plants of the Papaveraceæ. The distribution of protopine will be specially studied. This alkaloid does not occur in *P. orientale* or *P. lateritium*.

[With Walter Klee.]—*P. orientale* contains an *alkaloid*, m. p. 204—205°, which separates from ether in colourless crystals, and, since it is soluble in alkali, must contain a phenolic hydroxyl group. *P. lateritium* also contains a phenolic base, or mixture of bases, from which no crystalline substance could be separated. T. A. H.

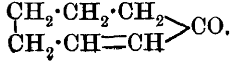
Corydalis Alkaloids. Corycavidine, a New Alkaloid of the Corycavine Series. Johannes Gadamer (*Arch. Pharm.*, 1911, **249**, 30—39).—The mixed amorphous alkaloids of *Corydalis cava* tubers, prepared as described already (Abstr., 1902, i, 306), on conversion into thiocyanates can be separated into two groups, one giving crystalline thiocyanates, soluble with difficulty in alcohol, and the other readily soluble, amorphous thiocyanates. From the second group a new alkaloid, corycavidine, closely related to corycavamine, has been isolated and characterised.

Corycavidine, $C_{22}H_{25}O_5N$, $[\alpha]_D^{20}$ +203·1° in chloroform, crystallises from hot chloroform with $1CHCl_3$ on addition of alcohol. When heated it changes at 209°, and melts at 212—213°. The change at 209° is into *i*-corycavidine (m. p. 193—195°, after re-crystallisation), and resembles that brought about by heating corycavamine (Abstr., 1902, i, 391). The *hydrochloride*, *nitrate*, and *sulphate* were prepared; the two former are crystalline. The *aurichloride*, $BHAuCl_4$, is a red powder, which sinters at 85° and decomposes at 170°.

Corycavidine contains two methoxyl groups, and a methyl group attached to the *N*-atom. It appears to be corycavamine, in which a dioxymethylene group is replaced by two methoxyl groups, and this view finds support in the similarity of the colour reactions of the two alkaloids and their similar behaviour on heating.

Corycavidine, like corycavamine, is unaffected by hot iodine solution. With methyl iodide it gives a *methiodide*, $B{\cdot}CH_3I,3H_2O$, m. p. 207—210° (decomp.), which is optically inactive, and forms small, colourless crystals from alcohol. When boiled with alkali hydroxide, the methiodide gives the corresponding *methine base*, m. p. 141·5—142·5°, which forms colourless crystals from ether, and with methyl iodide furnishes a methiodide, which was not isolated, but treated directly with alkali, when it decomposed, giving trimethylamine and a neutral substance. The latter polymerised very readily, forming a yellow, amorphous mass, and on oxidation with permanganate yielded a crystalline acid and a crystalline neutral substance, probably a glycol. T. A. H.

Constitution of Tropilen. Arthur Kötz and Richard Rosenbusch (*Ber.*, 1911, **44**, 464—466).—Tropilen, $C_7H_{10}O$, the final product of the "exhaustive methylation" of tropine, was supposed by Merling to be tetrahydrobenzaldehyde (Abstr., 1892, i, 358), and by Willstätter (Abstr., 1898, i, 540) to be *cyclo*heptenone,



$$\begin{matrix}CH_2{\cdot}CH_2{\cdot}CH_2 \\ | \\ CH_2{\cdot}CH{=}CH\end{matrix}\!\!>CO.$$

Willstätter's attempt to confirm this formula by the reduction of tropilen to suberone (Abstr., 1901, i, 649) was unsuccessful. By the use of Paal's reduction method with palladium as catalyst the authors have now effected this reduction and confirmed Willstätter's formula.

T. A. H.

Preparation of *iso*Sparteine. Action of Methyl Iodide on the Base. CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1911, **152**, 386—387).—A 90% yield of *iso*sparteine can be obtained from α-methylsparteine by heating the dihydrochloride of the latter at 220—230° in a current of hydrogen chloride.

When *iso*sparteine is boiled with methyl iodide in methyl-alcoholic solution, a mixture of two methiodides is formed; the α-compound has $[\alpha]_D$ $-16\cdot8°$, and is identical with the methiodide previously described (Abstr., 1908, i, 44), whilst the isometic iso*sparteine* α'-*methiodide* has $[\alpha]_D$ $-33\cdot3°$. The two substances are separated by taking advantage of the different solubilities of their hydriodides in water.

W. O. W.

***iso*Sparteine. A Case of Stereoisomerism of Nitrogen.** CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1911, **152**, 527—529. Compare preceding abstract).—The two isomeric α- and α'-methiodides of *iso*sparteine are now shown to owe their existence to a different spatial arrangement with regard to one nitrogen atom. If they correspond with the fixation of methyl iodide on two different nitrogen atoms, the bases arising by decomposition of the corresponding methyl*iso*sparteinium hydroxides should not be identical. It has been found, however, that α-methylsparteine is produced when either the α- or α'-hydroxide is heated in a vacuum. In the latter case a new base, *methyl*iso*sparteine*, $C_{16}H_{28}N_2$, is also formed. This has m. p. 24°, $[\alpha]_D$ $+23\cdot6°$, and may be separated from α-methylsparteine by mixing with methyl iodide in methyl-alcoholic solution, when *methyl*iso*sparteine dimethiodide*, $C_{16}H_{28}N_2,2MeI$, m. p. 281—282° (decomp.), is formed. A better method, which allows of isolating both bases, consists in heating with dilute sulphuric acid, when α-methylsparteine alone is converted into the methosulphate.

*Methyl*iso*sparteine dipicrate* has m. p. 203°. The *platinichloride* blackens at 240°, and has m. p. 256° (decomp.).

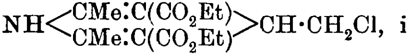
W. O. W.

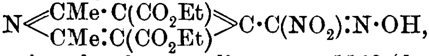
Synthesis of Pyrrole and Furfuran Derivatives from Dichloroethyl Ether, Ethyl Acetoacetate, and Ammonia. ERICH BENARY (*Ber.*, 1911, **44**, 493—496).—By the interaction of dichloroethyl ether, ethyl acetoacetate, and aqueous ammonia in the cold, a mixture of ethyl 2-methylpyrrole-3-carboxylate and ethyl 2-methylfurfuran-3-carboxylate is obtained. The mechanism of the reaction is precisely similar to that between chloroacetone, ethyl acetoacetate, and ammonia studied by Hantzsch (Abstr., 1890, i, 1165) and Feist (Abstr., 1902, i, 488).

Ethyl 2-methylpyrrole-3-carboxylate crystallises in colourless leaflets, m. p. 78—79°, and dissolves in concentrated sulphuric acid with a reddish-violet coloration. It is hydrolysed to the corresponding acid already described by Ciamician (*Ber.*, 1878, **14**, 1056).

Ethyl 2-methylfurfuran-3-carboxylate is an oil, b. p. 85—87°/20 mm. The corresponding acid forms colourless needles, m. p. 101—102° (Plancher and Albini, Abstr., 1904, i, 334). E. F. A.

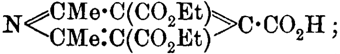
Synthesis of Pyridine Derivatives from Dichloroethyl Ether and Ethyl-β-aminocrotonate.

Erich Benary (*Ber.*, 1911, **44**, 489—493).—By the interaction of ethyl-β-aminocrotonate and 1 : 2-dichloroethyl ether, *ethyl* 2 : 6-*dimethyl*-4-*chloromethyldihydropyridine*-3 : 5-*dicarboxylate*,  $NH<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>CH\cdot CH_2Cl$, is obtained in tiny, colourless needles, m. p. 133—134°. On oxidation with dilute nitric acid (D 1·17), the corresponding *ethyl* 2 : 6-*dimethyl*-4-*chloromethylpyridine*-3 : 5-*dicarboxylate* is formed; it is a colourless, viscid oil, m. p. 197—198°. It was mixed with a small quantity of a chlorine-free substance crystallising in needles, m. p. 72—73°. A further by-product of the oxidation is *ethyl* 2 : 6-*dimethylpyridine*-3 : 5-*dicarboxylate*-4-*methylnitrolic acid*,



$$N\lessgtr\begin{matrix}CMe\cdot C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>C\cdot C(NO_2){:}N\cdot OH,$$

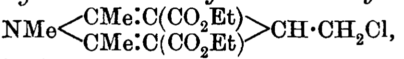
which crystallises in colourless needles, m. p. 110° (decomp.); it gives a red coloration with alkali hydroxide only in concentrated solution. When boiled with dilute nitric acid the *diethyl* ester of 2 : 6-*dimethylpyridine*-3 : 4 : 5-*tricarboxylic acid* is formed,



$$N\lessgtr\begin{matrix}CMe\cdot C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>C\cdot CO_2H;$$

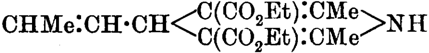
it crystallises in tiny needles, m. p. 181° (decomp.).

Ethyl 2 : 6-*dimethyl*-4-*iodomethylpyridine*-3 : 5-*dicarboxylate* is obtained by the interaction of the corresponding chloro-compound with sodium iodide in acetone solution; it crystallises in granular crusts, m. p. 77—78°.

Ethyl 1 : 2 : 6-*trimethyl*-4-*chloromethyldihydropyridine*-3 : 5-*dicarboxylate*,  $NMe<\begin{matrix}CMe{:}C(CO_2Et)\\CMe{:}C(CO_2Et)\end{matrix}>CH\cdot CH_2Cl$, from dichloroethyl ether and ethyl β-methylaminocrotonate, crystallises in four-sided platelets, m. p. 88—89°. E. F. A.

Condensation of Crotonaldehyde with Ammonia and Ethyl Acetoacetate.

E. Grishkewitsch-Trochimowsky (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1377—1380).—*Ethyl* 2 : 6-*dimethyl*-4-*allyldihydropyridine*-3 : 5-*dicarboxylate*,



$$CHMe{:}CH\cdot CH<\begin{matrix}C(CO_2Et){:}CMe\\C(CO_2Et){:}CMe\end{matrix}>NH,$$

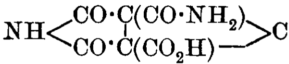
prepared by the condensation of crotonaldehyde with ammonia and ethyl acetoacetate, forms colourless crystals, m. p. 144·5—145·5°. When oxidised it yields a viscous, pale yellow liquid, b. p. about 205°/45 mm., and, when treated with platinum chloride in concentrated hydrochloric acid solution, it gives *ethyl* 2 : 6-*dimethyl*-4-*allylpyridine*-3 : 5-*dicarboxylate platinichloride*, $C_{16}H_{21}O_4N,H_2PtCl_6$, forming orange needles, m. p. 177·5—178°.

When the dihydropyridinedicarboxylic ester is hydrolysed and the salt subsequently subjected to dry distillation with slaked lime, it yields a colourless liquid, b. p. 175—178°, which is probably 2:4:6-*trimethylpyridine*; it forms a *platinichloride*, m. p. about 220° (decomp.), an *aurichloride*, and a *mercurichloride* compound, m. p. 155—155·5°.

T. H. P.

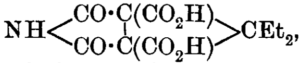
New Diethyltrimethylenepyrrole Derivatives. Mario Ghiglieno (*Atti R. Accad. Sci. Torino*, 1911, **46**, 87—95).—In order to test the accuracy of the explanation given (Abstr., 1910, i, 427) for the existence of two isomeric forms of 3 : 5-dicyano-4-methyl-4-ethyltrimethylenedicarbonimide and of similar methylethyl compounds, the author has examined various diethyl derivatives homologous with methylethyl derivatives already described (*loc. cit.*; Abstr., 1910, i, 505). The results confirm the hypothesis of spatial isomerism, since in no case could two isomeric diethyl derivatives be prepared.

The *mono-amide* of 3 : 5-*dicarboxy*-4 : 4-*diethyltrimethylenedicarbonimide*,



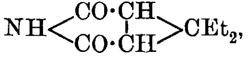
$NH<\begin{matrix}CO\cdot C(CO\cdot NH_2)\\ CO\cdot C(CO_2H)\end{matrix}>CEt_2$, prepared by the action of dilute sodium hydroxide solution on the corresponding 3:5-dicyano-compound, has m. p. 247—250° (Maquenne block), and behaves as a dibasic acid, owing to the mobility of the iminic hydrogen under the influence of the neighbouring groups; the second basicity is, however, weak, and, in *N*/10-solution, can only be estimated to the extent of about 50% by means of sodium hydroxide and phenolphthalein. The *silver*, $C_{11}H_{12}O_5N_2Ag_2,H_2O$, lead, copper, and barium salts are all sparingly soluble.

4 : 4-*Diethyltrimethylenedicarbonimide*-3 : 5-*dicarboxylic acid*,



$$NH<\begin{matrix}CO\cdot C(CO_2H)\\ CO\cdot C(CO_2H)\end{matrix}>CEt_2,$$

obtained by the action of nitrous acid on the preceding compound, forms colourless needles ($+1\frac{1}{2}H_2O$), the anhydrous acid having m. p. 188—189° (Maquenne block); it behaves as a dibasic acid, although not so sharply as the corresponding methylethyl homologue, and forms insoluble lead, copper, silver, and mercurous salts. When heated it loses $2CO_2$, forming 4 : 4-*diethyltrimethylenedicarbonimide*,

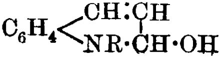


$$NH<\begin{matrix}CO\cdot CH\\ CO\cdot CH\end{matrix}>CEt_2,$$

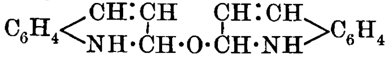
as a yellow, semi-fluid mass; this compound gives sparingly soluble *silver*, $C_9H_{12}O_2NAg$, lead, copper, and zinc salts.

T. H. P.

Constitution of the Pseudo-ammonium Bases. Adolf Kaufmann and Paul Strübin (*Ber.*, 1911, **44**, 680—690).—The constitution of the pseudo-ammonium bases has long been a subject of discussion (compare Hantzsch and Kalb, Abstr., 1900, i, 113). In particular, the first product formed on oxidation of the alkylquinolinium bases has been assumed to be a carbinol base,



$C_6H_4<\begin{matrix}CH:CH\\ NR\cdot CH\cdot OH\end{matrix}$ (Decker, Hantzsch), or an aldehyde base with the pyridine ring opened, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CHO$ (Roser, Gadamer, Reissert), or the anhydride of the carbinol,



$$C_6H_4{<}\begin{matrix}CH{:}CH \quad CH{:}CH\\ NH\cdot CH\cdot O\cdot CH\cdot NH\end{matrix}{>}C_6H_4$$

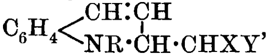
(La Coste, Hantzsch).

It is now shown that the carbinol at first formed slowly undergoes transformation into the isomeric aldehydeamine, which is an exceedingly reactive substance. The aldehyde group can be identified by the specific colour reactions with diazobenzenesulphonic acid; corresponding derivatives are also formed with phenylhydrazine, hydroxylamine, and aniline.

The aldehydeamine combines with alcohols, forming unstable additive products, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CH(OH)\cdot OR$, from which water is eliminated, and the closed-ring alcoholates formed. It forms an additive compound with the carbinol, which, on the elimination of water, is converted into the anhydride, dihydroquinolylquinolanol.

Alkali converts the aldehyde into an oxidation product (acid) and a reduction product (alcohol), from which water is eliminated and quinolone and dihydroquinoline are formed.

Two molecules of the aldehyde undergo a benzoin condensation, forming dyes which are probably identical with the *apo*cyanines.

The aldehyde combines further with substances containing a reactionary methylene or methyl group. Water is eliminated, and dihydroquinoline derivatives,  $C_6H_4{<}\begin{matrix}CH{:}CH\\ NR\cdot CH\cdot CHXY\end{matrix}$, are formed from the aldol intermediate product, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CH(OH)\cdot CHXY$, in addition to unsaturated substances, $NHR\cdot C_6H_4\cdot CH{:}CH\cdot CH{:}CXY$. Both types when oxidised form dyes belonging to the class of cyanines and *apo*cyanines.

Similar transformations to the above have been observed in the *iso*quinoline and pyridine series. Thus, with *iso*quinoline the pseudo-base is transformed into the aldehyde, $CHO\cdot C_6H_4\cdot CH{:}CH\cdot NHR$, which reacts as described above. When condensed with reactive methylene compounds, dihydro*iso*quinolines are formed closely related to the alkaloids.

*iso*Quinoline and pyridine differ from quinoline in that the aldehydes tend to lose alkylamine and form nitrogen-free alcohols or the isomeric aldehydes.

The *methochloride* of the pseudo-base from 6 : 8-dinitroquinoline is obtained by heating with the theoretical quantity of methyl sulphate, dissolving the fused mass in water, and precipitating with sodium chloride; it forms brownish-yellow crystals, m. p. 203° (decomp.). Alkali hydroxides, ammonia, and sodium carbonate precipitate the pseudo-base, *dinitromethylquinolanol*, from an aqueous solution of the salt as a light yellow, indefinitely crystalline substance; it is obtained from chloroform in yellow plates, m. p. 114°. When boiled with alcohols the *alcoholates* separate in well defined crystals; the *methyl ether* has m. p. 110°; the light yellow needles of the *ethyl ether* sinter at 124°. The pseudo-base, dissolved in the nascent state in benzene or toluene, readily separates again in light yellow flakes, which sinter at 199°, and have the composition, $C_{20}H_{16}O_9N_6$, of the anhydride, *dinitromethylquinoline oxide*; attempts to recrystallise it from ethyl alcohol result in the formation of the ethyl ether.

Dinitromethylquinolanol reacts with phenylhydrazine, forming a *phenylhydrazone*, crystallising in yellowish-brown needles, m. p. 141°. The corresponding *anil* separates in well formed, yellow needles, m. p. 186°. The evidence is insufficient to decide whether the pseudo-base has the carbinol or aldehyde structure.

On heating quinoline ethiodide, hydroxylamine hydrochloride, and potassium hydroxide, a *compound*, $C_{22}H_{25}ON_3$, crystallising in short, almost colourless needles, m. p. 214° (decomp.), was obtained, which appears to be a condensation product of two quinoline nuclei with one molecule of hydroxylamine. A red dye is also formed.

E. F. A.

Preparation of Bromo-fatty Acid Derivatives of Amino-aceto-*p*-phenetidines. CHEMISCHE WERKE VORM. DR. HEINRICH BYK (D.R.-P. 228835).—Aminoaceto-*p*-phenetidine has long been employed in pharmacy, and it is now found that its higher acyl derivatives containing bromine and an amino-residue have an enhanced therapeutic value.

*a-Bromo*iso*valerylaminoaceto*-p-*phenetidine*,

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NH\cdot CO\cdot CHPr^{\beta}Br,$$

slender, colourless needles, m. p. 155—156°, is prepared by slowly treating a cold benzene suspension of aminoaceto-*p*-phenetidine with a molecular proportion of *a*-bromo*iso*valeryl bromide, allowing the mixture to remain during several hours, removing the benzene in a vacuum, and subsequent crystallisation from alcohol.

F. M. G. M.

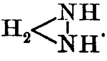
Strongly Coloured *holo*- and *meri*-Quinonoid Imonium Salts of Benzidine and their Use for Determining the Active Value of Oxidising Agents. WALTER MADELUNG (*Ber.*, 1911, **44**, 626—631).—The author does not agree with Willstätter and Kalb's view (*Ber.*, 1906, **39**, 3476) that *meri*-quinonoid derivatives are deeply coloured, whereas *holo*-quinonoid compounds are yellow (compare Willstätter and Piccard, Abstr., 1908, i, 475, 915; Schlenk and Knorr, 1909, i, 36, 808).

When an aqueous solution of benzidine is oxidised with halogens, permanganate, dichromate, or iron cyanate under such conditions that the solution is kept neutral, the product is a crystalline solid with a deep cornflower-blue colour, and is very sparingly soluble. This compound probably has a constitution analogous to Schlenk's *meri*-quinonoid salt of diphenoquinonedi-imine. When further oxidised the compound deepens in colour, and gives a deep violet-coloured product, which is regarded as the *holo*-quinonoid compound. When bromine water in presence of potassium bromide is used as oxidising agent, and an amount insufficient to completely precipitate the benzidine is used, it is found that the amount of bromine required to transform the blue into the violet product is equal to the amount of bromine required to oxidise the benzidine to the blue compound, and that the addition of more bromine water leads to the formation of a reddish-brown product, which is regarded as the quinonoid dibromoimide. When benzidine solution, or thiosulphate solution, is added to this, the change to the violet and then to the blue compound can be observed. It is suggested that Willstätter and Piccard's second chromate is in reality a *holo*-quinonoid derivative.

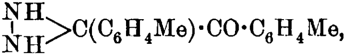
The salts of the *meri*- and *holo*-quinonoid compounds with mineral acids are quite stable at the ordinary temperature, but decompose when warmed and cannot be recrystallised. On addition of alkali they yield the yellow, readily soluble diphenoquinonedi-imine, which is readily decomposed by acids, for example, hydrochloric, yielding benzidine and the quinonoid dichlorobromide.

It is shown that when the blue compound formed by the action of a given amount of an oxidising agent of known concentration on benzidine is removed, acidified with hydrochloric acid, and the dichloroimine treated with excess of potassium iodide, an amount of iodine is liberated which corresponds exactly with the oxidising value of the original volume of oxidising agent employed. The method is recommended for the estimation of small amounts of oxidising agents. As the volume of iodine solution to be titrated can be quite small compared with the volume of the original solution, it is also recommended in cases where the original solution is coloured, for example, in the case of peroxydases and blood. J. J. S.

Colloidal Form of Nastvogel's Osazone. HENRY J. H. FENTON and WILLIAM A. R. WILKS (*Proc. Camb. Phil. Soc.*, 1911, **16**, 85—86).—A colloidal solution of Nastvogel's osazone of glyoxalcarboxylic acid is obtained by boiling phenylhydrazine dihydroxymaleate with water (Trans., 1905, **87**, 808). It is readily coagulated by minute quantities of electrolytes, moves to the anode in an electric field, is not precipitated by electronegative colloids, but yields a dark brown precipitate with colloidal ferric hydroxide; in general, it behaves as a negative colloid of the suspensoid class. The most remarkable property of the colloid is its extreme sensitiveness to hydrogen ions; a solution which is unaffected by several drops of 5*N*-sodium chloride is coagulated, under similar conditions, by one drop of *N*/10-hydrochloric acid, the hydrogen ion being about 300 times as effective as the sodium ion. It is suggested that a minute quantity of some basic substance is present in the colloidal solution, and that its "protective" influence is removed on neutralisation by the acid. C. S.

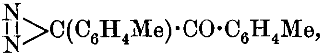
Action of Hydrazine Hydrate on Ortho-diketones. THEODOR CURTIUS and RICHARD KASTNER (*J. pr. Chem.*, 1911, [ii], **83**, 215—232).—Curtius and Thun (Abstr., 1891, 1355) have shown that hydrazine hydrate reacts with ortho-diketones, such as benzil, to form derivatives of the hypothetical hydrazimethylene,  $CH_2<\begin{matrix}NH\\ |\\ NH\end{matrix}$. The present work has been undertaken mainly to show that *p*-tolil behaves in a similar manner.

Hydrazi-p-*tolil* (p-*toluoyl*-p-*tolylhydrazimethylene*),



$$\begin{matrix}NH\\|\\NH\end{matrix}\!\!>C(C_6H_4Me)\cdot CO\cdot C_6H_4Me,$$

m. p. 139—140°, is obtained by heating an alcoholic solution of *p*-tolil with hydrazine hydrate (1 mol.). It yields deoxy-*p*-toluoin when heated under reduced pressure, and in benzene solution is oxidised by yellow mercuric oxide to *azo*-p-*tolil* (p-*toluoyl*-p-*tolylazomethylene*),

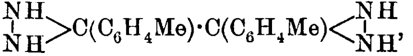


$\begin{matrix}N\\\|\\N\end{matrix}\!\!>C(C_6H_4Me)\cdot CO\cdot C_6H_4Me$, m. p. 84°, red crystals, which behaves like azobenzil (Curtius and Lang, Abstr., 1892, 451), being converted by bromine in carbon tetrachloride into *dibromodeoxy*-p-*toluoin*, $C_6H_4Me\cdot CO\cdot CBr_2\cdot C_6H_4Me$, m. p. 120°. When equal molecular quantities of deoxy-*p*-toluoin and hydrazine hydrate are heated on the water-bath, *bis*-p-*toluoyl*-p-*tolylazimethylene*,

$$[C_6H_4Me\cdot CH_2\cdot C(C_6H_4Me)\colon]_2N_2,$$

m. p. 155—156°, is produced.

Bishydrazi-p-*tolil* (*di*-p-*tolylbishydrazimethylene*),



$$\begin{matrix}NH\\|\\NH\end{matrix}\!\!>C(C_6H_4Me)\cdot C(C_6H_4Me)\!\!<\!\!\begin{matrix}NH\\|\\NH\end{matrix},$$

m. p. 137°, is obtained by heating *p*-tolil with a little alcohol and an excess of hydrazine hydrate at 100° for twenty-four hours; it yields 4 : 4′-dimethyltolane when its solution in benzene is treated with yellow mercuric oxide.

When a solution of hydrazibenzil in concentrated sulphuric acid is poured into water at 0°, the products obtained are benzil, benzaldehyde, benzaldazine, and bisbenzilketazine. The last substance, which is also produced by heating hydrazibenzil and benzil together at 200°, is identical with Curtius and Blumer's bisbenzoylphenylazimethylene obtained from benzoinhydrazine (Abstr., 1895, i, 600). *Bis*-p-*tolilketazine*, $N_2[\colon C(C_6H_4Me)\cdot CO\cdot C_6H_4Me]_2$, m. p. 248°, is similarly obtained from hydrazi-*p*-tolil and concentrated sulphuric acid, from hydrazi-*p*-tolil and *p*-tolil at 180°, and by heating *p*-toluoinhydrazine at 185° for five hours. (A by-product in the last reaction is *tetra*-p-*tolylpyrazine*, m. p. 287°. The corresponding by-product, $C_{28}H_{20}N_2$, obtained by Curtius and Blumer [*loc. cit.*] by heating benzoinhydrazine, is proved to be tetraphenylpyrazine, as suggested by Snape and Brooke [Trans., 1897, 71, 532].) p-*Toluoinhydrazine*,

$$C_6H_4Me\cdot CH(OH)\cdot C(C_6H_4Me)\colon N\cdot NH_2,$$

m. p. 147—148°, is obtained together with tetra-*p*-tolylpyrazine by heating toluoin and hydrazine hydrate for five hours on the water-bath and keeping the mixture for three weeks before treating it with ether to remove the second product.

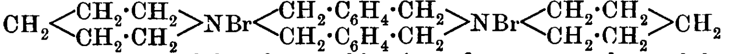
Bisbenzilketazine is not hydrolysed by boiling alcohol and dilute sulphuric acid or by dilute sulphuric acid at 160°, but is decomposed by the prolonged action of concentrated sulphuric acid, or rapidly by boiling aqueous alcoholic sodium hydroxide, yielding hydrazine and benzil. C. S.

Decomposition of Alloxan. Ross Aiken Gortner (*J. Amer. Chem. Soc.*, 1911, **33**, 85).—Wheeler and Bogert (Abstr., 1910, i, 466) have recorded explosions due to the decomposition of alloxan in closed bottles. The author has examined a sample of alloxan which had been kept for about a year. On the outside of the neck of the bottle was an incrustation which had evidently been forced out between the stopper and the bottle, and consisted chiefly of carbamide, oxalic acid, and alloxantin. There was considerable pressure in the bottle due to carbon dioxide, and some unaltered alloxan still remained. It is obvious, therefore, that the decomposition of alloxan takes place slowly at the ordinary temperature in accordance with certain well-known reactions. This confirms the explanation offered by Franklin (*J. Amer. Chem. Soc.*, 1910, **32**, 1362). E. G.

Constitution of Indirubin. LOUIS C. MAILLARD (*Bull. Soc. chim.*, 1911, [iv], **9**, 202—205. Compare Abstr., 1910, i, 138).—Polemical with Wahl and Bagard (this vol., i, 164). T. A. H.

Asymmetry of the Quinquevalent System N a$_2$ b c d. MAX SCHOLTZ (*Ber.*, 1911, **44**, 480—488. Compare Abstr., 1910, i, 634).—2-Phenyl-1 *o*-xylylene-6-methylpiperidinium bromide has been shown (Abstr., 1910, i, 634) to exist in two inactive stereoisomeric modifications. Similar compounds have been prepared from *o*-xylylene bromide and coniine, conhydrine, and α-stilbazoline, all of which contain a nitrogen atom common to two rings and attached to an asymmetric carbon atom. In neither case could more than one modification be observed.

Compounds of the general formula :



$$CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}NBr{<}\genfrac{}{}{0pt}{}{CH_2\cdot C_6H_4\cdot CH_2}{CH_2\cdot C_6H_4\cdot CH_2}{>}NBr{<}\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}{>}CH_2$$

have been prepared by the combination of *o*-, *m*-, and *p*-xylylenedipiperidide with *o*-, *m*-, and *p*-xylylene bromide. With the exception of that from *p*-xylylenedipiperidide and *p*-xylylene bromide, they are all of the type N a$_2$ b c d. The combination of *p*-xylylene dipiperidide with *m*-xylylene bromide yields two isomerides, one, m. p. 215°, readily soluble in alcohol, the other, m. p. 244°, which is formed in small proportion only, being sparingly soluble. The same two isomerides are formed by the combination of *m*-xylylene dipiperidide and *p*-xylylene bromide, in which case the amount of the less fusible isomeride is larger, although the more fusible form still predominates. The two dibromides also form different derivatives. They are not converted into one another on heating, and attempts to resolve them into optically active compounds were unsuccessful. They are prepared by mixing equivalent quantities of the components in chloroform solution ; after twenty-four hours the condensation product has either separated as a colourless mass, or it is precipitated by ether. The bromine cannot be estimated by direct titration, but good results are obtained by the Carius' method.

p-Xylylene dipiperidide, $C_6H_4(CH_2\cdot C_5NH_{10})_2$, has m. p. 90° (compare Manoukian, Abstr., 1901, i, 528, who gives 86°). m-*Xylylene*-p-*xylylene-dipiperidinium bromide* forms a microcrystalline α-isomeride, m. p. 215°, and a granular, crystalline β-isomeride, m. p. 244°

The α-isomeride forms the following salts : *platinichloride,* m. p.

234°; *aurichloride*, m. p. 165°, decomp. above 200°; *picrate*, m. p. 161—162°, decomp. 230°. The salts of the β-isomeride are *platinichloride*, m. p. 248°; *aurichloride*, m. p. 274° (decomp.); *picrate*, darkens at 220°, but is not melted at 300°.

o-*Xylylene*-m-*xylylenedipiperidinium bromide* does not form an isomeride; it is a sandy powder, m. p. 170—173° (decomp.); the *platinichloride* has m. p. 220° (decomp.); the *picrate*, m. p. 168—170°.

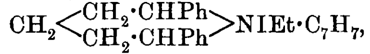
o-*Xylylene*-p-*xylylenedipiperidinium bromide* has m. p. 165° (decomp.); the *platinichloride* has m. p. 225° (decomp.); the *picrate*, m. p. 143—145°.

Di-p-*xylylenedipiperidinium bromide* is not melted at 310°; the *platinichloride* decomposes at 234°; *picrate*, m. p. 241° (decomp.).

o-*Xylyleneconhydrinium bromide* was obtained as a syrup. The *platinichloride* crystallises in golden-yellow cubes and octahedra, m. p. 232° (decomp.).

o-*Xylylenestilbazolinium bromide* is also a syrup; the *platinichloride* has m. p. 132°.

It was shown previously (Abstr., 1901, 483) that 2 : 6-diphenylpiperidine exists in two inactive forms. One of these, m. p. 71°, reacts with ethyl iodide and sodium hydroxide to form 2 : 6-*diphenyl*-1-*ethylpiperidine*, which crystallises in long, lustrous needles, m. p. 83°. It reacts with benzoyl iodide, one modification only of 2 : 6-*diphenyl*-1-*benzyl*-1-*ethylpiperidinium iodide*,



$$CH_2\left\langle\begin{matrix}CH_2\cdot CHPh\\CH_2\cdot CHPh\end{matrix}\right\rangle NIEt\cdot C_7H_7,$$

being obtained; this crystallises in colourless needles, m. p. 261°. Accordingly, 2 : 6-diphenylpiperidine, m. p. 71°, corresponds with the mesotartaric type, and cannot be resolved. E. F. A.

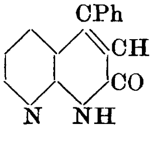
Syntheses of Derivatives of 1 : 8-Naphthyridine from α-Aminopyridine. F. CARLO PALAZZO and ASTORRE TAMBURINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 37—44).—By heating α-aminopyridine with ethyl acetoacetate for an hour and a-half in a sealed tube at 120—125°, α-*acetoacetylaminopyridine*,

$$C_5H_4N\cdot NH\cdot CO\cdot CH{:}CMe\cdot OH,$$

is obtained. It crystallises in colourless needles, m. p. 113° (softening towards 110°), is soluble in acids and alkalis, gives a green precipitate with ammoniacal copper acetate, and an intense reddish-violet coloration with ferric chloride. α-*Benzoacetylaminopyridine*,

$$C_5NH_4\cdot NH\cdot CO\cdot CH{:}CPh\cdot OH,$$

similarly prepared, crystallises in colourless needles, m. p. 110° (softening at 106°), and has properties similar to those of the acetoacetyl derivative. When heated for twenty to twenty-five minutes at 100° with concentrated sulphuric acid, it condenses to 4-*phenyl*-1 : 8-*naphthyrid*-2-*one* (annexed formula), which can be obtained on neutralising the solution, and forms colourless, silky needles, m. p. 150° (previously softening). The substance has only basic properties; it dissolves in acids, and is reprecipitated by alkals. It yields a *platinichloride*. It gives no coloration with ferric chloride. Acetoacetylaminopyridine behaves with



concentrated sulphuric acid like the benzoyl derivative, but for lack of substance the analogous naphthyridine could not be isolated.

R. V. S.

Quinoline Dyes. I. *apo*Cyanines. ADOLF KAUFMANN and PAUL STRÜBIN [and, in part, A. ANASTACHEWITCH, N. POPPER, and L. SZNAJDER] (*Ber.*, 1911, **44**, 690—701).—By the action of alkali on the quaternary salts of quinoline, particularly on warming, red to black dyes are formed, together with resins, in a manner analogous to the well-known cyanines and *iso*cyanines. The name *apo*cyanine is suggested for the new dyes, and distinction is made between the red *erythro*apo*cyanines* and the more yellow *xantho*apo*cyanines*, which are formed side by side. They are characterised by the fact that their aqueous solutions are not instantaneously decolorised by mineral acids.

When quinoline ethiodide is boiled with potassium hydroxide in methyl alcohol, the solution changes from yellow to red, then becomes reddish-violet, and yellow crystals of the *xantho*apo*cyanine* separate. These are separated by filtration, and, after a time, red needles of coppery lustre of the *erythro*apo*cyanine* crystallise, the proportion of the red dye being considerably greater than that of the yellow dye.

*Erythro*apo*cyanine*, $C_{22}H_{23}N_2I$, decomposes at 210—220°; the *nitrate* crystallises in dark red prisms, m. p. 169—170°. The homologous *dimethylerythro*apo*cyanine hydriodide* forms deep red, lustrous needles, m. p. 238° (decomp.).

The erythro*apo*cyanines are probably the monoacid salts of 2 : 2-diquinolenyls; they have weak basic properties. The neutral colourless salts are dissociated on dilution with water, and form the coloured basic salts. Oxidising agents destroy the double bond between the two quinoline nuclei, which appears to be the carrier of the chromophoric properties, with the formation of 2 : 2-diquinolyl derivatives.

Thus the *diethyl picrate* of a *diquinolyl*, $C_{34}H_{26}O_{14}N_8$, is obtained in slender, yellow needles, m. p. 186°, by the action of picric acid on diethyl-2 : 2-diquinolenyl hydriodide. At the same time, a more soluble red substance, m. p. 162°, is obtained, which is converted into the above picrate on oxidation; it possibly represents a neutral picrate of diquinolen. *Diethyldiquinolyl chromate* forms yellowish-red needles, and becomes black at 190°, m. p. 210° (decomp.).

2 : 2-*Diquinolyl diethiodide*, prepared by the action of iodine on diethyldiquinolenyl hydriodide, crystallises in long, citron-yellow needles, m. p. 198°. It yields the dipicrate described above. A second iodo-derivative, the *periodide*, $C_{22}H_{22}N_2I_7$, is formed in smaller quantity; it is a dark brownish-red, crystalline powder, m. p. 152° (decomp.).

A similar *perbromide*, $C_{22}H_{22}N_2IBr_6$, crystallises in lustrous, golden-yellow plates, m. p. 197—199°.

Diethyldiquinolenyl hydriodide was converted into the corresponding *chloride*, which is more soluble, and oxidised with cold alkaline potassium ferricyanide; the *oxidation product*, $C_{22}H_{20}O_2N_2$, forms slender, colourless needles, m. p. 176°. It has faintly basic properties and forms a *platinichloride*, m. p. 196—197°, which readily dissociates.

The corresponding product from dimethyldiquinolenyl hydrochloride forms yellow, rhombic crystals, m. p. 243°.

The xantho*apo*cyanines are more sparingly soluble, melt above 300°, have a yellowish-green fluorescence in solution, and are more stable towards mineral acids. They are not oxidised by iodine or potassium ferrocyanide.

The orange-yellow dye, $C_{22}H_{23}N_2I$, from quinoline ethiodide, crystallises in long, matted needles, m. p. 320° (decomp.); the corresponding yellow dye from quinoline methiodide crystallises in needles, m. p. above 300°. The *nitrate* separates in orange-yellow needles, which are partly decomposed on drying at 120°. The xantho*apo*cyanines have no basic properties; alkalis precipitate almost colourless bases, which rapidly change, have no definite melting point, and are characterised by the blue fluorescence when dissolved in alcohol or concentrated sulphuric acid. E. F. A.

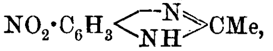
Tri-indylmethane Dyes. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1911, 71, 7—13. Compare Abstr., 1909, i, 846).—The dye obtained, as *sulphate*, on heating 2-methylindole-3-aldehyde with dilute sulphuric acid, whereby formic acid is formed, crystallises in long, reddish-violet needles, which sinter at 175°, m. p. 212° (decomp.). By treatment with ammonia, the *dye*, $C_{28}H_{23}N_3$, is obtained as bright yellow, narrow plates, m. p. 234—237°. The dye is even more readily formed in the cold from 2-methylindole, formic acid, and 20% sulphuric acid. It is also obtained by the condensation of methylindolealdehyde and methylindole in concentrated alcoholic solution with the addition of two drops of concentrated hydrochloric acid. On boiling with water at 230° under pressure, it is hydrolysed to these two components. The *leuco*-compound, $C_{28}H_{25}N_3$, is formed along with the dye by the last-described method; it has a faint rose tint, m. p. 319°. E. F. A.

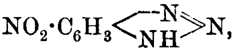
Reactions of 1-Chloro-2 : 6-dinitrobenzene. WALTHER BORSCHE and D. RANTSCHEFF (*Annalen*, 1911, 379, 152—182. Compare Abstr., 1909, i, 232).—The product described by Jungfleisch (*Jahresb.*, 1868, 345) as 1-chloro-2 : 6-dinitrobenzene is shown to be a mixture of 25% of this compound with 75% of the 2 : 4-dinitro-compound, and this accounts for the statement that the 2 : 6-compound is transformed into the 2 : 4- when impregnated with a crystal of the latter.

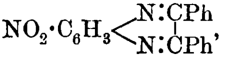
The separation of the two isomeric dinitro-derivatives is accomplished most readily by means of ethyl sodioacetoacetate, which reacts with the 2 : 4-compound much more readily than with the isomeride. The ethereal solution of the chloro-2 : 6-dinitrobenzene and the ethyl 2 : 4-dinitrophenylacetoacetate is extracted with water and then 2% sodium hydroxide solution, which removes the ester. 1-*Chloro-2 : 6-dinitrobenzene*, $C_6H_3Cl(NO_2)_2$, crystallises from alcohol in slender, yellow needles, m. p. 92°, and when finely divided has an irritating action on the mucous membrane. Its constitution has been proved by conversion into 2 : 6-dinitrophenol, 2 : 6-dinitrophenetole, and 2 : 6-dinitroaniline. The atom of chlorine is reactive, and can be replaced by various types of substituents.

2 : 6-*Dinitrophenyl ether*, $OPh\cdot C_6H_3(NO_2)_2$, prepared from sodium phenoxide and 1-chloro-2 : 6-dinitrobenzene, crystallises from alcohol in colourless plates, m. p. 99—100°. When reduced with an alcoholic solution of ammonium sulphide, the chloro-derivative yields *m*-nitroaniline, but with stannous chloride solution yields 2-chloro-*m*-phenylenediamine, $C_6H_7N_2Cl$, m. p. 85—86°, which forms a *dibenzoyl* derivative, $C_{20}H_{15}O_2N_2Cl$, m. p. 196—197°.

3-*Nitro*-o-*phenylenediamine*, $NO_2\cdot C_6H_3(NH_2)_2$, obtained by reducing 2 : 6-dinitroaniline with an alcoholic solution of ammonium sulphide, crystallises from dilute alcohol in dark red needles, m. p. 158—159°, and in the presence of pyridine yields a benzoyl derivative, $C_{13}H_{11}O_3N_3$, in the form of dark yellow, refractive needles, m. p. 206°.

4-*Nitro-2-methylbenziminazole*, 
$NO_2\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{N}{NH}}{>}CMe$, is formed when the nitro-*o*-phenylenediamine is boiled for several hours with acetic anhydride, and crystallises from dilute alcohol in compact, yellow needles, m. p. 217°. o-*Nitro*-1 : 2 : 3-*benztriazole*,


$$NO_2\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{N}{NH}}{>}N,$$

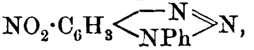
obtained by dissolving nitro-*o*-phenylenediamine in hydrochloric acid and treating with sodium nitrite solution, crystallises from alcohol in compact, glistening, brown needles, which decompose at 230°. The *o*-diamine also condenses with α-diketones; for example, when boiled with an alcoholic solution of benzil for several hours it yields 5-*nitro*-2 : 3-*diphenylquinoxaline*, 
$NO_2\cdot C_6H_3{<}{\genfrac{}{}{0pt}{}{N:CPh}{N:CPh}}$, which crystallises from a mixture of alcohol and chloroform, and has m. p. 169—170°. Its solution in concentrated sulphuric acid has a blood-red colour.

2 : 6-*Dinitrodimethylaniline*, $NMe_2\cdot C_6H_3(NO_2)_2$, obtained by the action of a 33% aqueous solution of dimethylamine on an alcoholic solution of 2 : 6-dinitrochlorobenzene, crystallises from dilute alcohol in slender orange-yellow needles, m. p. 78°, and when reduced with alcoholic ammonium sulphide yields 3-*nitro*-o-*phenylenedimethyldiamine*, $NO_2\cdot C_6H_3(NH_2)(NMe_2)$, as a dark red pasty mass. The corresponding *benzoyl* derivative, $C_{15}H_{15}O_3N_3$, crystallises in yellow needles, m. p. 114°.

Piperidine and chloro-2 : 6-dinitrobenzene in alcoholic solution yield 1-*di*-o-*nitrophenylpiperidine*,
$C_6H_3(NO_2)_2\cdot N{<}{\genfrac{}{}{0pt}{}{CH_2\cdot CH_2}{CH_2\cdot CH_2}}{>}CH_2$, which crystallises in long, brittle, yellow needles, m. p. 106—107°.

2 : 6-*Dinitrodiphenylamine*, $C_6H_3(NO_2)_2\cdot NHPh$, is formed when chloro-2 : 6-dinitrobenzene is boiled for several hours with an alcoholic solution of aniline and sodium acetate, and crystallises from alcohol in brilliant orange-red plates, m. p. 107—108°. An 80% yield of the corresponding 6-*nitro*-2-*aminodiphenylamine*, $C_{12}H_{11}O_2N_3$, is obtained by reducing the dinitro-compound with ammonium sulphide; it crystallises from alcohol in black prisms with a green

reflex, has m. p. 101°, and when finely divided has a dark red colour. With nitrous acid it yields 7-*nitro*-1-*phenyl*-1 : 2 : 3-*benztriazole*,

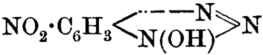


$$NO_2\cdot C_6H_3\left<\begin{array}{c}—N\\NPh\end{array}\right>N,$$

in the form of pale yellow needles, m. p. 152—153°. This latter does not yield a nitrocarbazole when heated (compare Ullmann, Abstr., 1904, i, 776), but when reduced with stannous chloride and concentrated hydrochloric acid in the presence of alcohol yields a mixture of 4-*chloro*-7-*amino*-1-*phenyl*-1 : 2 : 3-*benztriazole* and 7-*amino*-1-*phenyl*-1 : 2 : 3-*benztriazole*. The former crystallises from hot alcohol in pale green needles, m. p. 211°, but the latter could not be obtained in a pure form.

2 : 6-*Diaminodiphenylamine*, $C_6H_3(NH_2)_2\cdot NHPh$, obtained by reducing the dinitro-derivative with iron and dilute hydrochloric acid, crystallises from a mixture of ether and light petroleum in colourless prisms, which turn brown on exposure to the air and have m. p. 178°.

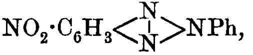
2 : 6-*Dinitrophenylhydrazine*, $C_6H_3(NO_2)_2\cdot NH\cdot NH_2$, crystallises from dilute alcohol in red needles, m. p. 144—145°; the *hydrochloride* crystallises from hot water in brilliant red needles, and with excess of alkali yields salts of 7-nitrobenztriazole, from which the triazole can be obtained by the action of nitric acid.

7-*Nitro*-1-*hydroxybenztriazole*,  $NO_2\cdot C_6H_3\left<\begin{array}{c}——N\\N(OH)\end{array}\right>N$, crystallises from hot water or dilute alcohol in orange-coloured needles, containing $1H_2O$, and decomposing with violence at 229°. 2:6-Dinitrophenylhydrazine condenses with quinones and quinoneoximes in the presence of dilute hydrochloric acid in much the same manner as the isomeric 2 : 4-dinitro-compound (Abstr., 1908, i, 66).

2 : 6-*Dinitro*-4′-*hydroxyazobenzene*, $C_6H_3(NO_2)\cdot N{:}N\cdot C_6H_4\cdot OH$, crystallises from dilute alcohol in brownish-yellow needles, m. p. 172°. p-*Benzoquinoneoxime*-2 : 6-*dinitrophenylhydrazone*,

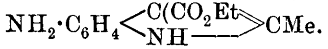
$$C_6H_3(NO_2)_2\cdot NH\cdot N{:}C_6H_4{:}N\cdot OH,$$

forms a brown, crystalline powder decomposing at 230°; it is readily transformed by dilute sodium hydroxide solution into 4 : 4′-*di*(2 : 6-*dinitrobenzeneazo*)-*azoxybenzene*, $ON_2[C_6H_4\cdot N{:}N\cdot C_6H_3(NO_2)_2]_2$, m. p. 255—256°, and is oxidised by a mixture of glacial acetic and nitric acids to 2 : 6 : 4′-*trinitroazobenzene*, $C_6H_3(NO_2)_2\cdot N_2\cdot C_6H_4\cdot NO_2$, which crystallises in slender, reddish-yellow needles, m. p. 168°.

4-*Nitro*-2-*phenyl*-2 : 1 : 3-*benztriazole*,  $NO_2\cdot C_6H_3\left<\begin{array}{c}N\\|\\N\end{array}\right>NPh$, obtained by heating an alcoholic solution of chloro-2 : 6-dinitrobenzene and phenylhydrazine with sodium acetate, crystallises from alcohol in glistening, yellow needles, m. p. 160°. 2 : 6-*Dinitrophenylpyridonium chloride*, $C_6H_3(NO_2)_2\cdot C_5NH_5Cl$, crystallises from alcohol in nearly colourless needles, m. p. 201°.

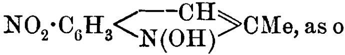
A small amount of 2 : 6 : 2′ : 6′-*tetranitrodiphenyl*, $C_{12}H_6(NO_2)_4$, is formed when chloro-2 : 6-dinitrobenzene is heated with nitrobenzene and copper powder (compare Ullmann and Bielecki, Abstr., 1901, i, 586) It crystallises from glacial acetic acid in slender, yellow needles, m. p. 217—218°. The chief by-product is 2 : 6-dinitrodiphenylamine.

1-Chloro-2 : 6-dinitrobenzene does not react so readily with ethyl sodioacetoacetate as the 2 : 4-isomeride, and in order to complete the reaction, the mixture must be heated for about four days. *Ethyl* 2 : 6-*dinitrophenylacetoacetate*, $C_{12}H_{12}O_7N_2$, crystallises from alcohol in compact, yellow needles, m. p. 90°. Its O-*benzoyl* derivative, $C_{19}H_{16}O_8N_2$, also forms yellow crystals, m. p. 130—131°, and when dissolved in concentrated sulphuric acid and diluted with water, yields 2 : 6-dinitrobenzyl methyl ketone. The ester does not react with ammonia, aniline, or phenylhydrazine, but when reduced with stannous chloride yields *ethyl* 4-*amino*-2-*methylindole*-3-*carboxylate*,



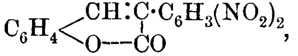
$$NH_2\cdot C_6H_4<\substack{C(CO_2Et)\\ NH}>CMe.$$

This crystallises from alcohol in colourless plates, m. p. 148°, which turn brown on exposure to the air. 2 : 6-*Dinitrobenzyl methyl ketone*, $C_6H_3(NO_2)_2\cdot CH_2\cdot COMe$, crystallises from alcohol in yellow needles, m. p. 106—107°. It does not react with diazonium salts, but forms a *phenylhydrazone*, $C_{15}H_{14}O_4N_4$, in the form of orange-red needles, m. p. 112°, which dissolve in alkalis, yielding deep blue solutions. When reduced with alcoholic ammonium sulphide, the ketone yields 4-*nitro*-1-*hydroxy*-2-*methylindole*,



$NO_2\cdot C_6H_3<\substack{CH\\ N(OH)}>CMe$, as orange-red needles, m. p. 186—187°, which react with sodium methoxide and methyl iodide, yielding the *methyl ether*, $C_{10}H_{10}O_3N_2$, in the form of greenish-yellow needles, m. p. 91—92°.

Ethyl 2 : 6-*dinitrophenylmalonate*, $C_{13}N_{14}O_8N_2$, crystallises from alcohol in compact, yellow needles, m. p. 54—55°, and when hydrolysed with acetic and sulphuric acids yields 2 : 6-*dinitrophenylacetic acid*, $C_6H_3(NO_2)_2\cdot CH_2\cdot CO_2H$, which crystallises from glacial acetic acid in yellow plates, m. p. 201—202° (decomp.). The *methyl* ester, $C_9H_8O_6N_2$, has m. p. 57°, and reacts with salicylaldehyde and a few drops of piperidine at 150°, yielding 2 : 6-*dinitrophenylcoumarin*,

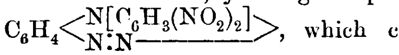


$$C_6H_4<\substack{CH:C\cdot C_6H_3(NO_2)_2\\ O\text{——}CO}\,,$$

as a yellow, crystalline powder, m. p. 233—234°.

1-Chloro-2 : 4-dinitrobenzene reacts with an alcoholic solution of potassium xanthate, yielding Beilstein and Kurbatoff's 2 : 4-dinitrophenyl sulphide (*Annalen*, 1879, **197**, 77). The 2 : 6-isomeride does not react in a similar manner.

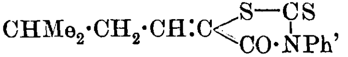
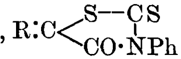
2 : 4-*Dinitrophenyl*-o-*phenylenediamine*, $C_{12}H_{10}O_4N_4$, obtained by the action of an alcoholic solution of *o*-phenylenediamine on chloro-2 : 4-dinitrobenzene, crystallises from alcohol in orange needles, m. p. 150—151°. The *hydrochloride* crystallises in brilliant, yellow plates and reacts with nitrous acid, yielding 1-o:p-*dinitrophenyl*-1 : 2 : 3-*benztriazole*,

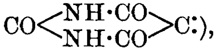


$C_6H_4<\substack{N[C_6H_3(NO_2)_2]\\ N:N}>$, which crystallises from glacial acetic acid in broad, yellow needles, m. p. 186—187°, but cannot be transformed into a carbazole derivative. J. J. S.

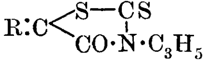
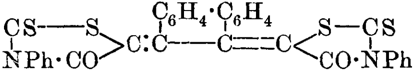
Action of Amidines on Cyanoguanidine. ADRIANO OSTROGOVICH (*Atti R. Accad Lincei*, 1911, [v], **20**, i, 182—186).—When a mixture of cyanoguanidine and acetamidine hydrochloride is gradually heated to 230°, and the temperature maintained at that point for a short time, ammonia is evolved, and on dissolving the reaction product in dilute hydrochloric acid, 4 : 6-diamino-2-methyl-1 : 3 : 5-triazine dihydrochloride (Ostrogovich, *Chem. Zentr.*, 1905, ii, 1360) is obtained. The yield is 65—70% of the theoretical, so that the method is convenient for the preparation of this substance. From benzamidine, 4 : 6-*diamino*-2-*phenyl*-1 : 3 : 5-*triazine* is similarly obtained in about the same yield. It crystallises in small, colourless needles, m. p. 225°, and is identical with the benzoguanamine of Elzanowski (*Diss.*, Freiburg [Switzerland], 1898). It gives a *platinichloride*, which crystallises in pale yellow needles, a *dichromate*, which forms orange-red needles, and a *hydrochloride*, $C_9H_9N_5,HCl,H_2O$, crystallising in lustrous, prismatic needles. The *picrate*, $C_9H_9N_5,C_6H_3O_7N_3$, forms yellow needles, m. p. 255—256°. R. V. S.

Substituted Rhodanic Acids and their Condensation Products with Aldehydes and Ketonic Substances. XI. EGON BUTSCHER (*Monatsh.*, 1911, 32, 9—19).

—Hitherto only the condensation products of substituted rhodanic acids with aromatic aldehydes and with furfuraldehyde have been described. The following substances have now been prepared: 5-*Valerylidene*-3-*phenylrhodanic acid*,  $\mathrm{CHMe_2{\cdot}CH_2{\cdot}CH{:}C}<\begin{array}{l}\mathrm{S—CS}\\ \mathrm{CO{\cdot}NPh}\end{array}$, m. p. 113°, yellow needles, is obtained by heating 3-phenylrhodanic acid and valeraldehyde for two hours in glacial acetic acid. The following compounds have been prepared in a similar manner from alloxan and the substituted rhodanic acids: 5-*Alloxan*-3-*phenylrhodanic acid*,  $\mathrm{R{:}C}<\begin{array}{l}\mathrm{S—CS}\\ \mathrm{CO{\cdot}NPh}\end{array}$ (where R =



$$\mathrm{CO}<\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{array}>\mathrm{C{:}}),$$

decomp. 270—280°, yellow needles. 5-*Alloxan*-3-*allylrhodanic acid*,  $\mathrm{R{:}C}<\begin{array}{l}\mathrm{S—CS}\\ \mathrm{CO{\cdot}N{\cdot}C_3H_5}\end{array}$, m. p. 166° (decomp.), yellow leaflets. 5-*Alloxan*-3-*methylrhodanic acid*, $C_8H_5O_4N_3S_2$, decomp. 220—225°, yellow needles. 5-*Alloxan*-3-p-*tolylrhodanic acid*, $C_{14}H_9O_4N_3S_2$, m. p. 270° (decomp.), microscopic, yellow needles. 5 : 5'-*Phenanthrenebis*-3-*phenylrhodanic acid*,  $\begin{array}{l}\mathrm{CS—S}\\ \mathrm{NPh{\cdot}CO}\end{array}>\mathrm{C{:}}\overset{\mathrm{C_6H_4{\cdot}}}{\mathrm{C}}—\overset{\mathrm{C_6H_4}}{\mathrm{C}}\mathrm{{=}C}<\begin{array}{l}\mathrm{S—CS}\\ \mathrm{CO{\cdot}NPh}\end{array}$, m. p. 291—292°, is obtained from phenanthraquinone and 3-phenylrhodanic acid (2 mols.) in hot glacial acetic acid; a *substance*, $C_{24}H_{18}O_2N_2S_4$, m. p. 216—218°, of similar constitution is obtained from 3-ethylrhodanic acid.

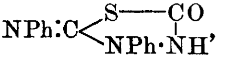
When 5-*p*-methoxybenzylidene-3-phenylrhodanic acid is hydrolysed by boiling baryta, the expected α-thiol-*p*-methoxycinnamic acid is obtained in the form of the corresponding *disulphide*,

$$[\mathrm{OMe{\cdot}C_6H_4{\cdot}CH{:}C(CO_2H)}]_2\mathrm{S_2},$$

m. p. 202—203°. In another experiment in which the hydrolysis was effected by alcoholic potassium hydroxide, the mercaptan was

isolated as its *benzyl* derivative,
$\mathrm{OMe{\cdot}C_6H_4{\cdot}CH{:}C(CO_2H){\cdot}S{\cdot}C_7H_7}$,
m. p. 131—134°. C. S.

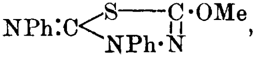
Intramolecular Changes. MAX BUSCH and OTTO LIMPACH (*Ber.*, 1911, **44**, 560—583).—Of the two isomeric substances obtained by the interaction of carbonyl chloride and $\beta\delta$-diphenylthiosemicarbazide (Marckwald and Sedlaczek (Abstr., 1896, i, 231), the labile, more fusible compound was shown by Busch, Reinhardt, and Limpach (Abstr., 1910, i, 142) to be 5-thio-*n*-1 : 4-diphenylurazole, and the stable isomeride to be 5-thiol-1 : 4-diphenyl*endo*oxydihydrotriazole. The latter still retains its constitution, but the labile compound, which is more conveniently obtained by the action of an excess of 20% carbonyl chloride in toluene on a benzene solution of $\beta\delta$-diphenylthiosemicarbazide at 60—70° (the two isomerides are separated as described, *loc. cit.*), is proved to be 3-*phenyl*-1 : 3 : 4-*thiodiazole*-5-*one*-2-*anil*,



$$\mathrm{NPh{:}C}\Big<\begin{matrix}\mathrm{S}\text{———}\mathrm{CO}\\ \mathrm{NPh}\cdot\mathrm{NH}\end{matrix},$$

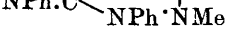
by the evidence quoted below. It reacts with phenylhydrazine or primary bases, yielding two products, one of which does not contain sulphur. Thus, with aniline on the water-bath, $\alpha\delta$-diphenylsemicarbazide and thiocarbanilide are formed, whilst with phenylhydrazine (2 mols.) the labile compound yields $\alpha\delta$-diphenylthiosemicarbazide and diphenylcarbazide. This facile fission of the ring suggests that the labile compound cannot be a urazole derivative, since true urazoles, such as 1-phenylurazole, 1 : 4-diphenylurazole, and 1 : 4-diphenyl-2-methylurazole, are stable to aniline or phenylhydrazine even at 150°. (5-Triol-1 : 4-diphenyl*endo*oxydihydrotriazole, the stable isomeride, is not attacked by boiling aniline.)

The key to the constitution of the labile compound is obtained by the behaviour of the substance on methylation. When heated with methyl iodide, it yields methyl mercaptan and 1 : 4-diphenyl-2-methylurazole, amongst other products. When kept overnight in contact with an excess of methyl sulphate, however, it yields two products, neither of which contains the group ·SMe. The by-product, m. p. 77—78°, is 5-*methoxy*-3-*phenyl*-1 : 3 : 4-*thiodiazole*-2-*anil*,



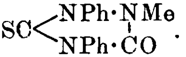
$$\mathrm{NPh{:}C}\Big<\begin{matrix}\mathrm{S}\text{———}\mathrm{C{\cdot}OMe}\\ \mathrm{NPh}\cdot\mathrm{N}\end{matrix},$$

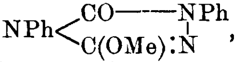
has basic properties, gives a quantitative yield of methyl iodide by Zeisel's method, and is probably identical with the methyl compound, m. p. 74·5—75·5°, obtained by Nirdlinger and Acree (Abstr., 1910, i, 785). The chief product of the methylation has m. p. 92°, is decomposed profoundly by hydriodic acid, and reacts with primary bases even more vigorously than its parent substance. It is decomposed by boiling 8% alcoholic potassium hydroxide, yielding $\beta\delta$-*diphenyl*-α-*methylthiosemicarbazide*, $\mathrm{NHMe{\cdot}NPh{\cdot}CS{\cdot}NHPh}$, m. p. 138°, which is transformed at 150° into the β-isomeride, $\mathrm{NHPh{\cdot}NMe{\cdot}CS{\cdot}NHPh}$, m. p. 176—177°, obtained by Marckwald. The formation of $\beta\delta$-diphenyl-α-methylthiosemicarbazide from the methylated product, m. p. 92°, proves that the latter must be either



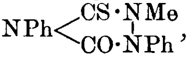
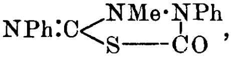
$$\mathrm{NPh{:}C}\Big<\begin{matrix}\mathrm{S}\text{———}\mathrm{CO}\\ \mathrm{NPh}\cdot\mathrm{NMe}\end{matrix}$$

or

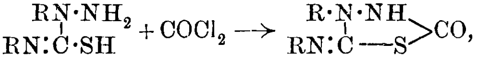
 $\mathrm{SC}<\begin{array}{l}\mathrm{NPh\cdot NMe}\\ \mathrm{NPh\cdot CO}\end{array}$. The latter constitution does not harmonise with the pronounced basic character of the substance, whilst the former is supported by the formation of the compound from carbonyl chloride and $\beta\delta$-diphenyl-α-methylthiosemicarbazide in benzene at 50—60°. The proof that the substance, m. p. 92°, has the former constitution is obtained by carefully heating the compound with alcoholic ammonia or potassium hydroxide; by this means it is converted into an *isomeride*, m. p. 165°, which has no basic properties and is easily desulphurised by mercuric oxide and benzene at 140—150°, yielding 1 : 4-diphenyl-2-methylurazole. Consequently the isomeride, m. p. 165°, has the latter of the two constitutions given above, the methylated product, m. p. 92°, has the former constitution, and, finally, therefore, the parent substance, the labile compound, formerly regarded as 1 : 4-diphenyl-5-thiourazole, must be 3-phenyl-1 : 3 : 4-thiodiazolone-2-anil, as mentioned above.

1 : 4-Diphenyl-2-methylurazole is conveniently obtained by warming 5-thiol-1 : 4-diphenyl*endo*oxydihydrotriazole with an excess of methyl sulphate and treating the product, still in the presence of methyl sulphate, with dilute sodium hydroxide; by the elimination of methyl mercaptan and the simultaneous entrance of a methyl group, 1 : 4-diphenyl-2-methylurazole is formed, together with a small quantity of 3-*methoxy*-1 : 4-*diphenyl*-1 : 2 : 4-*triazolone*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CO{-\!-\!-}NPh}\\ \mathrm{C(OMe){:}N}\end{array}$, m. p. 110—111°. The latter is stable to alcoholic alkalis, whilst 1 : 4-diphenyl-2-methylurazole is converted by 10% alcoholic potassium hydroxide into a mixture of approximately equal quantities of $\alpha\delta$-*diphenyl*-β-*methylsemicarbazide*, NHPh·CO·NMe·NHPh, m. p. 138° (which, like other members of the β-series, does not possess basic properties), and $\beta\delta$-*diphenyl*-α-*methylsemicarbazide*,

NHPh·CO·NPh·NHMe,

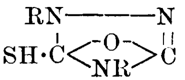
m. p. 140°. The attempt to prepare 5-thio-1 : 4-diphenyl-2-methylurazole from either of these compounds and thiophosphoryl chloride failed altogether with the β-compound. $\beta\delta$-Diphenyl-α-methylsemicarbazide and thiophosphoryl chloride in benzene solution, however, yield the *thiocarbonyl chloride*, NHPh·CO·NPh·NMe·CS·Cl, which loses hydrogen chloride at its m. p., 150°, and forms 3-*thion*-1 : 4-*diphenyl*-2-*methylurazole*,  $\mathrm{NPh}<\begin{array}{l}\mathrm{CS\cdot NMe}\\ \mathrm{CO\cdot NPh}\end{array}$, m. p. 165·5°. This substance, which yields 1 : 4-diphenyl-2-methylurazole by desulphurisation by mercuric oxide and alcohol, is also obtained by the action of alcoholic ammonia on 3-*phenyl*-4-*methyl*-1 : 3 : 4-*thiodiazolone*-5-*anil*,  $\mathrm{NPh{:}C}<\begin{array}{l}\mathrm{NMe\cdot NPh}\\ \mathrm{S{-\!-\!-}CO}\end{array}$, m. p. 102°, prepared by the interaction of carbonyl chloride and $\alpha\delta$-diphenyl-β-methylthiosemicarbazide in the same manner as 3-phenylthiodiazolone-5-anil from carbonyl chloride and $\beta\delta$-diphenylthiosemicarbazide.

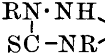
The preceding facts leave no doubt as to the course of the reaction between carbonyl chloride and $\beta\delta$-dialkylthiosemicarbazides. The labile compound first formed is a thiodiazoloneanil,

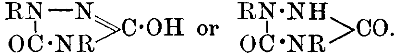


$$\begin{array}{l}RN\cdot NH_2\\ RN{:}C\cdot SH\end{array} + COCl_2 \rightarrow \begin{array}{l}R\cdot N\cdot NH\\ RN{:}C—S\end{array}\!\!>\!CO,$$

which is easily converted (by fusion or in alcoholic solution) into the stable thiol*endo*oxydihydrotriazole (annexed



formula), the thiourazole,  $\begin{array}{l}RN\cdot NH\\ SC-NR\end{array}\!\!>\!CO$, being an intermediate product. By desulphurisation the thiol*endo*oxydihydrotriazole regenerates the urazole ring,



$$\begin{array}{l}RN—N\\ OC\cdot NR\end{array}\!\!>\!C\cdot OH \text{ or } \begin{array}{l}RN\cdot NH\\ OC\cdot NR\end{array}\!\!>\!CO.$$

The authors deny that the interconversion of the salts of 5-thiol-1 : 4-diphenylurazole (*endo*oxy-5-thiol-1 : 4-diphenyldihydrotriazole) and 5-thion-1 : 4-diphenylurazole (3-phenyl-1 : 3 : 4-thiodiazolone-5-anil) is a reversible process, as stated by Nirdlinger and Acree (*loc. cit.*); they show that the change only proceeds in the direction, thiodiazolone ⟶ thioltriazole, and in aqueous solution is completed in twelve hours at 100° and in thirty-six hours at 80°. C. S.

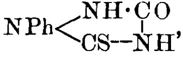
Derivatives of Hydrazodicarbonamide and of Urazole. Guido Pellizzari (*Gazzetta*, 1911, **41**, i. 30—38. Compare Abstr., 1907, i, 874).—[With L. Accame.]—From aminophenylcarbamide and potassium cyanate in aqueous solution in the presence of acetic acid, *phenylhydrazodicarbonamide*, $NH_2\cdot CO\cdot NPh\cdot NH\cdot CO\cdot NH_2$, is obtained as a colourless, crystalline precipitate, m. p. 221° (decomp.). When heated at its melting point the compound yields phenylurazole. The preparation of *phenylhydrazo-β-thiodicarbonamide*,

$$NH_2\cdot CO\cdot NPh\cdot NH\cdot CS\cdot NH_2,$$

is effected by mixing in alcoholic solution aminophenylcarbamide, hydrochloric acid, and ammonium thiocyanate. The precipitate of ammonium chloride is filtered off, and the liquid is boiled for three hours. The precipitate so obtained forms after recrystallisation colourless crystals, m. p. 235° (decomp.).

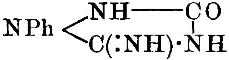
[With A. Laria-Botte.]—*Phenylhydrazo-a-thiodicarbonamide*,

$$NH_2\cdot CS\cdot NPh\cdot NH\cdot CO\cdot NH_2,$$

is prepared from aminophenylthiocarbamide and potassium cyanate in the presence of hydrochloric acid, and forms lustrous crystals, m. p. 213° (decomp.). A sample when heated began to evolve ammonia at 190°, and the evolution increased at 210°, at which temperature the substance was maintained for half an hour. From the product obtained on cooling, 1-*phenyl*-5-*thiourazole*,  $NPh<\begin{array}{l}NH\cdot CO\\ CS—NH\end{array}$, was isolated. It forms very small, yellowish-white crystals, m.p. 227—230°. Attempts to obtain the substance from carbamide and aminophenylthiocarbamide yielded only resinous products.

When aminophenylthiocarbamide is boiled in alcoholic solution for several hours, it is transformed into phenylsemithiocarbazide. The change can be explained on the lines of the well-known transformations of carbamide and thiocarbamide on heating.

The preparation of a salt of aminophenylguanidine is more easily effected by the interaction of cyanamide and phenylhydrazine hydrobromide than by the method formerly given (Abstr., 1897, i, 47), because the hydrobromides of the two products can be separated by crystallisation. Phenylaminoguanidine *hydrobromide* is recrystallised from water containing hydrobromic acid, and forms slightly coloured, small needles, m. p. 210°. Aminophenylguanidine *hydrobromide* crystallises in hexagonal tablets, m. p. 219°, and is more soluble in water than its isomeride, but less soluble in alcohol.

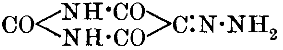
From aminophenylguanidine hydrobromide and potassium cyanate or thiocyanate no product could be prepared, and even with cyanamide the introduction of a second guanidine group could not be effected. When aminophenylguanidine hydrobromide and carbamide are heated together at 200° for half an hour, however, 5-*imino*-1-*phenylurazole*,  $\mathrm{NPh}\Big\langle\begin{array}{l}\mathrm{NH{-}{-}CO}\\ \mathrm{C(:NH)\cdot NH}\end{array}$, is obtained. It forms long, lustrous needles, m. p. 272—273° (decomp.), and is soluble in ammonia. From this solution it is precipitated by acetic acid, but it is soluble in dilute hydrochloric acid. From the mother liquors from its preparation a *substance*, m. p. towards 235—240°, was also isolated. R. V. S.

Condensations of Hydrazoic Acid with Cyanoformic Ester and with Cyanogen Bromide. III. E. OLIVERI-MANDALÀ (*Gazzetta*, 1911, 41, i, 59—63. Compare Abstr., 1910, i, 593).—Ethyl cyanoformate and a concentrated ethereal solution of hydrazoic acid when heated together under pressure for several days at 50° yield in small quantity ethyl tetrazolecarboxylate, $CN_4H\cdot CO_2Et$, which crystallises in small needles, m. p. 85—86° (previously softening). The substance has an acid reaction. When it is warmed with alcoholic potassium hydroxide, a substance is deposited, probably the potassium salt, which on addition of acid forms tetrazole.

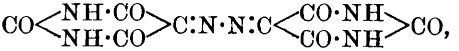
Cyanogen bromide and hydrazoic acid under similar conditions yield bromotetrazole, CN_4HBr, also in small amount. The substance after previously softening has m. p. 147—148° (decomp.). It has a strongly acid reaction, and does not lose bromine when treated with acids or with dilute alkalis. In the air, and especially in sunlight, it becomes yellow. R. V. S.

Some Derivatives of Alloxan. GUIDO PELLIZZARI and C. CANTONI (*Gazzetta*, 1911, 41, i, 21—29. Compare Abstr., 1887, 1100; 1889, 519).—Alloxanphenylhydrazone can be obtained directly from alloxan by the use of phenylhydrazine hydrogen sulphite. The preparation is effected by saturating with sulphur dioxide an aqueous solution of alloxan in which phenylhydrazine is suspended.

Hydrazine hydrogen sulphite, under similar conditions, yields, in the cold, *alloxan bisulphite*, which forms colourless crystals. When it is boiled with water a reddish-yellow *substance* is formed, which is also obtained in addition to alloxantin when alloxan reacts with hydrazine hydrate at the ordinary temperature. The slight solubility of the substance, its acid character, and the fact that it does not react with benzaldehyde accord with the formula (I),

(I.) 

$$\mathrm{CO}{<}\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}{>}\mathrm{C{:}N\cdot NH_2}$$

(II.) 

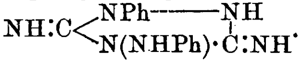
$$\mathrm{CO}{<}\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{NH\cdot CO}\end{matrix}{>}\mathrm{C{:}N\cdot N{:}C}{<}\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}{>}\mathrm{CO},$$

but the analytical figures agree with formula (II), which is, therefore, preferred by the authors.

Efforts have also been made to obtain substances of aldehydic nature by the action of alkalis or acids on phenylmethylpyrazolonealloxan in a manner similar to that which has been described in the case of other alloxan derivatives (compare Böhringer and Söhne, D.R.-P. 108026 [1898], 112174 [1899]). In no case was an aldehyde produced, and the formation of carbon monoxide or formic acid (which would accompany it) was not observed. When phenylmethylpyrazolonealloxan is boiled with hydrochloric acid (D 1·12, diluted with an equal volume of water), phenylmethylpyrazolonemalonylcarbamide (Abstr., 1889, 517) is first formed. This decomposes when the ebullition is continued, and a *hydrochloride* is obtained, of which the free *base* has m. p. 175—180°; phenylhydrazine oxalate and phenylmethylpyrazolone are also produced. R. V. S.

Action of Cyanogen Halides on Phenylhydrazine. III.

GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, i, 54—59. Compare Abstr., 1892, 1323; 1907, i, 873).—Another substance can be isolated from the mother liquors of the products of the reaction between phenylhydrazine and cyanogen bromide in aqueous solution. It forms transparent crystals of a reddish tinge, which contain alcohol of crystallisation, and have m. p. 180°. The compound is identical with that described in the first paper, resulting from the polymerisation of β-cyanophenylhydrazide, but since it is stable towards alkali and acid, it has not the constitution there assigned to it, but is the corresponding cyclic compound, *diphenylaminoguanazole*,



$$\mathrm{NH{:}C}{<}\begin{array}{l}\mathrm{NPh}\text{———}\mathrm{NH}\\ \mathrm{N(NHPh)\cdot C{:}NH}\end{array}.$$

The *hydrochloride* and *picrate* have the properties formerly described.

α-Cyanophenylhydrazide reacts with cyanogen bromide in alcoholic solution at the ordinary temperature in the course of several days, forming *tricyanophenylhydrazide*, to which the constitution

$$\mathrm{CN\cdot NPh\cdot N(CN)_2}$$

is provisionally given. It is a crystalline substance having a red or yellow tinge, and does not melt at 300°. The molecular weight in phenolic solution is normal. R. V. S.

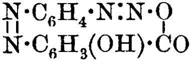
Peculiar Reactions of the Diazo-compound of *p*-Aminobenzeneazosalicylic Acid.

CARL BÜLOW [with KARL HAAS] (*Ber.*, 1911, **44**, 601—614).—Previously the author has observed that diazo-salts of certain substances containing the *p*-aminobenzeneazo-group yield intensely blue solutions by treatment with sufficient sodium carbonate or acetate. The source of this blue coloration has now been investigated in the case of the diazo-compound of *p*-aminobenzeneazosalicylic acid.

p-Acetylaminobenzeneazosalicylic acid,

$NHAc\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H$,

yellowish-brown prisms, m. p. 235°, obtained by coupling diazotised acetyl-*p*-phenylenediamine and salicylic acid in a solution containing sodium carbonate and hydroxide and acidifying the product, is hydrolysed best by concentrated sulphuric acid on the water-bath; the solution yields, after dilution with water, a *sulphate*, $(C_{13}H_{11}O_3N_3)_2,H_2SO_4$, from which sodium carbonate produces a sodium salt, which is decomposed by acetic acid, yielding p-*aminobenzeneazosalicylic acid*, a dirty, greyish-green powder, decomp. 232°. The aminoazo-compound is dissolved in dilute potassium hydroxide, treated with hydrochloric acid, and finally with sodium nitrite at 20—25°, whereby the *chloride* of the diazotised *p*-aminobenzeneazosalicylic acid is obtained in small, brick-red needles. By stirring a suspension of the chloride in cold water for four hours, a black *anhydride*, exploding at 132°, is obtained, to which the constitution



$$\begin{array}{l}N\cdot C_6H_4\cdot N\colon N\cdot O\\ \|\qquad\qquad\qquad\ |\\ N\cdot C_6H_3(OH)\cdot CO\end{array}$$

is ascribed.

When the diazo-chloride is added to an excess of aqueous sodium carbonate (not hydrogen carbonate, acetate, or hydroxide) at 0°, an intense blue solution is obtained, the colour of which persists for more than two hours and then becomes brown. By passing carbon dioxide into the blue solution, the colour changes to yellow; both solutions couple with *R*-salt. When the diazo-chloride is dissolved in dilute sodium hydroxide at 0° a blue solution is not obtained, but by passing in carbon dioxide the solution becomes blue, and finally yellow. These colour changes are explained by ascribing the blue coloration to the formation of the normal diazotate,

$ONa\cdot N\colon N\cdot C_6H_4\cdot N\colon N\cdot C_6H_3(OH)\cdot CO_2Na$,

and the yellow to the hydroxy-compound,

$OH\cdot N\colon N\cdot C_6H_4\cdot N\colon N\cdot C_6H_3(OH)\cdot CO_2Na$;

in sodium hydroxide the normal diazotate adds on NaOH to form

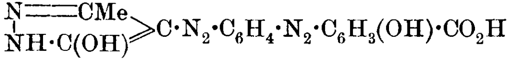
$ONa\cdot N(OH)\cdot NNa\cdot C_6H_4\cdot N\colon N\cdot C_6H_3(ONa)\cdot CO_2Na$,

which is converted by carbon dioxide successively into the blue and the yellow compounds.

*Ethyl acetoacetate-azobenzene-*p*-azosalicyclic acid,*

$CO_2Et\cdot CHAc\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H$,

m. p. 236° (decomp.), yellowish-brown needles, obtained by condensing the diazo-chloride of *p*-aminobenzeneazosalicylic acid with ethyl acetoacetate in dilute alcohol in the presence of sodium acetate, has been converted into the following substances. With 60% hydrazine hydrate in glacial acetic acid, it yields 5-*hydroxy*-3-*methylpyrazole*-4-*azobenzene*-4′-p-*azosalicylic acid*,



$$\left.\begin{array}{l}N{=\!=\!=}CMe\\ |\\ NH\cdot C(OH)\end{array}\right\rangle C\cdot N_2\cdot C_6H_4\cdot N_2\cdot C_6H_3(OH)\cdot CO_2H,$$

m. p. above 300°. With phenylhydrazine in hot glacial acetic acid it yields 5-*hydroxy*-1-*phenyl*-3-*methylpyrazole*-4-*azobenzene*-4′-p-*azosalicylic acid*, $C_{23}H_{18}O_4N_6$, m. p. 272—273° (decomp.). With 2:4-dinitrophenylhydrazine, it yields a *dinitrophenylhydrazone*, $C_{25}H_{22}O_9N_8$, m. p. 252—253° (decomp.), which is converted by hot acetic anhydride into *5-hydroxy-1-o*: p-*dinitrophenyl-3-methylpyrazole-4-azobenzene-4'*-p-*azosalicylic acid*, $C_{23}H_{16}O_8N_8$, m. p. 202—203°. With hydroxylamine in diluted acetic acid it yields *5-hydroxy-3-methyl*iso*oxazole-4-azobenzene-4'*-p-*azosalicylic acid*, m. p. 243—244°. By prolonged boiling with semicarbazide in diluted acetic acid, it yields *5-hydroxy-1-carbamido-3-methylpyrazole-4-azobenzene-4'*-p-*azosalicylic acid*,

$$C_{18}H_{15}O_5N_7,$$

m. p. above 280°. The colour reactions of these substances with various reagents are described. C. S.

Some Derivatives of *p*-Aminobenzhydrol. HENRY A. TORREY and C. W. PORTER (*J. Amer. Chem. Soc.*, 1911, **33**, 56—59).—The work described in this paper was carried out as part of an extensive investigation of the derivatives of *p*-aminobenzophenone.

Benzhydrol-4-azo-β-naphthol, $OH\cdot CHPh\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 169·5°, is a bright red dye, which is precipitated when a solution of β-naphthol in sodium hydroxide is added to the diazotisation product of *p*-aminobenzhydrol. The *compound*, $C_6H_5\cdot CO\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 185—186·5°, obtained in a similar manner from *p*-aminobenzophenone, is a dye of a much lighter red colour, and forms feathery crystals.

Benzhydrol-4-azodimethylaniline, $OH\cdot CHPh\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$, m. p. 145°, is a dye, which forms red, lustrous flakes; its *acetyl* and *benzoyl* derivatives were prepared.

Salicylidene-p-*aminobenzhydrol*, $OH\cdot CHPh\cdot C_6H_4\cdot N:CH\cdot C_6H_4\cdot OH$, m. p. 76—79°, obtained by heating a solution of *p*-aminobenzhydrol and salicylaldehyde in alcohol, forms yellow crystals. *Salicylidene*-p-*aminobenzophenone*, $C_6H_5\cdot CO\cdot C_6H_4\cdot N:CH\cdot C_6H_4\cdot OH$, is a yellow, crystalline solid, which is insoluble in solution of sodium hydroxide.

β-Naphtholaldehyde condenses with *p*-aminobenzhydrol to form the *compound*, $OH\cdot CHPh\cdot C_6H_4\cdot N:CH\cdot C_{10}H_6\cdot OH$, m. p. 167·5°, which is obtained in yellow crystals. The corresponding *compound*,

$$C_6H_5\cdot CO\cdot C_6H_4\cdot N:CH\cdot C_{10}H_6\cdot OH,$$

m. p. 152°, obtained from *p*-aminobenzophenone, also forms yellow crystals. E. G.

The Stability towards Light of Methylated Hydroxyazo-dyes. Some Derivatives of 1-Methoxynaphthalene. N. N. VOROSCHCOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1458—1465).—The introduction of an alkyl group into the hydroxy-group of a hydroxyazo-dye might be expected to result in an increase of the stability towards light, since the hydroxy-group is the most highly reactive of the molecule, and since replacement of its hydrogen by a metal is, in general, accompanied by increase of this stability.

Examination of the methoxy-derivatives corresponding with a number of hydroxyazonaphthalenesulphonic acids, prepared by Colombano's method (Abstr., 1907, i, 1091), shows, however, that the stability of these colouring matters towards light is not increased by the replacement of the hydroxy- by methoxy-groups.

Reduction of 1-sulphonaphthalene-4-azoanisole by means of zinc and acetic acid yields *p*-anisidine, which was identified through its acetyl derivative. In a similar manner, colouring matters containing the 1-methoxynaphthalene group may be converted into 4-*acetylamino*-1-*methoxynaphthalene*, $OMe\cdot C_{10}H_6\cdot NHAc$, which forms colourless prisms, m. p. 180—181°, and may also be prepared by reducing 4-nitro-1-methoxynaphthalene and subsequently acetylating.

Sodium 1-*methoxynaphthalene*-4-*sulphonate*, $OMe\cdot C_{10}H_6\cdot SO_3Na$, prepared by treating α-naphthol-4-sulphonic acid with methyl sulphate and sodium hydroxide, forms shining plates containing $3H_2O$, and the corresponding barium salt forms nacreous crystals.

4-*Nitro*-1-*methoxynaphthalene*, $OMe\cdot C_{10}H_6\cdot NO_2$, obtained by adding a mixture of sodium 1-methoxynaphthalene-4-sulphonate and sodium hydrogen carbonate to a solution of carbamide in nitric acid, forms yellow needles, m. p. 81°. T. H. P.

Azo-derivatives of 3-Phenyl*iso*oxazolone. ANDRÉ MEYER (*Compt. rend.*, 1911, **152**, 610—612. Compare Abstr., 1910, i, 593). —The following derivatives of Claisen's 4-benzeneazo-3-phenyl*iso*oxazolone (Abstr., 1891, 468) were prepared by dissolving phenyl*iso*oxazolone in aqueous alkali and sodium acetate, and adding the calculated amount of a diazonium salt. The required compound was obtained in theoretical yield by precipitation with acetic acid. All the substances described melt with decomposition.

4-m-*Nitrobenzeneazo*-3-*phenyl*isoo*xazolone*, $C_{15}H_{10}O_4N_4$, bright yellow needles, m. p. 200—201°; the p-*nitro*-compound crystallises in orange needles, m, p. 224—225°.

4-o-*Tolueneazo*-3-*phenyl*isoo*xazolone*, $C_{16}H_{13}O_2N_3$, orange needles, m. p. 151—152°; the p-*toluene* derivative has m. p. 177—178°. The m-*nitro*-p-*toluene* compound has m. p. 205—206°; the o-*nitro*-p-*toluene* compound forms deep orange needles, m. p. 213—214°. 4-m-*Xyleneazo*-3-*phenyl*isoo*xazolone*, $C_{17}H_{15}O_2N_3$, orange needles, m. p. 187°. 4-ψ-*Cumeneazo*-3-*phenyl*isoo*xazolone*, bright red needles, m. p. 215—216°. 4-α-*Naphthaleneazo*-3-*phenyl*isoo*xazolone*, $C_{19}H_{13}O_2N_3$, slender, brown needles, m. p. 172—173°; the β-derivative forms deep yellow needles, m. p. 202—203°. 4-o-*Carboxybenzeneazo*-3-*phenyl*isoo*xazolone*,

$$C_{16}H_{11}O_4N_3,$$

bright yellow needles, m. p. about 245°; the m-*carboxy-acid* has m. p. about 260°, and the p-*carboxyl acid*, m. p. about 290°. *Phenyldimethylpyrazoloneazophenyl*isoo*xazolone*, $C_{20}H_{17}O_3N_5$, ruby-red needles, m. p. 196—197°. *Diphenylbisazobisphenyl*isoo*xazolone*, $C_{30}H_{20}O_4N_6$, is a brick-red powder, m. p. above 300°. W. O. W.

The Refractive Indices of Certain Proteins. III. Serum Globulin. IV. Casein in Alcohol–Water Mixtures. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1910, **8**, 441—448, 507—511. Compare Abstr., 1910, i, 526, 793).—The value of *a* for serum globulin under different conditions varies from 0·00229 to 0·00119, and for casein from 0·00157 to 0·00125. W. D. H.

Hydrolysis of the Protein of Linseed. F. W. FOREMAN (*J. Agric. Science*, 1911, **3**, 358—382; *Proc. Camb. Phil. Soc.*, 1911, **16**, 87—88).—The protein of linseed meal, extracted with 0·2% potassium hydroxide, contains 17·45% nitrogen. When hydrolysed with hydrochloric acid (D 1·16), the following substances were obtained: alanine, 1·03; valine, 12·71; leucine and *iso*leucine, 3·97; proline, 2·85; phenylalanine, 4·14; aspartic acid, 1·65; glutamic acid, 11·58; tyrosine, 0·65; arginine, 6·06; histidine, 1·66; lysine, 1·19; and ammonia, 1·94%. Small amounts of glycine, serine, and tryptophan were also found.

The most striking result is the high amount of valine; the highest percentage hitherto obtained by the hydrolysis of proteins seems to be only 2%. N. H. J. M.

Thymic Acid. HERMANN STEUDEL and P. BRIGL (*Zeitsch. physiol. Chem.*, 1910, **70**, 398—403).—By the action of dilute nitric acid in the cold on thymus-nucleic acid, the alloxuric bases are eliminated and a compound, $C_{33}H_{51}O_{31}N_5P_4$, remains, for which the name *thymic acid* is suggested. This contains all the phosphoric acid of nucleic acid in an organic complex, is dextrorotatory, and forms a barium salt. It does not reduce Fehling's solution after purification. When hydrolysed, it yields thymin and uracil in the proportions required by the formula given. E. F. A.

The Action of Dilute Acids and Salt Solutions on Gelatin. HENRY R. PROCTER (*Koll. Chem. Beihefte*, 1911, **2**, 243—284).—The action of solutions on the connective tissue is complicated by their capillary absorption between the fibres of collagen, of which it mainly consists. To avoid this difficulty, the author has studied the action of solutions or thin sheets of gelatin, which is a chemically closely related substance. In opposition to the view that gelatin jelly has ordinarily the microscopic cellular structure attributed to it by Bütschli and van Bemmelen, normal jelly is considered to be a network of protein molecules, in which the absorbed liquid is dissolved and subjected to its molecular attractions and internal pressure. The swelling of gelatin is thus an osmotic phenomenon, which, however, is influenced not only by the presence of altered products formed by hydrolysis, but also by the solid elasticity dependent on its volume at the moment of solidification.

Gelatin jelly is insoluble in alcohol, and semipermeable to it, and its dehydration is due to the external osmotic pressure of the alcohol. If, however, alcohol is incorporated with gelatin solution before "setting," it forms a mixture, which, although apparently homogeneous, must really be an emulsion of diluted alcohol. Such a jelly swells in water more than a purely aqueous one, since the alcohol globules become diluted in equilibrium with the jelly. Such jellies would probably show microscopic cellular structure.

Swelling with acids is a more complex phenomenon, and apparently involves chemical combination as well as osmotic action. Gelatin, which absorbs only seven or eight times its weight of pure water, may absorb over fifty times its weight of 0·005*N*-hydrochloric acid solution, but it contracts again when the acid solution is concentrated, absorbing only twenty times its weight of 0·2*N*-acid. In more concentrated solutions the jelly dissolves.

The amount of acid in the jelly increases with that in the outer solution, and is always in excess of that corresponding with the solution absorbed. Since only a portion of the absorbed acid can be estimated by titration with methyl-orange as indicator, it is evident that part of the acid is in some way combined. Assuming that the concentration of the free acid in the absorbed solution is the same as that in the outer solution, and deducting this from the total acid in the jelly, it is found that the acid "fixed" by 1 gram of dry gelatin increases rapidly up to a concentration of about $0·005N$-acid, and afterwards remains nearly constant. This constant value corresponds with about 0·78 mg. mol. of acid per gram of gelatin.

In hydrochloric acid solutions of greater concentration than $0·005N$, the swelling is repressed by increasing the concentration of the chlorine ion. By addition of sodium chloride, this repression can be carried almost to dehydration, although neutral gelatin is swollen by salt solutions. The total acid in the contracted jelly is diminished by that expelled, but the "fixed" acid is increased, and sodium chloride is expelled from the solution absorbed. The effect is evidently due to osmotic forces, although, since both hydrogen and sodium chlorides and their ions diffuse freely through gelatin, the condition of equilibrium would appear to resemble that which is set up in the distribution of a substance between immiscible solvents.

It is assumed that the amphoteric gelatin forms a hydrolysable chloride in equilibrium with the acid having a much greater affinity for water than for neutral gelatin. If x is the molar concentration of the external acid, β the number of millimols. in the jelly per gram of gelatin, and k the hydrolytic constant, then $\beta = x/x + k$ is the proportion of unhydrolysed salt. Taking β as 1·28 and k as 0·005, a curve representing the values of fixed acid is obtained, which corresponds closely with the experimental curve when the swelling is repressed by large quantities of sodium chloride, although it is higher than the experimental curve in the absence of salt. The assumption that the free acid in the absorbed solution is of the same concentration as the outer solution is, however, not strictly permissible, for the chlorine ion concentration in the ionised gelatin chloride must be equal to that of the outer solution, and since the gelatin ion cannot diffuse, this equality can only result from the expulsion of water and acid.

The experimental curve of swelling can be represented by the expression $7·8\sqrt{x/x+k}$, and the curve of total acid absorbed by $(7·8x^{\frac{1}{2}}/x+k)+0·8$, or by the adsorption formula $\eta = 87x^{0·41}$. If the hydrolytic constant k be taken as 0·005, the ionisation constant of neutral gelatin is of the order of 1×10^{-12}.

Similar considerations to the above are applicable to the equilibrium between gelatin and solutions of weak acids and their salts, data for which are also recorded in the paper. H. M. D.

Trypsin and Pancreas Nucleo-protein. Leonor Michaelis and Heinrich Davidsohn (*Biochem. Zeitsch.*, 1911, **30**, 481—504).—The isoelectric point of trypsin was determined by two methods, namely, by dissolving the trypsin in solutions with different hydrogen ion concentrations and determining the range of concentration in which it is neither distinctly anodic or cathodic when in an electric field (method of electrocataphoresis), and by determining the hydrogen ion concentration in which aggregation most readily takes place. In the former experiment a silver anode in concentrated sodium chloride, and, as cathode, copper wire and a moderately concentrated cupric chloride solution were employed. By the first of the above-mentioned methods, the isoelectric point was found to be about $H=1\cdot35\times10^{-4}$, and by the second, $2\cdot6\times10^{-4}$. This is almost the same as the isoelectric point found for Hammarsten's α-nucleo-protein, and differs considerably from that of the β-nucleo-protein ($H=1\cdot2\times10^{-3}$), and of the protein which can be obtained from this ($H=1\cdot7\times10^{-5}$). Furthermore, no organ other than the pancreas yields a substance of the same isoelectric point. If trypsin be aggregated from its solution under the optimal conditions, a strong trypsin preparation is obtained, as the greater part of the enzyme is carried down in the precipitate, which does not give the normal protein reactions. From the results, the authors conclude that there is probably an intimate chemical relationship between trypsin and α-nucleo-protein. S. B. S.

Optically Active Compounds of Phosphorus. JAKOB MEISENHEIMER and LEO LICHTENSTADT (*Ber.*, 1911, **44**, 356—359. Compare Abstr., 1909, i, 20).—It has been shown previously that the bases obtained from *d*- and *l*-hydroxyphenylmethylethylammonium chlorides, OH·NMeEtPhCl, by the action of barium hydroxide are optically active, but it was left uncertain whether they had the formula O:NMeEtPh or $NMeEtPh(OH)_2$. The conclusion is now arrived at that the crystalline solid is an amine oxide, but that in aqueous solution the dihydroxy-form is present. A cyclic amine oxide, kairoline oxide, has been observed to behave similarly, and the same process has been investigated with phosphine oxides.

Phenylmethylethylphosphine oxide, O:PMeEtPh, prepared by the addition of methyl iodide to ethyldiphenylphosphine and subsequent boiling with water, is a colourless, hygroscopic substance crystallising in needles, m. p. about 50°, b. p. above 360° without decomposition. With *d*-bromocamphorsulphonic acid a well crystallised salt is formed, having m. p. 94—95° and $[\alpha]_D$ +67·4°, which values did not change on fractional crystallisation. The value for the rotation indicates the presence of an optically-active phosphorus ion.

d-*Methylethylphenylphosphine oxide* is obtained by the action of ammonia on the salt in benzene solution in crystalline needles, $[\alpha]_D$ +23·1° in water, and 33·8° in benzene.

Accordingly, the free phosphine oxide is optically active, and the satisfaction of the five valencies of phosphorus with only four different radicles is sufficient to give asymmetric compounds. E. F. A.

Organic Chemistry.

$\beta\gamma$-Dimethylhexane. LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1911, **33**, 520—531).—In continuation of the work on the octanes (Abstr., 1907, i, 169; 1908, i, 493, 593; 1909, i, 125, 350), $\beta\gamma$-dimethylhexane has been synthesised by the two following methods: (1) Ethyl dimethylacetoacetate on hydrolysis yields dimethylacetone (β-methyl-γ-butanone), which on treatment with magnesium propyl bromide gives $\beta\gamma$-dimethyl-γ-hexanol. This compound is converted into γ-iodo-$\beta\gamma$-dimethylhexane by the action of iodine in presence of amorphous phosphorus, and on reducing this substance with zinc and hydrochloric acid, $\beta\gamma$-dimethylhexane is produced. (2) Ethyl methylpropylacetoacetate on hydrolysis yields γ-methyl-β-hexanone, which on treatment with magnesium methyl iodide is converted into $\beta\gamma$-dimethyl-β-hexanol. From the latter compound, β-iodo-$\beta\gamma$-dimethylhexane is prepared, which on reduction gives $\beta\gamma$-dimethylhexane.

$\beta\gamma$-Dimethyl-γ-hexanol, $CHMe_2{\cdot}CMe(OH){\cdot}CH_2{\cdot}CH_2Me$, b. p. 158—158·2°/758 mm., has a eucalyptus-like odour. *$\beta\gamma$-Dimethylhexane*, $CHMe_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2Me$, b. p. 113·8—114°/758 mm., is a colourless, mobile liquid, which has a rather strong odour, D_{15}^{15} 0·7246, and n_D^{25} 1·4075.

γ-Methyl-β-hexanone has b. p. 136—137°/760 mm. *$\beta\gamma$-Dimethyl-β-hexanol*, $OH{\cdot}CMe_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2Me$, b. p. 150—151°/756 mm., is a colourless liquid with an odour recalling that of musty apples.

The physical constants of eight octanes are compared, and it is shown that these compounds fall into three classes according to the number of methyl groups they contain, *n*-octane containing two, the methylheptanes three, and the dimethylhexanes four methyl groups. The volatility increases with the number of methyl groups present. The position of the methyl group in the methylheptanes makes only a slight difference in the boiling point, but the density increases as the methyl group is moved successively from the β- to the γ- or δ-position.

E. G.

Pyrogenic Decomposition of *s*-Tetrachloroethane and Trichloroethylene. O. NICODEMUS (*J. pr. Chem.*, 1911, [ii], **83**, 312—322).—The liquid under examination is heated nearly to the boiling point in a flask through which a current of purified carbon dioxide is drawn; the gas and vapour pass into a quartz combustion tube packed with pumice and heated electrically by about six metres of nickel wire (1 mm. thick, resistance 2·2 ohms) wound round the tube and insulated by asbestos cord, loss of heat being diminished by wrapping the tube and wire in layers of asbestos paper. The current is supplied at 72 volts; the temperature desired is attained after one and a-half to two hours, and is determined by a platinum-iridium thermocouple. The quartz tube is connected with a series of condensing vessels consisting of a large Woulf's bottle, two washing-bottles containing ether (in ice), two containing water, and the gasometer. The gas and vapour pass through the tube at such a rate that the deposition of carbon in the tube is as small as possible, and the vapour streaming into the Woulf's bottle has a light brown colour. The products obtained by the decomposition of *s*-tetrachloroethane at 700° under these conditions cannot be separated satisfactorily by fractional distillation; consequently, the author collects fractions at every 10°, and treats each with bromine in sunlight, whereby the saturated chlorinated components are unattacked, whilst the unsaturated constituents are converted into chlorobromo-derivatives of high boiling point, the separation of which is readily effected by fractional distillation. In this way the author has obtained *s*-dichloroethylene, 1—5%; chloroform, 5—8%; carbon tetrachloride, 5—8%; trichloroethylene, 50—60%; tetrachloroethylene, 5—10%; pentachloroethane, 1—3%; and hexachloroethane, 1—3%, the percentages being calculated on the amount of crude decomposition products; the remainder consists of carbon and hexachlorobenzene.

Under conditions similar to the preceding, trichloroethylene decomposes violently, and yields dichloromethane (a trace); dichloroethylene, 5—10%; chloroform, 5—10%; tetrachloroethylene, 5—10%; carbon tetrachloride, 5—10%; *αββββ*-tetrachloroethane, 3—5%; pentachloroethane, 3—5%; and hexachloroethane (a trace). When the decomposition is performed slowly a large quantity of carbon and hexachlorobenzene is produced; by rapid distillation, free chlorine is formed together with dichloroacetylene (?), which partly polymerises and partly explodes in the delivery tube. The fraction, b. p. 180—230°, contains about 15% of *αααγδδ-hexachloro-Δ^β-butylene*,

$CCl_3{\cdot}CH{:}CCl{\cdot}CHCl_2$ (?),

b. p. 210—212° (decomp.) or 98—99°/17 mm., D_{30}^{30} 1·6610, the constitution of which is deduced from the facts that quinoline eliminates hydrogen chloride (1 mol.), yielding a *substance*, C_4HCl_5, b. p. 227—230° or 130°/80 mm., sodium ethoxide produces an *ether*, $C_3HCl_3(OEt)_3$, b. p. 240—245°/120 mm., and reduction by zinc and acetic acid gives products from which allyl chloride and trichloropropylene have been isolated. The fraction, b. p. 240—300°, contains pentachlorobenzene, m. p. 85—86° (identified by conversion into pentachloronitrobenzene by nitration), and 2 : 3 : 4-*trichlorobenzylidene chloride*, $C_6H_2Cl_3{\cdot}CHCl_2$, m. p. 83—84°, b. p. 275—280°, which is converted by hydrochloric acid into the trichlorobenzaldehyde, m. p. 91°. The fraction, b. p. 300—340°, representing 20—25% of the crude products of decomposition, consists almost entirely of hexachlorobenzene, but also contains about 0·3—0·5% of 2 : 3 : 5 : 6-*tetrachlorobenzotrichloride*, $C_6HCl_4{\cdot}CCl_3$, m. p. 101—102°, b. p. 320—330°, which is not attacked by chlorine, bromine, or potassium permanganate, but is oxidised by chromic acid to chloranil, and is converted by alcoholic potassium hydroxide into the *ester*, $C_6HCl_4{\cdot}C(OEt)_3$, b. p. 240—245°/120 mm. C. S.

Tribromo*tert.*-butyl Alcohol, $C_4H_7OBr_3$. THOMAS B. ALDRICH (*J. Amer. Chem. Soc.*, 1911, **33**, 386—388).—Willgerodt (Abstr., 1882, 492) has described the preparation of chloro*tert.*-butyl alcohol (chloretone) by the action of alkali hydroxide on a mixture of chloroform and acetone. An account is now given of the corresponding tribromo-derivative (brometone), the pharmacological action of which has been studied by Houghton and Aldrich (Abstr., 1903 ii, 315).

Tribromo*tert.*-butyl alcohol, $CBr_3\cdot CMe_2\cdot OH$, m. p. 167—176°, forms white crystals, has a camphor-like taste and odour, is slowly volatile in the air, and can be distilled with steam. This compound, like the trichloro-derivative, contains varying amounts of water, which are present in the form of a solid solution (compare Cameron and Holly, Abstr., 1899, i, 323). Attempts have been made to convert tribromo-*tert.*-butyl alcohol into α-hydroxy*iso*butyric acid, which was obtained by Willgerodt (*loc. cit.*) from the trichloro-derivative, but, although an organic acid was produced, the quantity was too small for it to be identified. E. G.

Method for Preparing Certain True Acetylenic Alcohols.

Robert Lespieau (*Compt. rend.*, 1911, **152**, 879—881).—The next higher homologue of butinene-γ-ol has been prepared by the method previously described, which appears to be of general application (Abstr., 1910, i, 149).

Δ^{α}-Pentinene-γ-ol, $OH\cdot CHEt\cdot C\vdots CH$, b. p. 125°/761 mm., has D^{15} 0·8926, n_D 1·4347. It forms a crystalline precipitate with aqueous silver nitrate, soluble in excess, having the composition

$$C_5H_7OAg,AgNO_3.$$

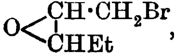
The precipitate formed with cuprous chloride is soluble in ammonia; on treatment with iodine it yields *$\alpha\alpha\beta$-tri-iodo-Δ^{α}-penten-γ-ol*,

$$OH\cdot CHEt\cdot CI{:}CI_2,$$

m. p. 142—144°. *β-Bromo-Δ^{α}-penten-γ-ol*, $OH\cdot CHEt\cdot CBr{:}CH_2$, has b. p. 165—166°/755 mm., $D^{15\cdot5}$ 1·351, n_D 1·482; the *phenylurethane* has m. p. 42—44°.

Acetylenic alcohols can also be obtained, although not in good yield, by the action of acraldehyde on zinc alkyl derivatives or organo-magnesium halides.

$\alpha\beta$-Dibromopentan-γ-ol, heated with sodium ethoxide, gave the *oxide*,



$$O<\begin{matrix}CH\cdot CH_2Br\\ |\\ CHEt\end{matrix}$$

, b. p. 165—166°/768 mm., $D^{15\cdot5}$ 1·4096, n_D 1·4725.

W. O. W.

Quantitative Dehydration of Pure Pinacone.

Maurice Delacre (*Bull. Soc. chim.*, 1911, [iv], **9**, 240—247).—Couturier has pointed out that quantitative yields of pinacolin should be obtained by the dehydration of pinacone (Abstr., 1893, i, 244), and this conclusion has been confirmed by Richard and Langlais (Abstr., 1910, i, 455). In the present paper details are given of the yields obtained by the use of sulphuric and oxalic acids as dehydrating agents, and it is shown that high yields are obtainable when pure pinacone is employed, and if this condition is fulfilled Friedel's process gives results as good as those obtained by methods suggested more recently. T. A. H.

Pyrogenic Decomposition of Metallic Xanthates. ALEXANDRE HÉBERT (*Compt. rend.*, 1911, **152**, 869—871. Compare Fleicher and Hankó, Abstr., 1878, 29).—A tabular statement shows the relative proportions of the principal products obtained by decomposing at 350° the xanthates of potassium, barium, iron, cobalt, nickel, zinc, copper, lead, mercury, silver, and tin. The gases liberated consist of hydrogen sulphide and carbon dioxide, with small quantities of combustible gases containing carbon monoxide.

The liquid products as a rule contain carbon disulphide, carbon oxysulphide, ethyl alcohol, ethyl hydrogen sulphide, and ethyl sulphide and disulphide. In the case of the nickel and silver salts, however, the liquid is composed almost entirely of ethyl xanthate, and the dry distillation of the nickel salt is recommended as a useful method for preparing this substance. W. O. W.

Catalytic Scission of Esters by Certain Metallic Oxides. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **152**, 669—673. Compare Senderens, Abstr., 1908, i, 494, 495; 1909, i, 127, 286; Colson, Abstr., 1909, i, 302).—If the catalyst is heated above 330° during the esterification of acids by the method previously described (this vol., i, 258), the yield of ester is diminished; at 400°, the principal reactions are those involving decomposition of the acid and alcohol.

When the vapour of an ester is passed over the catalyst, decomposition may occur in several ways. In each case it is supposed that an unstable salt and alkyloxide are first formed, and that the course of the subsequent reactions depends on the relative stability of these substances. They are produced in accordance with the equation: $2MO + 2R{\cdot}CO_2{\cdot}C_nH_{2n+1} = (R{\cdot}CO_2)_2M + (C_nH_{2n+1}O)_2M$. (1) If the salts are equally unstable, a ketone and ethylenic hydrocarbon (2 vols.) with carbon dioxide (1 vol.) and water are formed, for example, when ethyl acetate is passed over alumina. (2) When the alkyl oxide is more stable the water formed in (1) reacts with it, giving an alcohol. Thus ethyl, propyl, and *iso*butyl acetates, propyl propionate, and ethyl hexoate, in presence of thorium oxide, yield a ketone and alcohol with approximately equal volumes of hydrocarbon and carbon dioxide. At high temperatures, however, the alcohol undergoes dehydrogenation. (3) When the converse holds, as, for example, when titanium oxide is the catalyst, the salt $(R{\cdot}CO_2)_2M$, is decomposed by water, yielding the acid. (4) If the ester is a benzoate or toluate, or if boric anhydride is used as catalyst, exclusive formation of acid and unsaturated hydrocarbon occurs. Thus ethyl valerate is decomposed by boric anhydride at 400° into ethylene and valeric acid. W. O. W.

Density of Soap Solutions. E. C. V. CORNISH (*Zeitsch. physikal. Chem.*, 1911, **76**, 210—211).—The measurements were made by the pyknometer method at 90°. Some of the results are as follows: Sodium palmitate, $N/1$ $D_4^{90} = 0{\cdot}9625$, $N/2$ 0·9658, $N/10$ 0·9654, $N/100$ 0·9655; sodium stearate, $N/2$ 0·9599, $N/10$ 0·9629, $N/100$ 0·9639. D_4^{90} for water is 0·9653. G. S.

Constitution of Soap Solutions: Solutions of "Sodium Palmitates." JAMES W. MCBAIN and MILLICENT TAYLOR (*Zeitsch. physikal. Chem.*, 1911, **76**, 179—209. Compare Abstr., 1910, ii, 177). —The high electrical conductivity of aqueous solutions of sodium palmitate at 90° (*loc. cit.*) shows that the normal soaps are not simple colloids. The nature of the dissolved electrolyte is not conclusively established; it is certain that free sodium hydroxide is present, and presumably normal sodium palmitate is present in ordinary solution, and acid sodium palmitate mainly in the colloidal form. As the conductivity does not alter with time, there is a completely reversible equilibrium between electrolyte, hydrosol, and coagulum. The molecular conductivity-dilution curve of sodium palmitate is unlike any previously observed in aqueous solution, inasmuch as it shows a pronounced maximum in half-normal and a distinct minimum between *N*/5- and *N*/10-solution. The conductivity of solutions containing sodium hydroxide and sodium palmitate in varying proportions has also been investigated; the results show that even in normal solution sodium palmitate is considerably hydrolysed.

The solubility of palmitic acid and of acid sodium palmitate in water has been investigated. If it is assumed that the palmitic acid is dissociated to the extent of 50% in aqueous solution, the concentration of the undissociated acid, and also of the ions, is about $0{\cdot}6 \times 10^{-5}$ mol. per litre at 90°. The conductivity of a saturated solution of acid sodium palmitate is due mainly to ionised normal and acid palmitate, and to a much smaller extent to the presence of sodium hydroxide.

The precipitate obtained by "salting out" sodium palmitate with sodium hydroxide consists mainly of sodium acid palmitate with proportions of the normal palmitate depending upon the conditions of precipitation.

The boiling point and vapour-pressure methods are inapplicable to the investigation of soap solution, owing to the great difficulty of removing adsorbed air. G. S.

Direct Synthesis of the Glycerides. G. GIANOLI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 348).—The author points out that the method described by Bellucci and Manzetti in a recent paper under this title (this vol., i, 259) is not new, for it was introduced by him on the large scale in 1891, and was referred to in a recent publication (Gianoli, *Atti VI. Congr. chim. appl.*, 1907, **3**, 51). R. V. S.

Mode of Formation of Ethyl Chloroethoxyacetate. Use of this Ester in the Synthesis of α-Alkyloxy-acids. EDMOND E. BLAISE and L. PICARD (*Compt. rend.*, 1911, **152**, 960—962).—In an attempt to prepare diethoxyacetyl chloride by the action of thionyl chloride on diethoxyacetic acid, a liquid was obtained giving on fractionation an anhydride of glyoxylic acid, with the chloride, OEt·SOCl, and a liquid, b. p. 79—81°/10 mm. The latter has the composition of the expected chloride, but proved to be *ethyl chloroethoxyacetate*,

$$OEt{\cdot}CHCl{\cdot}CO_2Et.$$

This yields α-alkyloxy-esters on treatment with zinc alkyl halides; thus zinc propyl iodide furnishes ethyl α-ethoxyvalerate.

Ethyl chloroethoxyacetate is not formed in the chlorination of ethoxyacetic acid, but may be prepared by the action of thionyl chloride on the alcoholate of ethyl glyoxylate. The production of the ester from diethoxyacetic acid is probably preceded by the formation of the chloride, which then undergoes transformation, involving interchange of the chlorine atom with an ethoxy-group. W. O. W.

Keto-enolic Tautomerism. KURT H. MEYER (*Annalen*, 1911, **380**, 212—242).—I. *The Quantitative Estimation of Keto-enolic Tautomerides.*—It is shown, by experiments with compounds which exist in both the ketonic and enolic forms, that the unsaturated hydroxylic compound reacts instantaneously with an alcoholic solution of bromine, and that the amount of bromine used up corresponds with the formation of a dibromide. The ketonic forms, on the other hand, are coloured by the first drop of bromine solution, and the colour disappears gradually. The compounds experimented with were the two forms of dibenzoylacetylmethane, mesityl-oxide-oxalic ester and diacetylsuccinic ester, and the pairs of compounds, anthranol and anthrone, anthraquinol and hydroxyanthrone.

When other solvents are used, for example, benzene or chloroform, the difference between the ketonic and enolic forms is not so marked (compare also Lapworth, Trans., 1904, **85**, 30). The reaction between the enol and bromine undoubtedly consists in the formation of a dibromide (compare Lippmann, *Zeitsch. Chem.*, 1869, 5, 29), although such products cannot be isolated, as hydrogen bromide is immediately liberated and a bromo-ketone is formed.

The amount of the enolic compound in a mixture of the tautomeric forms can also be determined by the aid of bromine. A simple method consists in titrating the alcoholic solution with an alcoholic solution of bromine of known concentration, until the colour of the bromine remains permanent. The method has the disadvantage that alcoholic solutions of bromine rapidly deteriorate. A more general method consists in titrating with an alcoholic solution of bromine of unknown concentration, and then determining the amount of bromo-ketone formed. This is accomplished by adding potassium iodide solution and warming gently, when iodine is liberated, owing to the reduction of the bromo-ketone to ketone. The iodine liberated is titrated by means of standard thiosulphate without the aid of starch. The reaction probably consists in the addition of hydrogen iodide to the carbonyl group, and the replacement of bromine by iodine and ultimately in the elimination of iodine from the di-iodo-compound : $O{:}\overset{|}{C}{\cdot}CBr{<} \longrightarrow OH{\cdot}\overset{|}{C}I{\cdot}CI{<} \longrightarrow OH{\cdot}\overset{|}{C}{:}C{<} + I_2$.

When a *N*/50-solution of either the enolic or ketonic form of dibenzoylacetylmethane in alcohol is kept for twelve hours, an equilibrium mixture containing 75% of the enolic compound is obtained. In the case of the enolic form of methyl mesityl-oxide-oxalate, $CMe_2{:}CH{\cdot}CO{\cdot}CH{:}C(OH){\cdot}CO_2Me$, rather more than one molecule is used up before the red colour of the bromine persists for a moment or two. This is probably due to the addition of bromine to the second ethylene linking. Benzoylacetone reacts with a carbon disulphide solution of bromine, yielding a *hydrobromide* of the ketone, which gives up hydrogen bromide on exposure to the air.

II. *Tautomerism of Ethyl Acetoacetate.*—Titrations of freshly-prepared solutions of ethyl acetoacetate indicate the presence of 7·71% of the enolic form. Similar results are obtained for the following solvents when the solutions are titrated immediately after they are prepared: methyl, ethyl, propyl and amyl alcohols, and chloroform at – 15°, provided the titration is made in the presence of an excess of alcohol. These results indicate that the liquid ester contains 7·71% of enol and 92·29% of ketone (compare Hantzsch, Abstr., 1910, i, 811; Brühl, 1905, i, 407). Different results are obtained when the solutions are kept for some time. The following numbers indicate the percentage of enol present after forty-eight hours at 18°: Water 0·4, glacial acetic acid 5·74, methyl alcohol 6·87, acetone 7·3, chloroform 8·2, nitrobenzene 10·1, ethyl alcohol 12, ethyl acetate 12·9, benzene 16·2, ether 27·1, carbon disulphide 32·4, and hexane 46·4. In all cases an appreciable excess of ethyl alcohol was added before the titration with the bromine solution.

In solution a rise of temperature favours the formation of the ketonic form, for example, boiling methyl and ethyl alcoholic solutions contain respectively 4·74 and 7·5% of enol. Heating the liquid ester to 80° for an hour scarcely affects the equilibrium, but the freshly distilled ester contains 20—25% of enol.

When an alkaline solution of ethyl acetoacetate is acidified, an oil is precipitated which gradually dissolves. The oil is the enolic form, which is then transformed into the keto-form (99·6%), and these phenomena are in harmony with Dimroth's conclusion (this vol., ii, 31) that the relative proportions of the two components in a given solution when equilibrium is reached depend on the relative solubilities of the components. The enol, on the other hand, is readily soluble in hexane or light petroleum, and is removed when the liquid ester is shaken three times with twice its volume of well-cooled hexane; the residual oil after freeing from hexane contains only 1·5% of the enol.

The solubility of the keto-form in water at 0° is 11·6%, and in 2% sodium chloride solution 10·9%. The solubility of the enol in 2% sodium chloride solution is 0·5%. The value for the van 't Hoff-Dimroth constant G is thus 0·09.

The velocity of transformation has been calculated by means of the equations: $k_1 + k_2 = 1/(t_2 - t_1)\log s - x_1/s - x_2$ and $k_1/k_2 = C_2/C_1$. Where k_1 is the velocity constant of ketonisation, k_2 that of enolisation, s the value of x when equilibrium is attained, and C_1 and C_2 the concentrations of the two forms in the equilibrium mixture. For liquid ester which has been freshly distilled, the value for k_1 is 0·00055, and k_2 0·000046 at 15°.

In aqueous solution the values are $k_1 = 2·4$, and $k_2 = 0·010$ at 0°. The velocity of enolisation can also be determined by the rate of addition of bromine to the ketone, since this includes the enolisation of the ketone and the instantaneous addition of bromine to the enol (compare Lapworth, *loc. cit.*).

In 99·8% ethyl alcohol, $k_1 = 0{\cdot}077$, and $k_2 = 0{\cdot}0105$ at 0°; in hexane, $k_1 = 0{\cdot}0041$, and $k_2 = 0{\cdot}0035$ at 0°.

Acids have a catalytic action; thus, in aqueous 0·1*N*-hydrochloric acid at 0°, $k_2 = 0{\cdot}018$; in non-ionising solvents the catalytic effect is much more marked. For example, when the ester is shaken for a few seconds with hexane containing a little hydrogen bromide, 45—46% of enol is found. It is suggested that the action of the acid is due to its addition and subsequent removal: $O{:}\overset{|}{C}{\cdot}\underset{|}{\overset{|}{C}}H \longrightarrow OH{\cdot}\overset{|}{C}Br{\cdot}\underset{|}{\overset{|}{C}}H \longrightarrow OH{\cdot}\overset{|}{C}{:}\underset{|}{\overset{|}{C}}$.

The frequency of the molecular change has been calculated by Dimroth's method, and the conclusion is drawn that the ultraviolet absorption bands characteristic of the ester cannot be due to the oscillations between the keto- and enolic forms (compare Baly and Desch, Trans., 1905, **87**, 768; Hantzsch, Abstr., 1910, i, 811).

Experiments have been made with the following tautomeric substances, the numbers indicating the % of enol present in the liquid at the ordinary temperature: Methyl acetoacetate 4·1, methyl methylacetoacetate 3·16, ethyl bromoacetoacetate 4·0, methyl benzoylacetate 16·3, ethyl benzoylacetate 31·9, ethyl acetonedicarboxylate 16·8, acetylacetone 80·4, benzoylacetone (solid) 99, dibenzoylmethane (solid), 102. J. J. S.

Some Reactions of Calcium Oxalate. WILLIAM OECHSNER DE CONINCK and A. RAYNAUD (*Bull. Soc. chim.*, 1911, [iv], **9**, 301—306).—Calcium oxalate, CaC_2O_4,H_2O, undergoes the following reactions: On gentle warming chlorine reacts quantitatively, giving calcium chloride and carbon dioxide. Bromine and iodine react similarly. On warming with concentrated hydrochloric acid, it dissolves completely, a small quantity of carbon dioxide being evolved only on boiling. With dry hydrogen chloride at a red heat, carbon monoxide and dioxide are evolved. Hydrobromic acid and hydrogen bromide react similarly to the chlorine compounds. Concentrated nitric acid reacts according to the equation: $CaC_2O_4 + 3NHO_3 = Ca(NO_3)_2 + NO_2 + H_2O + 2CO_2$. Concentrated sulphuric acid gives the ordinary reaction with oxalates.

Calcium oxalate loses its water of crystallisation only at temperatures above 100°; towards a red heat, carbon dioxide commences to be evolved, carbon being liberated at the same time. At a bright red heat, carbon monoxide is evolved, the evolution of gas taking place suddenly. Sodium and potassium oxalates behave similarly towards heat.

The action of a red heat on mixtures of calcium oxalate with various oxides has been studied. With silica, carbon dioxide only is evolved and calcium silicate formed, either SiO_2,CaO or $3SiO_2,2CaO$, or a mixture of both, according to the proportions taken. Boron trioxide gives carbon dioxide and a calcium borate of indefinite composition. Titanium dioxide gives carbon dioxide and a residue of indefinite composition. Uranium trioxide hydrate, UO_3,H_2O, gives calcium carbonate, carbon dioxide, and uranium dioxide; the green oxide of uranium, U_3O_8, acts similarly. With stannic oxide a mixture of carbon monoxide and dioxide is evolved, leaving a residue of calcium stannate and calcium oxide. Ferric oxide, as also black oxide of iron, Fe_3O_4, gives calcium carbonate, ferrous oxide, and carbon dioxide. With lead dioxide, carbon dioxide is evolved, a mixture of calcium oxide, red lead, and litharge remaining. Red lead reacts similarly, the lead compound remaining being litharge. Manganese dioxide gives carbon dioxide, calcium oxide, and the oxide Mn_3O_4. Antimonious oxide is reduced to antimony, carbon dioxide being evolved and calcium oxide formed. Bismuth oxide is similarly reduced to the oxide BiO.

Careful heating of a mixture of calcium oxalate and barium peroxide gives a residue of calcium oxide, barium oxide, and barium carbonate, carbon dioxide being evolved. T. S. P.

Yttrium Potassium Oxalate. L. A. PRATT and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1911, **33**, 488—492).—Cleve and Höglund (this Journ., 1873, 136) described two yttrium potassium oxalates, $Y_2(C_2O_4)_3,4K_2C_2O_4,12H_2O$ and $Y_2(C_2O_4)_3,K_2C_2O_4,H_2O$.

A study has been made of the solubility of yttrium oxalate in potassium oxalate solutions at 25°, and the accompanying solid phases have been examined. Varying quantities of potassium and yttrium oxalates were shaken with 75 c.c. of water until equilibrium was established. The results of the experiments are tabulated and plotted as curves. It has been found that the only yttrium potassium oxalate formed at 25° is the salt, $Y_2(C_2O_4)_3,4K_2C_2O_4,12H_2O$. This compound can exist in contact with an aqueous solution of potassium oxalate containing more than 27·5 grams of the oxalate per litre. E. G.

Condensations in the Mesoxalic Ester Series. RICHARD S. CURTISS and EARLE K. STRACHAM (*J. Amer. Chem. Soc.*, 1911, **33**, 396—400).—In an earlier paper (Curtiss and Spencer, Abstr., 1909, i, 763), an account has been given of the preparation and reactions of methyl oxomalonate. A study has now been made of the corresponding ethyl ester.

Ethyl oxomalonate, $CO(CO_2Et)_2$, b. p. 117°/31 mm., obtained by distilling ethyl dihydroxymalonate with phosphoric oxide, is a green oil, which has D_{20}^{20} 1·119, and, when cooled with a mixture of solid carbon dioxide and ether, crystallises in aggregates of radiating, colourless plates, m. p. below $-30°$. When the ester is treated with hydrogen chloride at $-60°$ to $-70°$, it is converted into a white, crystalline mass, which melts between $-29°$ and $-10°$ with evolution of hydrogen chloride, and consists of a mixture of additive compounds containing HCl, 2HCl, and 3HCl respectively. Hydrogen bromide unites with the ester in a similar manner. Methyl oxomalonate combines with only 1 mol. of a halogen hydride (Curtiss and Spencer, *loc. cit.*).

When ethyl oxomalonate is treated with urethane, *ethyl carbethoxyaminotartronate*, $OEt·CO·NH·C(CO_2Et)_2·OH$, m. p. 32—33°, is produced, which forms colourless crystals, and yields a *disodium* salt, probably of the enolic form. If this ester is left in contact with phosphoric oxide for twenty-four hours, a colourless, crystalline *compound*, m. p. 121·5°, is formed, which is being investigated.

Carbamide reacts with ethyl oxomalonate with production of a crystalline *substance*, m. p. 132—133°, which appears to consist of *ethyl carbamidotartronate*, $NH_2\cdot CO\cdot NH\cdot C(CO_2Et)_2\cdot OH$, together with about 5% of carbamide. E. G.

The Solution Densities of Dextrose, Lævulose, and Maltose.

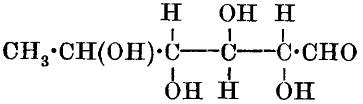
ARTHUR R. LING, LEWIS EYNON, and JOSEPH H. LANE (*7th Intern. Congr. Appl. Chem.*, London, 1909, Sect. I., 137—138).—The specific gravities of solutions of dextrose, lævulose, and maltose are tabulated for concentrations from 1 to 24%, specially purified sugars having been used for the determinations. C. H. D.

Digestive Ferments for Hexotrioses and for Stachyose.

HENRI BIERRY (*Compt. rend.*, 1911, **152**, 904—906. Compare this vol., i, 263).—Although the enzymes of the digestive system of vertebrates are without action on trioses, these sugars are hydrolysed with facility by ferments present in the gastro-intestinal juice of molluscs and crustaceans. The juice from *Helix* and *Astacus* hydrolyses raffinose, gentianose, rhamninose, and the tetrose stachyose. W. O. W.

*iso*Rhodeose.

EMIL VOTOČEK (*Ber.*, 1911, **44**, 819—824. Compare Abstr., 1910, i, 223, 274).—*iso*Rhodeose from purgic acid has the annexed constitutional formula, and is the optical antipode of Fischer's *iso*rhamnose. On oxidation with nitric acid, the same trihydroxyxyloglutaric acid is formed as is obtained from *iso*rhamnose. Crystalline *iso*rhodeose has $[\alpha]_D$ +31·5° (*iso*rhamnose having $[\alpha]_D$ −30°); it does not form insoluble hydrazones.



$$CH_3\cdot CH(OH)\cdot\overset{H}{\underset{OH}{C}}-\overset{OH}{\underset{H}{C}}-\overset{H}{\underset{OH}{C}}\cdot CHO$$

*iso*Rhodeosephenylosazone has m. p. 186—187°; 0·2 gram dissolved in 10 c.c. of a mixture of pyridine and alcohol in a 100 mm. tube has α −2·9°; under similar conditions the phenylosazone of rhamnose (identical with that of *iso*rhamnose) has α −3·5°. *iso*Rhodeose-*p*-bromophenylosazone has m. p. 221·5—222°.

Further proof of the constitution is afforded by the oxidation of *iso*rhodeose to *iso*rhodeonic acid, conversion of this into *anti*rhamnonic acid by means of pyridine, reduction to *anti*rhamnose, addition of hydrogen cyanide, forming *anti*rhamnohexonic acid, and oxidation of this to mucic acid. The intermediate products were not isolated, but mucic acid was identified. E. F. A.

Photochemical Synthesis of Carbohydrates. I. Sorbose.

GIUSEPPE INGHILLERI (*Zeitsch. physiol. Chem.*, 1911, **71**, 105—109).—Tubes containing 40% formaldehyde and crystallised oxalic acid were exposed to sunlight for fourteen months. The product contained a carbohydrate, which separated in regular orthorhombic crystals, m. p. 98°, and formed a phenylosazone crystallising in dark yellow, stellate crystals, m. p. 164°. The phenylmethylosazone was dark yellow. The carbohydrate was optically inactive; it is assumed to be sorbose.

E. F. A.

Stereochemical Configuration of the Sugars Fucose and Rhodeose. C. S. Hudson (*J. Amer. Chem. Soc.*, 1911, **33**, 405—410). —The constitution and configuration of fucose and rhodeose have been established by Mayer and Tollens (Abstr., 1907, i, 588) and Votoček (Abstr., 1906, i, 378, 483; 1910, i, 223).

In an earlier paper (Abstr., 1910, i, 220), the author has pointed out a relation between the constitution and optical rotatory power of the sugar lactones, and has shown that it can be applied to the determination of the constitution of the sugars. By means of this relation, it is now shown that, since rhodeonic and rhodeohexonic lactones are strongly lævorotatory (Krauz, Abstr., 1910, i, 224), rhodeose and fucose must have the configurations which have already been assigned to them. E. G.

Colorimetric Method of Determining the Molecular Size of Polysaccharides. Leonhard Wacker (*Zeitsch. physiol. Chem.*, 1911, **71**, 143—152. Compare Abstr., 1908, i, 135; 1909, i, 633).—The intensity of the colour given by carbohydrates with *p*-phenylhydrazinesulphonic acid in presence of sodium hydroxide, when that of dextrose is 100, varies after inversion from 107·1 in the case of a carbohydrate with three hexoses to 110·9 in that of a polysaccharide with one hundred hexoses. The mean value is 109, and this divided by the colour intensity shown by the polysaccharide before inversion by acid gives the number of hexoses in the molecule. Lævulose and carbohydrates yielding lævulose on hydrolysis give a somewhat deeper coloration. The influence of acids and alkali on the intensity of the colour for the various sugars is shown to be negligible.

The method shows erythro- and acro-dextrin to contain four hexoses; starch, seven hexoses, and glycogen, eight or nine hexoses.
E. F. A.

Cellulose. Hydrocellulose. H. Jentgen (*Zeitsch. angew. Chem.*, 1911, **24**, 585—586).—A reply to Schwalbe (this vol., i, 115).
T. S. P.

Mercerisation of Cellulose. Oswald Miller (*Ber.*, 1911, **44**, 728—731).—Mainly a reply to the criticisms of Cross (this vol., i, 114) of previous work of the author (this vol., i, 17).

The fact that mercerised cellulose, when kept over fused calcium chloride at 23—25°, loses its water at a gradually diminishing rate, supports the view that mercerised cellulose is not a hydrate, but contains adsorbed water. F. B.

Nitrous Esters of Cellulose. M. Marqueyrol and D. Florentin (*Bull. Soc. chim.*, 1911, [iv], **9**, 306—309).—The experimental evidence given by Nicolardot and Chertier (Abstr., 1910, i, 818) in support of the existence of nitrous esters of cellulose is not satisfactory for several reasons: (*a*) It is improbable that nitrous esters could be formed in a nitric acid medium. (*b*) It is well known that nitrated celluloses with a low nitrogen content are insoluble in the usual solvents for guncotton, namely, ethyl acetate, acetone, etc. (*c*) Various investigators have shown that the nitric esters of cellulose when saponified with aqueous or alcoholic alkali give rise to considerable quantities of nitrite, since reduction accompanies the saponification.

It is furthermore shown that if cellulose is nitrated by the prolonged action of nitric acid (D_4^{15} = *ca.* 1·5) to which excess of carbamide has been added to destroy all the nitrous acid present, or formed during the reaction, products are obtained which cannot be nitrous esters, but which nevertheless possess the properties ascribed to these compounds by Nicolardot and Chertier. T. S. P.

Action of Ultra-violet Radiations on Starch. L. MASSOL (*Compt. rend.*, 1911, **152**, 902—904).—Soluble starch becomes hydrolysed when its aqueous solution is exposed to the light from a quartz-mercury lamp. Changes in the rotatory power of the solution show that the transformation is probably into dextrins and maltose, although the amount of sugar isolated was insufficient for identification. The hydrolysis is not due to the small amount of hydrogen peroxide formed under the action of the rays. W. O. W.

Catalytic Transformation of Starch Paste. AUGUSTE FERNBACH and JULES WOLFF (*7th. Intern. Congr. Appl. Chem.*, 1909, Sect. VI B, 124—128).—When to 50 c.c. of 5% starch-paste a few drops of hydrogen peroxide (corresponding with 5 mg. of oxygen) and of a ammonia solution (corresponding with 4 mg. of ammonia) are added, the paste rapidly becomes liquid, and in about fifteen minutes has a viscosity comparable to that of water. Other alkalis act similarly; there appears to be an optimum quantity of these, and, if excess is added, the liquefaction is retarded. There is partial neutralisation of the alkali during the change corresponding with 1·6 mg. of ammonia per gram of starch. A similar liquefying effect is exercised by hydrogen peroxide and certain salts (Wolff, Abstr., 1908, i, 137).

The optimum reaction in presence of fixed quantities of hydrogen peroxide and ferrous sulphate takes place when sodium hydroxide is added until the mixture is very faintly alkaline to methyl-orange. The slightest excess of acid very materially retards the liquefaction. Lactic and succinic acids in equivalent proportions are only one-third as harmful as succinic acid.

Ferric sulphate has only one-half to one-third the activity of ferrous sulphate. Copper sulphate is about twice as active as ferrous sulphate, and its effect is less susceptible to the presence of acids, sodium hydroxide having no influence. Manganese sulphate is very slightly active. Mono- and di-sodium phosphate retard the change, particularly the latter.

The minimum quantity of hydrogen peroxide in time brings about liquefaction, provided the reaction remains neutral or feebly alkaline, but this is probably due to the influence of impurities in the starch.

When a large proportion of hydrogen peroxide is used at 70—75°, the starch after two hours no longer gives an iodine coloration, the liquid has a marked reducing power, and is acid. The reducing substance is insoluble in alcohol, and is precipitated from a concentrated solution by copper sulphate. E. F. A.

Characteristic Properties of Amylose and Amylopectin. Mme. Z. Gatin-Gruzewska (*Compt. rend.*, 1911, **152**, 785—788. Compare Abstr., 1908, i, 320; Maquenne, *ibid.*).—The envelope of a potato-starch grain consists of amylopectin associated with inorganic substances. Neither crude nor pure amylopectin shows the phenomenon of ageing or spontaneous precipitation from solution on cooling (Maquenne and Roux's retrogradation). On the other hand, amylose has this property, the precipitation being more complete the purer the substance. When starch paste is cooled, the hydrosol granules of amylose are precipitated, and carry with them the gel of amylopectin, in which they are suspended. W. O. W.

Oxidation of Humic Acid. A. G. Dojarenko (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VII., 11—18).—When humic acid is oxidised with 30% hydrogen peroxide, a part of the nitrogen is detached in the forms of ammonia and soluble amides and amino-acids. The amide- and amino-acid nitrogen pass into the oxidised form of humus compounds, perhaps *apo*crenic acid, whilst the rest of the nitrogen of humic acid, the "humin nitrogen," serves as source of ammonia and simple amides. The properties of humic acid, as regards the production of assimilable nitrogen when oxidised, can be ascertained from the amounts of the different forms of nitrogen, especially the amount of "humin nitrogen."

The solution of humic acid in alkalis results in the production of *apo*crenates and crenates, and also in the breaking off of nitrogen in the form of ammonia and other simple compounds. The former are derived from amide- and amino-acid nitrogen, whilst the "humin nitrogen" yields the less complex nitrogen compounds. N. H. J. M.

Preparation of Ethyl Oxalhydrazinate. Robert Stollé (*Ber.*, 1911, **44**, 776—777).—*Ethyl oxalhydrazinate*, $CO_2Et\cdot CO\cdot NH\cdot NH_2$, is formed by the action of hydrazine hydrate on an alcoholic solution of ethyl oxalate at $-10°$ to $-15°$, and is most readily isolated as its *benzylidene* derivative, $CO_2Et\cdot CO\cdot NH\cdot N:CHPh$, which crystallises from alcohol in colourless, refractive needles, m. p. 133°. The *oxalate*, $CO_2Et\cdot CO\cdot NH\cdot NH_2,H_2C_2O_4$, crystallises from hot alcohol, and reduces hot Fehling's solution. J. J. S.

Sodium Derivatives of Bromo-amides and their Rôle in Hofmann's Reaction. Charles Mauguin (*Ann. Chim. Phys.*, 1911, [viii], **22**, 297—369. Compare Abstr., 1909, i, 892).—A further study of these compounds, the preparation of which has already been described. Owing to their explosive character, the preparation is not free from danger.

When bromoacetamide is prepared by Hofmann's method, the product consists of a mixture of the anhydrous compound (slender needles, m. p. 106°) with a monohydrate. The latter separates from warm solutions in orthorhombic, hemimorphic crystals (compare François, Abstr., 1909, i, 13, 140). *Bromo*iso*butyramide*, prepared by adding bromine (2 mols.) and potassium hydroxide (1 mol.) to the amide (2 mols.) in chloroform at −15°, forms monoclinic needles, m. p. 92°.

The sodium derivatives of bromoamides react with urethanes in benzene solution, giving substituted allophanates of the type

$$NHR\cdot CO\cdot NH\cdot CO_2R',$$

termed by the author ureocarbonic esters (compare Diels and Jacoby, Abstr., 1908, i, 613). Thus urethane and sodium bromoacetamide form *ethyl methylcarbamidecarboxylate*, $NHMe\cdot CO\cdot NH\cdot CO_2Et$, needles, m. p. 134°; this compound was also obtained by the action of ethyl chlorocarbonate on methylcarbamide. The *methyl* ester crystallises in lamellæ, m. p. 163°; the *propyl* ester has m. p. 130°. Sodium bromopropionamide gives *methyl ethylcarbamidecarboxylate*,

$$NHEt\cdot CO\cdot NH\cdot CO_2Me,$$

needles subliming at 40—50°, m. p. 95°; the ethyl ester has m. p. 72° (Jacoby, Thesis, 1907, gives 64—65°); the *propyl* ester has m. p. 81°; the iso*butyl* ester, lamellæ, m. p. 87°; the iso*amyl* ester, needles, m. p. 67—68°. *Methyl* iso*propylcarbamidecarboxylate* forms monoclinic prisms, m. p. 70°; the *ethyl* ester, m. p. 40°.

Amides react with their sodium bromo-derivatives, forming ureides of the type $NHR\cdot CO\cdot NH\cdot COR$; thus acetamide yields acetylmethylcarbamide. Butyramide furnishes a mixture of acetylmethylcarbamide, butyrylpropylcarbamide and *acetylpropylcarbamide*, $NHPr^{\alpha}\cdot CO\cdot NHAc$, micaceous lamellæ, m. p. 115°.

When oxamethane is warmed with an aqueous solution of potassium bromoacetamide there is formed urethane, ethyl allophanate, and the *potassium* salt of a new ureide, $CO_2Et\cdot NH\cdot CO\cdot NH\cdot CO\cdot CO_2K$, crystallising in slender needles. The *copper* and *silver* salts are sparingly soluble; on treating the latter with ethyl iodide, the *ester*,

$$CO_2Et\cdot NH\cdot CO\cdot NH\cdot CO\cdot CO_2Et,$$

was obtained. This substance occurs in brilliant needles, m. p. 146°; its constitution was established by a study of its behaviour towards water, alcohol, and ammonia, as well as by the action of these substances on the potassium salt. The latter is decomposed by water, giving potassium oxalate and ethyl allophanate.

Ethyl malonate and sodium bromoacetamide react to form acetylmethylcarbamide and ethyl ethylenetetracarboxylate.

The paper contains crystallographic details, illustrated by diagrams, of most of the substances mentioned. W. O. W.

The Catalytic Action of Potassium Carbonate on the Absorption of Nitrogen by Calcium Carbide.

GINO POLLACCI (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. II, 278—282).—It is known that the absorption of nitrogen by calcium carbide is accelerated by calcium fluoride (Foerster and Jacoby, Abstr., 1907, i, 397) and by various chlorides (Bredig, Fraenkel, and Wilke, *ibid.*, 396, 903). It is now found that potassium carbonate has an accelerating action, lowering the temperature at which absorption takes place, the best result being obtained when 4% of potassium carbonate is added. There is no advantage in raising the pressure of the nitrogen above one atmosphere. C. H. D.

Action of Nitrous Acid on Aminoguanidine and on Semicarbazide. Difference between the Tetrazen, $C_2H_8ON_2$, and Azoimides in their Behaviour Towards Hydriodic Acid. KARL A. HOFMANN, HEINRICH HOCK, and HEINRICH KIRMREUTHER (*Annalen*, 1911, **380**, 131—147).—The compound obtained by the action of sodium nitrite on a solution of aminoguanidine dinitrate, and termed aminoguanidine diazohydroxide (Abstr., 1910, i, 232) or guanyldiazoguanyltetrazen (*ibid.*, 446), is formed in larger quantity when an excess of sodium nitrite is used. The compound cannot contain the hydrate of an azoimide, $NH\!:\!\underset{|}{C}\cdot N_3,H_2O$, as carbamideimideazoimide, $NH_2\cdot C(\!:\!NH)\cdot N_3$, and carbamic acid azoimide, $NH_2\cdot CO\cdot N_3$, are readily decomposed by acids, alkalis, and silver salts, yielding hydrazoic acid.

Hydriodic acid reacts with hydrazoic acid and azoimides, yielding nitrogen, amine, and free iodine, $N_2\!:\!NR + 2HI = N_2 + NH_2R + I_2$, but with the derivative from aminoguanidine the acid merely forms the pale yellow iodide, or with a mixture of hydrochloric and hydriodic acids the chloroperiodide, $(C_2H_{10}N_7)_2ClI_3$. The compound is thus a base, and yields salts by the introduction of acid in place of water. It is regarded as a β-nitrosohydrazine derivative with the formula: $NH_2\cdot C(NH)\cdot NH\cdot NH\cdot N\!:\!N\cdot C(\!:\!NH)\cdot NH\cdot NH\cdot NO$, and in the formation of salts water is eliminated and a terminal diazo-group is formed. The nitroso-compound (tetrazen) is extremely stable, and is not attacked by sodium acetate solution, nitrous acid, sodium hydrogen sulphite, ammonium hydrogen sulphide, hydroxylamine, hydrazine sulphate, phenylhydrazine, hydrogen peroxide, formaldehyde, acetone, benzaldehyde, aniline, pyridine, or acetic anhydride. When reduced with stannous chloride and hydrochloric acid, it yields tetrazylhydrazine, which is isolated as its benzylidene derivative (Thiele, Abstr., 1893, i, 441). The sulphate, $(C_2H_7N_{10})_2SO_4$, crystallises in long, colourless prisms, and is hydrolysed by water; the acid sulphate yields the double *sulphate*, $C_2H_7N_{10}\cdot SO_4H,Ag_2SO_4$, in the form of glistening, doubly refractive needles. The *double* salt, $C_2H_7ON_{10}Ag,AgNO_3,3H_2O$, crystallises in pale yellow, glistening needles, and when boiled with dilute hydrochloric acid evolves nitrogen (3 atoms). With ammonia, the silver salt yields silver cyanamide and the silver derivative of tetrazylazoimide.

The *iodide*, $C_2H_7N_{10}I$, forms pale yellow, flat needles, only slightly pleochroic, and is extremely explosive. The *periodide*, $C_2H_7N_{10}I_5$, forms glistening, greenish-black, rhombohedral crystals, and the *chloroiodide*, $(C_2H_7N_{10})_2ClI_3$, forms pointed prisms, strongly pleochroic, from pale yellow to deep black, and also doubly refractive.

Semicarbazide hydrochloride and sodium nitrite yield the azoimide of carbamic acid, which is decomposed by copper acetate solution, yielding hydrazoic acid in the form of the *double* salt, $N_3\cdot Cu\cdot C_2H_3O_2$. This forms long, dark green needles, and when kept under water yields copper hydrazoate.

Semicarbazide hydrochloride and sodium nitrite in the presence of sodium acetate yield hydrazoic acid hydrazodicarbonamide (Thiele, Abstr., 1892, 1298), as represented by the equation:

$$NH_2\cdot CO\cdot NH\cdot NH_2 + NO\cdot OH + NH_2\cdot NH\cdot CO\cdot NH_2 = \\ NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2 + N_3H + 2H_2O.$$

The formation of guanylnitrosoguanyltetrazen from aminoguanidine dinitrate and sodium nitrite probably proceeds in a similar manner.

J. J. S.

Reaction of Iodoacetonitrile with Silver Nitrate. S. K. Loy and Salomon F. Acree (*Amer. Chem. J.*, 1911, **45**, 224—230).—It has been stated by Acree and Shadinger (Abstr., 1908, ii, 163) that in the reactions between urazoles and alkyl halides, it is probable that, in some cases, the anion first unites with the alkyl halide to form an unstable complex anion, which then decomposes, thus:

(1) $CH_3I + Ag^{\cdot} + NO'_3 \rightleftarrows CH_3I,NO'_3 + Ag^{\cdot} \longrightarrow CH_3{\cdot}NO_3 + Ag^{\cdot} + I'$.

(2) $CH_3I + AgNO_3(\text{or } Ag^{\cdot} + NO'_3) \rightleftarrows CH_3I,AgNO_3 \longrightarrow CH_3{\cdot}NO_3 + AgI$.

It was shown that in certain urazole reactions not more than traces of the complex salt could be present. In order to obtain evidence as to the existence of appreciable quantities of such a salt in solution, a study has been made of the double compound, $AgNO_3,CH_2I{\cdot}CN$, obtained by Scholl and Steinkopf (Abstr., 1907, i, 116) by the action of silver nitrate on iodoacetonitrile. Assuming that the complex salt is not more highly ionised than silver nitrate, and that the complex ion $NO'_3{\cdot}ICH_2{\cdot}CN$ must migrate more slowly than the NO'_3 ion, it follows that if the complex salt is actually formed and decomposes slowly enough to be studied, the conductivity of a standard solution of silver nitrate should be reduced on the introduction of acetonitrile to a degree depending on the amount of complex salt formed.

Measurements have therefore been made of the conductivity of aqueous mixtures of silver nitrate and iodoacetonitrile in comparison with solutions of silver nitrate of the same concentration. The conductivities have also been determined of solutions in methyl alcohol, ethyl alcohol, and acetone. The results show that the double compound, $AgNO_3,CH_2I{\cdot}CN$, does not exist to any appreciable extent in such mixtures, and its rapid precipitation from solutions of its components must therefore be due to its small solubility and not to its appreciable concentration at any moment.

E. G.

Direct Preparation of Metallic and Organic Sulphonates from Crude Sulphonation Products. Alphonse Seyewetz and L. Poizat (*Bull. Soc. chim.*, 1911, [iv], **9**, 247—253).—An extension of Gattermann's method (Abstr., 1891, 1226) for the preparation of sulphonates without the intervention of the barium salt.

The precipitation of sodium salts of sulphonic acids when sodium chloride is added to crude sulphonation products is due to the slight solubility of these salts in the excess of sulphuric acid present. This property is shown by all salts of sodium, which are decomposed by sulphuric acid and by similar salts of the alkali and other metals, and also of certain organic bases, and a large number of metallic benzenesulphonates have been prepared by this method and are described in this paper.

Hydroxylamine benzenesulphonate, colourless leaflets, and p-*aminophenyl benzenesulphonate,* colourless needles or leaflets, were also obtained in like manner. The corresponding *salts* of *phenylhydrazine*, m. p. 176°, and of *carbamide,* m. p. 162—163°, were obtained by adding the respective bases suspended in water to the crude sulphonation product; both are crystalline. These four salts are best purified by crystallisation, first from water and then from alcohol.

T. A. H.

Conversion of Benzenesulphondibromoamide into Dibromobenzenesulphonamide by means of Concentrated Sulphuric Acid. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1911, **45**, 219—223).—It has been shown by Benedikt (Abstr., 1879, 717) that when tribromophenol bromide is treated with concentrated sulphuric acid, it is converted into tetrabromophenol.

Since benzenesulphondibromoamide shows many analogies to tribromophenol bromide, it was considered of interest to ascertain whether it is similarly transformed by sulphuric acid. It has been found that a reaction occurs instantly at the ordinary temperature with liberation of traces of bromine and formation of a dibromobenzenesulphonamide, m. p. 194°, which is probably the *p*-dibromo-compound. A small quantity of another substance, m. p. 135—140°, is simultaneously produced, which contains 36% of bromine, but has not yet been identified.

E. G.

Triphenylmethyl. XX. MOSES GOMBERG and DONALD D. VAN SLYKE (*J. Amer. Chem. Soc.*, 1911, **33**, 531—549).—In earlier papers (Gomberg, Abstr., 1907, i, 504; 1909, i, 144) it has been stated that triphenylmethane compounds exist in both benzenoid and quinonoid forms. The present work was undertaken with the object of ascertaining whether ortho-quinonoid nuclei occur in the products of tautomerisation, or whether only para-quinonoid rings are formed. If the former is the case, the halogen atom should be just as reactive in the ortho-position as it has been found to be in the para-position in the tautomerised products, whilst if the *o*-halogen is inert it may be concluded that ortho-quinonoid modifications are not produced.

o-*Chlorotriphenylcarbinol*, $C_6H_4Cl\cdot CPh_2\cdot OH$, m. p. 95°, obtained by the action of ethyl *o*-chlorobenzoate on magnesium phenyl bromide, forms white crystals; the *chloride* has m. p. 136°, and the *ethyl ether*, m. p. 77°. o-*Chlorotriphenylmethylaniline*, $C_6H_4Cl\cdot CPh_2\cdot NHPh$, has m. p. 121°. o-*Chlorotetraphenylethane*, $C_6H_4Cl\cdot CPh_2\cdot CH_2Ph$, prepared by Gomberg and Cone's method (Abstr., 1906, i, 414), has m. p. 165·5°.

o-*Bromotriphenylcarbinol*, $C_6H_4Br\cdot CPh_2\cdot OH$, m. p. 104°, obtained by the action of ethyl *o*-bromobenzoate on magnesium phenyl bromide, forms white crystals; the *chloride* was also prepared. The *ethyl ether* has m. p. 69—70°. o-*Bromotriphenylmethylaniline*,

$$C_6H_4Br\cdot CPh_2\cdot NHPh,$$

has m. p. 126°, and o-*bromotetraphenylethane*, $C_6H_4Br\cdot CPh_2\cdot CH_2Ph$, m. p. 153°.

Di-p-*chloro*-o-*bromotriphenylcarbinol*, $C_6H_4Br\cdot C(C_6H_4Cl)_2\cdot OH$, m. p. 107°, obtained by the action of magnesium *p*-chlorophenyl iodide on ethyl *o*-bromobenzoate, forms white crystals; the *chloride* has m. p. 165°, and the *ethyl ether*, m. p. 107°. *Di*-p-*chloro*-o-*bromotriphenylmethylaniline*, $C_6H_4Br\cdot C(C_6H_4Cl)_2\cdot NHPh$, has m. p. 212°, and *di-*

p-*chloro*-o-*bromotetraphenylethane*, $C_6H_4Br{\cdot}C(C_6H_4Cl)_2{\cdot}CH_2Ph$, m. p. 162°.

Di-p-*chloro*-p-*bromotriphenylcarbinol*, $C_6H_4Br{\cdot}C(C_6H_4Cl)_2{\cdot}OH$, has m. p. 106°; the chloride has already been described (Abstr., 1907, i, 506); the *ethyl ether* has m. p. 188°. *Di*-p-*chloro*-p-*bromotriphenylmethylaniline*, $C_6H_4Br{\cdot}C(C_6H_4Cl)_2{\cdot}NHPh$, has m. p. 182°.

The action of molecular silver on the halogen-substituted triphenylmethyl chlorides has been studied, with the following results (compare Gomberg and Cone, Abstr., 1906, i, 824). Not a trace of the halogen in the ortho-position was removed in any case, and there is therefore no indication of the formation of an *o*-quinonoid nucleus. The total amounts of halogen in the para-position removed, in relation to the number of *p*-halogen atoms present, are in accord with Gomberg and Cone's results. Bromine in the para-position is more reactive towards molecular silver than is chlorine. The colorations produced by the action of molecular silver on the *o*-halogen derivatives are deeper and more brilliant than those produced with the corresponding para-derivatives.

Experiments have been made to ascertain the action of silver sulphate on ortho- and para-halogen derivatives of triphenylmethyl chloride, and Gomberg's conclusion (Abstr., 1907, i, 505) that the coloured triphenylmethyl sulphates have a quinonoid structure is confirmed. One para-halogen atom, and one only, becomes unstable, and can be readily removed by further action of the silver. The orthohalogen atoms are not affected. When one or two nuclei contain bromine and the other nucleus or nuclei chlorine, all in the paraposition, the transformation of the sulphate into the quinonoid form in methyl sulphate solution takes place almost entirely in the brominated nuclei.

The para-halogen atoms in the acid sulphates, unlike those in the normal sulphates, cannot be removed by the action of silver sulphate, owing to the sulphuric acid in the acid sulphates being directly combined with the para-halogen of the quinonoid nucleus.

When *o*-bromo- and di-*p*-chloro-*o*-bromo-triphenylmethyl chlorides are treated with sulphur dioxide and silver chloride in sealed tubes, no silver bromide is produced in either case.

There was not any evidence of the formation of *o*-quinonoid nuclei in any of the experiments with the *o*-bromo-derivatives, and the conclusion is therefore drawn that only *p*-quinonoid rings are formed.

E. G.

Decacyclene and its Alleged Property of Dissolving Graphite. MAURICE PADOA (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 345—347).—The yield of decacyclene by the method of Dziewonski (Abstr., 1903, i, 431) is poor. If, however, the sulphur and acenaphthene are heated together in a sealed tube for two hours at 200°, the high pressure then reduced, and the heating resumed for an hour at 250°, a yield of 12 grams of decacyclene is obtained for every 100 grams of acenaphthene. From an observation of the cooling curve, the m. p. was found to be 389·5°.

When in repetition of Ostromisslensky's experiment (Abstr., 1907, ii, 864) the hydrocarbon was heated at 500° for an hour with various samples of graphite, decomposition occurred. If a lower temperature was employed (430°), the cooling curve was that of the pure substance, and the graphite was recovered unchanged. R. V. S.

Colorations Produced by the Interaction of Aromatic Amino- and Nitro-compounds. JOHANN WALTER (*Zeit. Farb.-Ind.*, 1911, Reprint).—A description is given of the colorations produced when commercial dimethylaniline is treated with picric acid, styphnic acid, nitronaphthalene, nitrobenzene, *m*-dinitrobenzene, *o*- and *p*-nitrotoluenes, and dinitro-α-naphthol. Nitronaphthalene is coloured reddish-orange by dimethylaniline (or, better, by dimethyl- or diethyl-*p*-toluidine), the solution being yellow or orange-yellow; the reaction possibly could be used to detect the addition of nitronaphthalene to oils.

The colorations produced by the following aromatic bases on filter-paper soaked in a solution of trinitrotoluene in toluene and dried are described: dimethylaniline, aniline, *o*-toluidine, *p*-toluidine, ethylaniline, benzylethylaniline, dimethyl-α-naphthylamine, diethylaniline, amylaniline, dimethyl-*p*-toluidine, diethyl-*p*-toluidine, dimethyl-*o*-toluidine, nitrosodimethylaniline, diphenylamine, quinoline, tetramethyldiaminodiphenylmethane, tetramethyldiaminobenzophenone, diaminotriphenylmethane, tetramethyldiaminotriphenylmethane, hexamethyltriaminotriphenylmethane, α-naphthylamine, β-naphthylamine, anthranilic acid, *p*-aminobenzoic acid, dimethyl-*p*-aminobenzoic acid and its amide, anilide, and ethyl ester, *o*-tolylglycine, ethyl phenylglycine, phenylaminoacetonitrile, diethyl-*m*-aminophenol, *m*-aminophenol, indigotin, and tetramethyl-*m*-phenylenediamine. The prepared filter-paper did not give colorations with acridine, indolecarboxylic acid, phthalimide, benzamide, acetamide, acetanilide, carbamide, and bisphenylmethylpyrazolone.

Many of the preceding substances are only the commercial preparations; consequently, too much reliance must not be placed on the colorations. By a systematic study and comparison of the colorations produced by pure materials, the author thinks it should be possible to ascertain the presence of definite groups, their position, and method of union in substances of unknown or doubtful constitution. One or two interesting suggestions are made in the paper. The use of ether in the extraction of large volumes of dilute aqueous solutions of certain substances (dimethylaniline is the instance quoted) may be avoided by shaking the solution with trinitrotoluene, filtering, and decomposing the precipitate with dilute acid, whereby the substance is isolated (after basification, if necessary).

Dimethylaniline or dimethyl- or diethyl-*p*-toluidine probably could be used to detect trinitrotoluene in explosives.

When a solution of dimethylaniline in benzene is distilled on the water-bath, the presence of dimethylaniline in the distillate can be shown by the yellow coloration produced by trinitrotoluene. This proves that the solvent recovered by the distillation of a solution in a solvent of low b. p. is not pure, as is frequently assumed to be the case.

The naphthionic acid used in the preparation of dyes must be of good quality and free from α-naphthylamine in particular; the presence of the latter can be detected by the brownish-red coloration produced by trinitrotoluene paper. C. S.

Quantitative Investigations on the Nitration of Aniline. ARNOLD F. HOLLEMAN, J. C. HARTOGS, and T. VAN DER LINDEN (*Ber.*, 1911, **44**, 704—728).—The authors have investigated the composition of the products obtained when aniline and its acyl derivatives are nitrated under various conditions.

By nitrating aniline at −20° in sulphuric acid solution, *m*- and *p*-nitroanilines are produced in approximately equal quantities; the amount of the ortho-compound varies from 1—2%. When the nitration is effected by adding aniline nitrate to sulphuric acid, the amount of *m*-nitroaniline diminishes, whilst that of the ortho- and para-isomerides increases.

Formanilide, when nitrated with pure nitric acid, yields 2:4-dinitroformanilide; with 80% nitric acid the product consists of *o*- and *p*-nitroformanilides, the latter being present in the greater proportion; on nitration at −20° with the calculated amount of nitric acid in sulphuric acid solution, the product consists almost exclusively of the para-isomeride. Similar results were obtained in the nitration of acetanilide and of benzanilide.

The product obtained by nitrating acetanilide with acetyl nitrate at −25° consists of 76·7% of ortho-, 4·1% of meta-, and 20·2% of para-nitroacetanilide; the relative proportions are very similar when the nitration is carried out in carbon tetrachloride solution.

Since the concentration of the nitric acid employed has a considerable influence on the relative proportions of the isomerides, the effect of partly or wholly replacing the water by acetic acid was studied. In the case of acetanilide partial replacement of the water by acetic acid causes an increase in the amount of the para- and a diminution in that of the ortho-isomeride. By nitrating acetanilide with pure nitric acid containing 20% of glacial acetic acid, the product consists entirely of 2 : 4-dinitroacetanilide.

By the removal of water from aniline nitrate by means of acetic anhydride at 0°, *o*-nitroaniline is formed to the extent of 82·1%, meta- 2·9%, and para 15%.

The product obtained by the interaction of 74% sulphuric acid and phenylnitroamine at −20° consists almost exclusively of *o*-nitroaniline.

From these results the authors draw the conclusion that by the direct nitration of aniline and its derivatives the product consists mainly of the para-compound, together with small quantities of the ortho-compound. This is, however, modified by two causes: (1) the formation of aniline sulphate and the introduction of acyl groups in the amino-group, both of which lead to the formation of the meta-substituted product; (2) the intermediate formation of phenylnitroamine, which gives rise to *o*-nitroaniline.

For the determination of the relative amounts of the three nitroanilines in a mixture, thermal methods of analysis were employed. The freezing-point curves of binary mixtures of the three nitroanilines, together with certain portions of the eutectic lines leading from the three binary eutectics to the ternary eutectic point, were first determined. The composition of a mixture of the nitroanilines was then deduced from these portions of the ternary diagram by determining the first and second freezing-points of the mixture.

Since the freezing point of any one of the nitroanilines is depressed to the same extent by the addition of equal quantities of either of the other two isomerides, the composition of a ternary mixture may be determined by adding a sufficient quantity of one of the nitroanilines to the mixture, so that this isomeride crystallises out at the initial freezing point. From the position of this point on the binary freezing-point curves, the relative amount, in the original mixture, of that isomeride which crystallises out may be calculated.

An apparatus for the determination of freezing points is described. It closely resembles Thiele's melting-point apparatus, but the open tube of the latter is inserted in one of the side limbs, which is widened and contains a test-tube in which is placed the mixture, the freezing point of which is to be determined. F. B.

Unsymmetrical Aromatic Derivatives of Oxamide. II.

HERMANN SUIDA, jun. (*Monatsh.*, 1911, **32**, 197—223).—In continuation of the former investigation (Abstr., 1910, i, 665), unsymmetrical oxanilides have been prepared containing the $-CO_2H$, $-NH_2$, $-OH$, and $-N:NPh$ groups. Also a phenyl-α-naphthyloxamide has been obtained containing a nitro-group in each nucleus. An oxanilide monosulphonate could not be obtained from ethyl oxanilate and aminobenzenesulphonate. In all cases the yields were very unsatisfactory. In some cases the desired reactions become subordinated to other reactions, for example, in the interaction of ethyl oxanilate with *p*-phenylenediamine or with *m*-aminophenol. The material so far obtained is insufficient to determine the influence of the substituents on the course of fission with alcoholic potassium hydroxide.

Oxanilide-o-*carboxylic acid*, $NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot CO_2H,H_2O$, is obtained by heating ethyl oxanilate and anthranilic acid for three hours at 140—150°; it forms colourless, shining needles, m. p. 226—227°; the water of crystallisation is lost at 105—110°. With dichromate and sulphuric acid it gives a blood-red colour (Tafel's reaction). The *ammonium* salt is an acid salt,

$$C_{15}H_{12}O_4N_2,C_{15}H_{11}O_4N_2\cdot NH_4,$$

and loses ammonia a few degrees below 226—227°. The *potassium* salt, $C_{15}H_{11}O_4N_2K,4H_2O$, forms rhombic needles [$b:c = 1:0.347$]. The *silver*, *calcium*, *barium*, and *copper* salts were also prepared. Under the action of alcoholic potassium hydroxide the acid decomposes into aniline and kynuric acid (oxalylanthranilic acid).

p-*Phenylazo-oxanilide*, $NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot N:NPh$, results from the interaction of ethyl oxanilate and *p*-aminoazobenzene at 130—150°, and repeated extraction of the cold fusion with benzene. It forms ochre-yellow crystals, m. p. 256—257°, and gives a dark carmine colour with Tafel's reaction. Alcoholic potassium hydroxide decomposes it into *p*-aminoazobenzene and oxanilic acid.

p-*Amino-oxanilide*, $NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot NH_2$, could not be prepared by the reduction of either *p*-nitro-oxanilide or *p*-phenylazo-oxanilide. It is obtained by the condensation of ethyl oxanilate and *p*-phenylenediamine at 150—155° in an atmosphere of carbon dioxide. If the condensation is carried out in the air, a deep blue mass is obtained. The amino-oxanilide is obtained from this as colourless prisms and plates, m. p. 215°, by extraction with alcohol; it gives a dull carmine-red colour, with a brownish tinge, with Tafel's reaction. The *hydrochloride*, $C_{14}H_{13}O_2N_3,HCl$, and the *sulphate*, $(C_{14}H_{13}O_2N_3)_2,H_2SO_4$, are prepared by adding the respective acids to the hot alcoholic solution of the base. Alcoholic potassium hydroxide decomposes the oxanilide into aniline, *p*-phenylenediamine, oxanilic acid, and *p*-amino-oxanilic acid.

The residue insoluble in alcohol is also practically insoluble in all organic solvents, but soluble in hot concentrated sulphuric acid. It could not be identified.

By the nitration of phenyl-α-naphthyloxamide (*loc. cit.*) with concentrated nitric acid ($D = 1\cdot4$), a mixture of p-*nitrophenyl*-4-*nitro*-α-*naphthyloxamide*, $NO_2\cdot C_6H_4\cdot NH\cdot C_2O_2\cdot NH\cdot C_{10}H_6\cdot NO_2$, and o-*nitrophenyl*-4-*nitro*-α-*naphthyloxamide*, is obtained. The former compound is the chief product of reaction, and can be separated from the latter by recrystallisation from glacial acetic acid; it forms slender, yellow needles, which sinter at 230° (decomp.); it does not give Tafel's reaction. The latter compound gives a dark brownish-red colour with Tafel's reaction. Fission with alcoholic potassium hydroxide gives the *p*- and *o*-nitroanilines respectively, and 4-nitro-1-naphthylamine; the acids formed at the same time could not be separated and identified.

Ethyl oxanilate and *m*-aminophenol interact readily at 150—160°. The main product of the reaction is extracted with alcohol, and gives pale rose-coloured, monoclinic tablets, m. p. 246—247°. Analysis points to the formula $4C_{14}H_{12}O_3N_2-H_2O$, that is, an anhydride compound formed from three molecules of *m*-hydroxyanilide and one molecule of oxanilide. This formula is confirmed by the preparation of a *triacetyl* derivative, $C_{64}H_{54}O_{15}N_8$, m. p. 176—178°, although the ebullioscopic determination of the molecular weight in glacial acetic acid points to the simple formula $C_{14}H_{12}O_3N_2$. With alcoholic potassium hydroxide, aniline, *m*-aminophenol, and oxalic acid are formed. On shaking with dilute aqueous sodium hydroxide, m-*hydroxyoxanilide*,

$$NHPh\cdot C_2O_2\cdot NH\cdot C_6H_4\cdot OH,$$

is continually extracted, and this compound is also obtained from the alcoholic mother liquors of the above-mentioned anhydride compound. If forms peach-red coloured leaflets, m. p. 246°, and is decomposed by alcoholic potassium hydroxide into oxanilic acid, *m*-hydroxyoxanilic acid, aniline, and *m*-aminophenol. T. S. P.

Keto-ester Additive Products with Arylamines and Alcohols.

Richard S. Curtiss, Harry S. Hill, and R. H. Lewis (*J. Amer. Chem. Soc.*, 1911, **33**, 400—405).—Curtiss and Spencer

(Abstr., 1909, i, 763) have given an account of a study of the action of alcohols and amines on methyl oxomalonate. The investigation has now been extended to ethyl oxomalonate.

When ethyl oxomalonate is treated with arylamines, additive compounds of the type $R\cdot NH\cdot C(CO_2Et)_2\cdot OH$ are first produced, which are capable of undergoing further reaction with formation of compounds of the type $(NHR)_2C(CO_2Et)_2$.

In the case of aniline, evidence was obtained of the formation of the compound $NHPh\cdot C(CO_2Et)_2\cdot OH$, but this substance could not be isolated, as it immediately reacts with another molecule of aniline with production of ethyl dianilinomalonate (Curtiss, Abstr., 1897, i, 556).

o- and *p*-Toluidine react with ethyl oxomalonate to form *ethyl* o-*toluidinotartronate*, $C_6H_4Me\cdot NH\cdot C(CO_2Et)_2\cdot OH$, m. p. 92°, and *ethyl* p-*toluidinotartronate*, m. p. 95°, which crystallise in radiating needles; the *acetyl* derivative of the latter compound has m. p. 150°. *m*-Toluidine also reacts with ethyl oxomalonate, but the product was not obtained in a pure condition. When a solution of ethyl *p*-toluidinotartronate in dry ether is treated with phosphoric oxide, a thick, green oil is produced, the properties of which resemble those of methyl phenyliminomalonate (Curtiss and Spencer, *loc. cit.*); when left in the air, it absorbs moisture, and is reconverted into ethyl *p*-toluidinotartronate. Phosphorus trichloride also reacts with ethyl *p*-toluidinotartronate, with production of ethyl *p*-tolyliminomalonate,

$$C_6H_4Me\cdot N{:}C(CO_2Et)_2,$$

which is decomposed by potassium carbonate into *p*-toluidine and ethyl mesoxalate.

Benzylamine reacts with ethyl oxomalonate, but the product could not be isolated in a pure state.

When ethyl oxomalonate (1 mol.) is treated at $-13°$ with methyl, ethyl, or benzyl alcohol (1 mol.), a colourless syrup is obtained in each case, which dissociates into the original constituents on heating, and cannot be crystallised or distilled. These compounds are doubtless *ethers* of ethyl dihydroxymalonate, $OH\cdot C(CO_2Et)_2\cdot OR$, corresponding with the product obtained by Curtiss and Spencer (*loc. cit.*) by the action of ethyl alcohol on methyl oxomalonate. E. G.

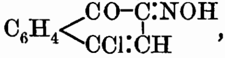
Isomerism and Polymorphism. EINAR BIILMANN (*Ber.*, 1911, **44**, 827—837).—The classification of isomerism by Kruyt (Abstr., 1910, ii, 285) into three classes, for example, phase isomerism, component isomerism, and dynamic isomerism. is criticised as quite unnecessary, dynamic isomerism, being regarded as only a special case of phase isomerism. Two substances of the same molecular composition are either identically constructed (polymorphic) or of different structure (isomeric).

Isomerisation, denoting the conversion of a substance *A* into another *B* of the same composition, is either spontaneous and complete, or when a mixture of *A* and *B* is formed, whichever was originally taken, it is reciprocal.

Homochromoisomerism (Hantzsch, Abstr., 1910, i, 474), in which the isomerides differ in m. p. and solubility, but are identical chemically and optically, is considered to be completely explained by the ordinary conceptions of polymorphism. The case of picrylphenylmethylamine studied by Hantzsch (*loc. cit.*), which exists in two modifications, m. p. 108—110° and m. p. 128—129° respectively, has been further investigated.

The amine, m. p. 128°, crystallised from benzene, yields the amine, m. p. 108°, but contrary to Hantzsch, the reverse change could not be effected. The two amines are converted into one another by fusion and innoculation. The amine, m. p. 108°, when heated at 100° or at a temperature above 108°, is converted into the amine, m. p. 128°. The reverse change takes place when the amine, m. p. 128°, is heated for a short time above this temperature and quickly cooled. E. F. A.

Chlorination of α-Naphthol. ARNOLD REISSERT (*Ber.*, 1911, **44**, 865—869).—4-Chloro-α-naphthol, which cannot be obtained by the direct chlorination of α-naphthol, is readily produced by treating a methyl-alcoholic solution of 1-hydroxy-2-naphthoic acid with chlorine (1 mol.) at 30—40°, and heating the resulting *4-chloro-1-hydroxy-2-naphthoic acid*, m. p. 234°, with aniline and naphthalene at 170—180°, whereby carbon dioxide is eliminated.

4-Chloro-1-hydroxy-2-naphthoic acid reacts with boiling aqueous sodium nitrite to form a *compound*, $C_{10}H_6O_2NCl,C_{11}H_7O_3Cl$, of chlorohydroxynaphthoic acid and 4-chloro-β-naphthaquinoneoxime. *4-Chloro-β-naphthaquinoneoxime*,  $C_6H_4<\begin{array}{l}CO-C{:}NOH\\ \quad\;\;|\\ CCl{:}CH\end{array}$, m. p. 157°, pale yellow needles, is obtained by treating an alcoholic solution of 4-chloro-1-naphthol at 0° with concentrated hydrochloric acid and sodium nitrite; it is purified by means of its sparingly soluble, red *sodium* salt.

C. S.

4-Nitroresorcinol. HUGO KAUFFMANN and W. KUGEL (*Ber.*, 1911, **44**, 753—756).—The nitro-derivatives of dihydric phenols are most readily prepared by nitrating their monobenzoates. Resorcinol monobenzoate yields two isomeric nitro-derivatives, but both yield 4-nitroresorcinol (Weselsky and Benedikt, Abstr., 1881, 727) on hydrolysis.

Resorcinol monobenzoate crystallises from benzene, and has m. p. 133°; it is best nitrated by dissolving in ten times its weight of glacial acetic acid, cooling to 20—22°, adding nitric acid (D 1·2), and allowing the temperature to rise to 36—38° and then diluting with its own volume of water. It is essential to work under specific conditions, as otherwise resinous masses or the original compound are obtained. The 1 : 3 : 4-*derivative* is sparingly soluble in chloroform, and crystallises from 50% alcohol in colourless needles, m. p. 189°; it dissolves in dilute sodium carbonate, yielding a yellow solution; the isomeric 1 : 3 : 6-*derivative* is readily soluble in chloroform, crystallises from glacial acetic acid in yellow needles, m. p. 124°, and with sodium carbonate yields a sparingly soluble, orange-coloured sodium derivative. 4-Nitroresorcinol has m. p. 122° (not 115°), and its dimethyl ether, m. p. 75°. J. J. S.

New Series of Aromatic Sulphur Compounds. THEODOR ZINCKE (*Ber.*, 1911, **44**, 769—771).—Compounds of the type

$C_6H_5{\cdot}SCl$ can be obtained by the action of chlorine on the benzyl ethers of aromatic mercaptans. The reaction is entirely different from that between the corresponding methyl ethers and chlorine (Abstr., 1909, i, 644; 1910, i, 314; this vol., i, 40). The same type of compound is also formed by the action of chlorine on the mercaptans or their disulphides.

4 : 4′-*Dichlorothioldiphenyl*, $SCl{\cdot}C_6H_4{\cdot}C_6H_4{\cdot}SCl$, crystallises from carbon tetrachloride in yellow prisms, m. p. 115°, and decomposes at 140°. 4 : 6-*Dichloro*-1 : 3-*dichlorothiolbenzene*, $C_6H_2Cl_2(SCl)_2$, obtained by the action of chlorine on a chloroform solution of 1 : 3-dithiolbenzene, crystallises from hexane in yellow needles, m. p. 103°. o-*Nitrochlorothiolbenzene*, $NO_2{\cdot}C_6H_4{\cdot}SCl$, prepared by the action of chlorine on *o*-*o*′-dinitrodiphenyl disulphide suspended in carbon tetrachloride, crystallises in long, yellow needles, m. p. 75°. The chlorine derivatives are transformed into disulphides when boiled with alcohol or treated with aqueous alkali solutions. They also react with acetone, the chlorine of the $\cdot SCl$ group being replaced by $\cdot CH_2{\cdot}CO{\cdot}CH_3$.

The corresponding bromine derivatives are not so easy to prepare, and the compound described by Otto (*Annalen*, 1868, **145**, 329) as $C_6H_5{\cdot}SBr$ is shown to be the disulphide $(C_6H_4Br)_2S_2$. J. J. S.

Action of Ethyl Alcohol on Toluene-*p*-diazonium Hydrochloride and of Sulphuric Acid on *p*-Tolyl Ethyl Ether.

PERCIVAL RUDOLPH ROBERTS and GELLERT ALLEMAN (*J. Amer. Chem. Soc.*, 1911, **33**, 391—396).—In an earlier paper (Alleman, Abstr., 1904, i, 202), it was shown that *p*-tolyl methyl ether can be readily obtained by the action of methyl alcohol on *p*-toluenediazonium sulphate, and that when treated with sulphuric acid, it is converted into *p*-methoxytoluene-*m*-sulphonic acid. Attempts to prepare *p*-tolyl ethyl ether in a similar manner did not yield good results, but a method is now described by which it can be obtained in a yield of 35% of the theoretical.

The diazonium compound is prepared from *p*-toluidine hydrochloride instead of the sulphate, as the former is more soluble in ethyl alcohol. The ethyl ether is thus obtained as an oil, b. p. 187—191°, $[n]_D^{15}$ 1·51069, which is identical with the compound described by Engelhardt and Latschinow (*Zeitsch. Chem.*, 1869, 619).

p-Tolyl ethyl ether reacts with concentrated sulphuric acid at the ordinary temperature with formation of p-*ethoxy*-m-*toluenesulphonic acid*, $OEt{\cdot}C_6H_3Me{\cdot}SO_3H$, m. p. 92—92·5°, which forms colourless, transparent crystals; its *barium*, *potassium*, *sodium*, *calcium*, *zinc*, *nickel*, *copper*, and *lead* salts are described. E. G.

Hexahydrohippuric Acid.

MARCEL GODCHOT (*Bull. Soc. chim.*, 1911, [iv], **9**, 261—264).—The preparation of hexahydrohippuric acid and of a number of its derivatives is described.

*cyclo*Hexanecarboxyl chloride, b. p. 179—180°/760 or 100°/40 mm. (compare Meyer and Scharvin, Abstr., 1897, i, 612), reacts with glycine to form *hexahydrohippuric acid*, $C_6H_{11}{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$, m. p. 152°, which crystallises in colourless needles, is sparingly soluble in water, alcohol, or ether, but much more so on warming, reddens litmus, and gives a characteristic *copper* salt. The *methyl* ester, m. p. 100—101°, and the *ethyl* ester, m. p. 75—76°, both crystallise in needles. The *amide*, m. p. 195—196°, obtained from the ethyl ester by the action of ammonia solution, separates from warm water in small crystals. On distillation at atmospheric pressure with zinc chloride, the acid furnishes *cyclo*hexanecarboxylonitrile, b. p. 184—185°/760 mm. (compare Demjanoff, Abstr., 1904, i, 410).

T. A. H.

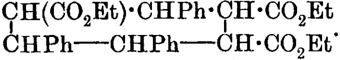
Ethyl Polycinnamate. Carl Liebermann and Milan Zsuffa (*Ber.*, 1911, **44**, 841—849).—In connexion with attempts to accelerate the rate of spontaneous polymerisation of the esters of cinnamic acid, the authors have prepared methyl, *iso*amyl, benzyl, allyl, and *octyl* cinnamates. The last is obtained by boiling equal molecular quantities of cinnamyl chloride and octan-β-ol in three times the weight of benzene to which pyridine (1·5 mol.) is added, and has b. p. 240°/60 mm. However, only the ethyl and the *iso*amyl esters polymerise to an extent suitable for practical purposes. After many trials, the following process is adopted, by which polymerised ethyl cinnamate is obtained in comparatively large quantities. Ethyl cinnamate, about 100—200 grams, is distilled under ordinary pressure, and the distillate is inoculated with the polymeride and heated for some days at 80—85°. The liquid becomes gelatinous, and contains about 6% of the isomeride; the latter is precipitated by ether and removed, whilst the unchanged ester, after being recovered, is redistilled and again treated as above. In this way about 20% of the ethyl cinnamate can be converted into its polymeride.

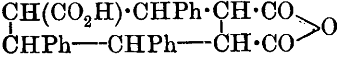
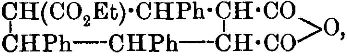
The esters of polycinnamic acid are white, infusible, friable substances, which are almost insoluble in all solvents, and are odourless even after very long keeping. When heated, ethyl polycinnamate at first blackens, but as depolymerisation occurs, the distillation proceeds smoothly, and almost the whole of the polymeride is obtained as ethyl cinnamate.

Ethyl polycinnamate resists hydrolysis even by prolonged boiling with concentrated aqueous or alcoholic potassium hydroxide, acetic and 50% sulphuric acids, or *p*-toluidine. The hydrolysis can be effected, although not completely, by the following two methods. The polymeride is covered with a little acetic anhydride, and heated for ten to twelve hours at 160° with hydriodic acid, D 1·96, whereby ethyl iodide is produced; the product is washed with very dilute sulphurous acid and with very dilute alkali, is dissolved in boiling water, and the polycinnamic acid is precipitated in gelatinous flocks by hydrochloric acid. In the second method the ethyl polycinnamate is intimately mixed with aluminium chloride and antimony chloride, and is heated for some hours on the water-bath, and finally at 130—140° for two to three hours; the product is digested with 25% hydrochloric acid, washed with 35% tartaric acid and with water, and is finally dissolved in hot alkali and precipitated as above.

Polycinnamic acid (?), m. p. above 260°, is stable to alkaline potassium permanganate. Its analysis points to the composition $C_{27}H_{22}O_5$, that is, 3 mols. of cinnamic acid minus 1 mol. of water, whilst titration with *N*/10-sodium hydroxide and phenolphthalein shows that it is dibasic.

The authors make the following deductions from the preceding results. Ethyl polycinnamate, which is undoubtedly a true polymeride of ethyl cinnamate, probably has the constitution :



The polycinnamic acid (?) obtained by its hydrolysis would then be  Since, however, an acid of this constitution would be either mono- or tri-basic, and, moreover, since in the ester the carbethoxy-group between the two CHPh groups very probably is unattacked during hydrolysis, polycinnamic acid (?) might have the constitution: , a formula which does not agree quite as well as the former with the analytical results, but has the advantage of representing polycinnamic acid (?) as the anhydride of a dibasic acid. C. S.

The Utilisation of Carbalkyloxy-derivatives for the Estimation of Hydroxyl Groups.

K. C. R. DANIEL and MAXIMILIAN NIERENSTEIN (*Ber.*, 1911, **44**, 701—704).—The method of estimation consists in hydrolysing the carbalkyloxy-derivative by heating it with 50% pyridine at 115—120°, and weighing the carbon dioxide evolved, the gas being freed from pyridine vapour by passing through a tube containing a mixture of oxalic acid and calcium chloride. A sketch of the apparatus employed is given.

The following new compounds, prepared according to Fischer's method, are described :

m-*Ethylcarbonatobenzoic acid*, $CO_2Et{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H$, crystallises in needles, m. p. 98°.

p-*Nitrophenyl ethyl carbonate*, $CO_2Et{\cdot}O{\cdot}C_6H_4{\cdot}NO_2$, forms needles, m. p. 67—68°.

4-*Ethylcarbonato*-m-*nitrobenzoic acid*, $CO_2Et{\cdot}O{\cdot}C_6H_3(NO_2){\cdot}CO_2H$, crystallises in pale yellow cubes, m. p. 176—177°. F. B.

Carbamides Derived from α-Amino-*p*-hydroxyphenylacetic Acid and its Methyl Ether.

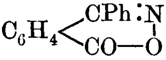
JULES ALOY and CHARLES RABAUT (*Bull. Soc. chim.*, 1911, [iv], **9**, 253—255. Compare Abstr., 1910, i, 558).—Phenylcarbamide and carbamide derivatives of these two acids have been prepared, similar to those obtained by Hugounenq and Morel from tyrosine and leucine (Abstr., 1906, i, 85).

The sodium salt of α-amino-*p*-hydroxyphenylacetic acid reacts with phenylcarbimide to form diphenylcarbamide and a mixed *carbamide*, $NHPh{\cdot}CO{\cdot}NH{\cdot}CH(CO_2H){\cdot}C_6H_4{\cdot}OH$, m. p. 193°, which is sparingly soluble in water, readily so in alcohol, and insoluble in ether or chloroform. α-Amino-*p*-methoxyphenylacetic acid gives a similar derivative, m. p. 198° (approx.). When the sodium salts of the two amino-acids are treated with carbonyl chloride, they give rise to the corresponding symmetrical *derivatives* of carbamide, $CO[NH{\cdot}CH(CO_2H){\cdot}C_6H_4{\cdot}OH]_2$

and $CO[NH·CH(CO_2H)·C_6H_4·OMe]_2$ respectively. Both are amorphous, pale yellow powders; the second has m. p. 150° (decomp.).
T. A. H.

Preparation of 3:5-Di-iodotyrosine from Iodoproteins. II. The Obtaining of the Same from Iodoglidin. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **71**, 200—203. Compare this vol., i, 203).—It has been shown previously that 3:5-di-iodotyrosine is obtained from the commercial iodised protein called iodo-albacid. The same product is also obtained from iodo-glidin, an iodised protein containing 9·2% of iodine in organic combination, prepared from wheat.
W. D. H.

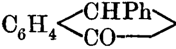
Reduction of the Anhydroxime of *o*-Benzoylbenzoic Acid. ROBERT EVSTAFIEFF ROSE (*J. Amer. Chem. Soc.*, 1911, **33**, 388—391).—The oxime of *o*-benzoylbenzoic acid, like those of other compounds containing a carboxyl group in the ortho-position to the carbonyl group, cannot exist in the free state, but, when liberated from its alkali salts, is instantly converted into the anhydride,



$C_6H_4<\begin{matrix}CPh:N\\ CO—O\end{matrix}$

(Thorp, Abstr., 1893, i, 446, 589).

This anhydro-compound has m. p. 161—163°. When reduced with zinc dust and glacial acetic acid, it yields a stable, crystalline *lactam*,



$C_6H_4<\begin{matrix}CHPh\\ CO\end{matrix}>NH$, m. p. 218—220°, which furnishes an *acetyl* derivative, m. p. 153—155°. If the lactam is heated with concentrated sulphuric acid for four hours at 160—170°, a sulphonic acid is produced, which yields a *barium* salt, $(C_{14}H_{10}O_4NS)_2Ba,2H_2O$. On distilling the lactam with zinc dust, a strongly fluorescent, oily product was obtained, which contained carbazole; the fluorescent substance was not present in sufficient quantity to enable it to be identified.
E. G.

Benzoylphenylacetamide. TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1911, **33**, 517—520).—By the action of benzoyl chloride on phenyl-phenylethenylamidine, Wheeler, Johnson, and McFarland (Abstr., 1903, i, 859) obtained benzoylphenylacetamide, m. p. 129—130°. Benzoylphenylacetamide was previously described by Colby and Dodge (Abstr., 1891, 409), who obtained it by heating benzonitrile with phenylacetic acid, or phenylacetonitrile with benzoic acid, and found its m. p. to be 171°. On repeating Colby and Dodge's experiments, it has been found that the product obtained is not benzoylphenylacetamide, but a mixture of dibenzamide and diphenyldiacetamide.

Benzoylphenylacetamide, m. p. 129—130°, can be prepared in nearly theoretical yield by the action of benzoylcarbimide on phenylacetic acid at the ordinary temperature, and the product thus obtained is identical with that described by Wheeler, Johnson, and McFarland (*loc. cit.*).

When benzoylthiocarbimide is heated with phenylacetic acid at 104—110°, diphenyldiacetamide is produced.

Benzoylcarbimide reacts readily with β-phenylpropionic acid, with formation of β-phenylpropionylbenzamide, m. p. 104—105° (Colby and Dodge, *loc. cit.*). E. G.

Fulgides. Hans Stobbe (*Annalen*, 1911, **380**, 1—129. Compare Abstr., 1904, i, 588, 589, 672, 673; 1905, i, 857; 1906, i, 22, 91, 92, 101, 183, 278, 279, 361, 960; 1908, ii, 339).—I. *Relation between Colour and Constitution of Fulgides.*—The absorption spectra of chloroform solutions of the following compounds have been determined, using a Nernst lamp placed 30 cm. from a 10 mm. layer of a 1/32*N*-solution and giving an exposure of three minutes: α-phenyl-, α-*p*-tolyl-, α-cumyl-, α-*o*-nitrophenyl-, α-*m*-nitrophenyl-, α-*o*-anisyl-, α-anisyl-, α-veratryl-, and α-piperonyl-δδ-dimethyl-fulgide; α-phenyl-αδδ-triphenylfulgide; αδ-diphenyl-, αδ-diphenyl-δ-methyl-, αα-diphenyl-δδ-dimethyl-, α-anisyl-δ-phenyl-, α-piperonyl-δ-phenyl-, αδ-dicumyl-, αδ-dianisyl-, αδ-diveratryl-, αδ-dipiperonyl-, and αδδ-triphenyl-fulgide; α-*p*-tolyl-, α-cumyl-, α-*p*-chlorophenyl-, α-*o*-nitrophenyl-, α-*m*-nitrophenyl-, α-*p*-nitrophenyl-, α-*o*-anisyl-, α-anisyl-, α-veratryl-, and α-piperonyl-δδ-diphenylfulgide; ααδδ-tetraphenylfulgide. Photographs of the absorption spectra and the value of the absorption limit in the violet end of the spectrum are given. The absorption depends on three factors: (*a*) the unsaturated (quinonoid) structure of the fulgide ring; (*b*) the number of aryl groups present, and (*c*) the nature and position of the auxochromes present in the aryl groups. An increase in the number of aryl groups increases the absorption in the violet end; the presence of alkyl, nitro-, and methoxy-groups also tends to increase the absorption, more especially when they are in the para-position. When present in the meta-position the effect is only slight. By suitably varying *b* and *c*, it is possible to obtain fulgides with any desired nuance.

The colour tone can also be altered by the introduction of a large number of olefine linkings in the fulgide molecule; for example, by introducing styryl in place of phenyl groups. Thus α-phenyl-δδ-dimethylfulgide is sulphur-yellow, whereas the corresponding α-styryl compound is golden-yellow; the αδ-diphenyl compound is lemon-yellow, and the α-styryl-δ-phenyl derivative orange; the αδδ-triphenyl compound, orange-red, and the α-styryl-δδ-diphenylfulgide, ruby-red (compare also Fittig and Batt, Abstr., 1904, i, 744). Naphthylfulgides have deeper colours than the corresponding phenyl derivatives, and, similarly, the α-diphenylenefulgides have deeper colours than the corresponding α-diphenyl compounds.

II. *Thermochromic Phenomena* (compare Stobbe and Vigier, Abstr., 1904, i, 672; Hantzsch, 1906, i, 353; Senier and Shepheard, Trans., 1909, **95**, 1943).—The colours of the various fulgides have been examined at the ordinary temperature, at −80° to −180°, and at higher temperatures, namely, 70° to 140°. A rise of temperature produces a change in colour, indicated by the order: greenish-yellow, yellow, orange, brown, red, purple, violet, blue, and a fall in temperature a change in the opposite direction. For any given compound each temperature has a corresponding colour tone, and the colour of the compound always returns to the tone corresponding with the temperature at which it is kept. The changes which the pale yellow monoarylfulgides undergo are not so marked as those characteristic of the deeper coloured polyaryl compounds, that is, the latter compounds are more sensitive to thermochromic influences. The solid fulgides are also phototropic (Abstr., 1908, ii, 339), and the deepening in colour produced by exposure to light can be removed by a slight increase in temperature, and by a further rise of temperature a second deepening of the colour is produced. The conclusion is drawn that all compounds which are both phototropic and thermochromic undergo two distinct reversible changes which are characterised by colour alterations.

III. *Monoarylfulgenic Acids and their Fulgides.*—By the condensation of an aromatic aldehyde with ethyl tetraconate in the presence of sodium ethoxide a single fulgenic acid is usually obtained.

Cuminaldehyde, however, yields two stereoisomeric α-cumyl-δδ-dimethylfulgenic acids (Abstr., 1906, i, 22), together with an isomeric lactonic acid, and *p*-chlorobenzaldehyde yields mainly a lactonic acid. All the monoarylfulgenic acids are oxidised by permanganate to oxalic acid, acetone, and the aldehyde from which they were synthesised. Acetyl chloride transforms the acids into their yellow anhydrides, each acid yielding as a rule a corresponding fulgide. The two stereoisomeric cuminyldimethylfulgenic acids yield stereoisomeric fulgides; the *allo*-fulgide has a somewhat broader absorption band ($\lambda = 412\mu\mu$) than the isomeride ($\lambda = 407\mu\mu$). α-Phenyl-δδ-dimethylfulgenic acid yields two stereoisomeric fulgides, the one colourless and the other yellow; both have the same m. p. and the same chemical properties, but the colours of their solutions are different.

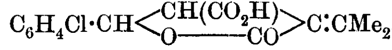
[With ALFRED LENZNER].—*α-Veratryl-δδ-dimethylfulgenic acid,*

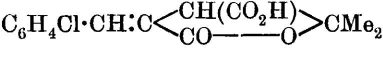
$$CMe_2{:}C(CO_2H)\cdot C(CO_2H){:}CH\cdot C_6H_3(OMe)_2,$$

crystallises from water in nodular masses, m. p. 194·5° (decomp.) after sintering at a lower temperature; the corresponding *fulgide*, $C_{16}H_{16}O_5$, crystallises from light petroleum in yellow prisms, resembling sodium picrate, and has m. p. 127·5°. *α-Piperonyl-δδ-dimethylfulgenic acid,* $CMe_2{:}C(CO_2H)\cdot C(CO_2H){:}CH\cdot C_6H_3{:}O_2{:}CH_2$, separates as colourless crystals from ethyl acetate, and has m. p. 203—204°; when reduced with sodium amalgam in alkaline solution, it yields *ε-piperonyl-β-methyl-*Δ^{β}*-pentene-γδ-dicarboxylic acid,*

$$CH_2O_2{:}C_6H_3\cdot CH_2\cdot CH(CO_2H)\cdot C(CO_2H){:}CMe_2,$$

which crystallises from 10% acetic acid, and has m. p. 135° (decomp.). *α-Piperonyl-δδ-dimethylfulgide,* $C_{15}H_{12}O_5$, forms yellow crystals, m. p. 145—146°. A by-product, formed in the preparation of the fulgenic acid, crystallises from chloroform in yellow needles, m. p. 191°, and is probably *dimethylenedioxystilbene,* $C_2H_2(C_6H_3{:}O_2{:}CH_2)_2$; it yields a *dibromide,* m. p. 173°.

[With EMIL WAHL.]—The *lactonic acid,* obtained by condensing *p*-chlorobenzaldehyde with ethyl tetraconate and sodium ethoxide in the presence of anhydrous ether, is either *γ-p-chlorophenyl-α-*iso*propylene-paraconic acid,*  $C_6H_4Cl\cdot CH<\begin{matrix}CH(CO_2H)\\ O\text{——————}CO\end{matrix}>C{:}CMe_2$, or *α-p-chloro-benzylidene-γγ-dimethylparaconic acid,*



$$C_6H_4Cl\cdot CH{:}C<\begin{matrix}CH(CO_2H)\\ CO\text{——————}O\end{matrix}>CMe_2.$$

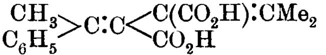
It crystallises from ether, has m. p. 220°, and when warmed with acetyl chloride the greater portion is recovered unaltered, but a small amount of *a*-p-*chlorophenyl-δδ-dimethylfulgide* is obtained as pale yellow crystals, m. p. 133°, and $\lambda = 415\mu\mu$.

IV. *The Stereoisomeric Ethyl Phenylmethylitaconates and their Colour Reactions* (compare Abstr., 1904, i, 503).—The *cis*-acid with concentrated sulphuric acid yields a yellow methylindoneacetic acid, the solution of which in sulphuric acid has a deep violet coloration. The normal and acid esters of the *cis*-acid give the same coloration. The *trans*-acid and its esters, on the other hand, dissolve in concentrated sulphuric acid, yielding yellow solutions, and this difference in coloration affords a basis for determining whether in such compounds the phenyl and carboxyl groups are in the *cis*- or *trans*-positions with respect to one another.

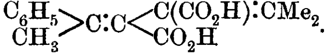
[With FERDINAND GADEMANN.]—Ethyl phenylmethyl*iso*itaconate (Abstr., 1899, i, 902) is best prepared from the silver salt of the ethyl hydrogen ester, and has b. p. 305—307°.

[With ROBERT ROSE.]—*Ethyl phenylmethylitaconate*, $C_{16}H_{20}O_4$, when prepared by the hydrogen chloride or sulphuric acid catalytic method contains a certain amount of anhydride; it is best prepared from the silver salt, and is a pale yellow oil, b. p. 314—316°. The corresponding *methyl* ester, $C_{14}H_{16}O_4$, has b. p. 182·5—183°/20 mm.

V. *The Stereoisomeric Phenyltrimethylfulgenic Acids and their Fulgides.*—[With FERDINAND GADEMANN.]—*a*-Phenyl-*a*δδ-trimethylfulgenic acid exists in two stereoisomeric modifications:



$$\begin{matrix}CH_3\\C_6H_5\end{matrix}\!\!>C{:}C<\!\!\begin{matrix}C(CO_2H){:}CMe_2\\CO_2H\end{matrix}$$

and, *allo*,  $\begin{matrix}C_6H_5\\CH_3\end{matrix}\!\!>C{:}C<\!\!\begin{matrix}C(CO_2H){:}CMe_2\\CO_2H\end{matrix}$. The fulgenic acid alone is obtained by the condensation of acetone with ethyl phenylmethyl*iso*itaconate, whereas a mixture of the two stereoisomeric fulgenic acids and phenylmethylitaconic acid is obtained when acetone is condensed with ethyl phenylmethylitaconate and sodium ethoxide. Acetophenone and ethyl dimethylitaconate condense in the presence of sodium ethoxide, yielding a mixture of the two fulgenic acids.

*a-Phenyl-a*δδ-*trimethylfulgenic acid* crystallises from water in small, colourless needles, m. p. 221—223° (decomp.), and gives an intense violet coloration with sulphuric acid. With acetyl chloride, it yields *a-phenyl-a*δδ-*trimethylfulgide*, $C_{15}H_{24}O_3$, which forms colourless crystals with a yellowish-green reflex, and has m. p. 112—113°. *a-Phenyl-a*δδ-*trimethyl*allo*fulgenic acid* is identical with the compound described by Stobbe and Rose (Abstr., 1905, i, 857) as δ-phenyl-*aa*δ-trimethylfulgenic acid, and has m. p. 208—210° (decomp.). Details for its preparation are given. The corresponding *allo*fulgide is identical with the compound described as δ-phenyl-*aa*δ-trimethylfulgide. It forms lemon-yellow needles, m. p. 132—133°, and is the stable form, as it can be obtained from its stereoisomeride (1) by exposing a chloroform solution containing a little iodine to sunlight; (2) by prolonged boiling of its xylene solution; (3) by heating with naphthalene for twelve hours at 190°. An *N*/32-chloroform solution of the *allo*fulgide has a rather broader absorption band ($\lambda = 405\mu\mu$) than a similar solution of its isomeride ($\lambda = 402\mu\mu$). As in the case of many other pairs of stereoisomeric fulgides, the more stable and less fusible compound is the more deeply coloured.

VI. *Diarylated Fulgenic Acids and their Fulgides.*—Good yields of αδ-diarylated fulgenic acids can be obtained by condensing the ester of a γ-arylated itaconic acid with an aromatic aldehyde in the presence of an alcoholic solution of sodium ethoxide, or of the solid ethoxide and anhydrous ether. Hydroxy-acids of the type

$$R{\cdot}CH(OH){\cdot}CH(CO_2H){\cdot}C(CO_2H){:}CHR',$$

are sometimes formed. Although the fulgenic acid can exist theoretically in three ($R = R'$) or four stereoisomeric forms, the acids obtained are usually homogeneous. The same acids can also be synthesised by condensing ethyl succinate with an excess of an aromatic aldehyde in the presence of sodium ethoxide (compare Abstr., 1906, i, 102). This method is less expensive, but is complicated by the formation of various by-products, for example, γ-arylated paraconic and itaconic acids, lactonic acids isomeric with the fulgenic acids, and aromatic monobasic acids and alcohols formed by the action of the alkali on the aldehyde. The various aldehydes react differently with ethyl succinate. Benzaldehyde, p-*iso*propylbenzaldehyde, anisaldehyde, and piperonaldehyde give 40% yields of the corresponding diarylated fulgenic acids. Low temperatures (− 10° to − 17°) favour the formation of these acids, whereas higher temperatures tend to form resins or substituted itaconic acids. Veratraldehyde gives but a poor yield of diveratrylfulgenic acid, and nitrobenzaldehydes yield resins. Practically all the acids can be reduced to the corresponding diarylated butanedicarboxylic acids, which yield colourless anhydrides. The lactonic acids formed during the condensation of aromatic aldehydes with itaconic esters can be transformed into the isomeric fulgenic acids by boiling with sodium ethoxide solution, and it is probable that in all cases lactonic acids are intermediate products in the formation of fulminic acids.

[With ROBERT ROSE.]—*Ethyl hydrogen αδ-diphenyl-δ-methylfulgenate*, $C_{21}H_{20}O_4$, prepared by allowing a solution of benzaldehyde, γ-phenyl-γ-methylitaconic ester, and sodium ethoxide in ethyl alcohol to remain for four hours at the ordinary temperature, forms colourless, rhombic crystals, m. p. 172—173°. The corresponding *acid* crystallises from 50% acetic acid in colourless prisms, m. p. 212—214° (decomp.) after softening at 180°, and appears to be a mixture of the acid with a monohydrate. *αδ-Diphenyl-δ-methylfulgide*, $C_{19}H_{14}O_3$, crystallises from ether in glistening, lemon-yellow, hexagonal prisms, m. p. 148°.

[With GEORG POSNJAK.]—αα-Diphenyl-δδ-dimethylfulgenic acid (Abstr., 1905, i, 857) can also be prepared by condensing acetone with diphenylitaconic ester and sodium ethoxide, and its solution in concentrated sulphuric acid has a deep green colour, similar to that of diphenylitaconic acid in sulphuric acid, and in both cases an indone derivative is formed.

[With KARL KAUTZSCH and TH. BADENHAUSEN.]—*δ-Phenyl-α-piperonylfulgenic acid*, $CH_2O_2{:}C_6H_3{\cdot}CH{:}C(CO_2H){\cdot}C(CO_2H){:}CHPh$, is obtained mixed with the corresponding hydroxy-acid by condensing piperonaldehyde and phenylitaconic ester. The mixture forms pale yellow, nodular masses from ether, m. p. 203—206° (decomp.), and the corresponding *fulgide*, $C_{19}H_{12}O_5$, crystallises from a mixture of ether and chloroform in pale orange-coloured prisms, m. p. 169—170°.

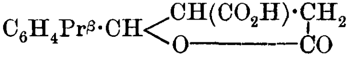
VII. *aδ-Dicumylfulgenic Acids, Cumylitaconic Acid, and Cumylparaconic Acid.*—[With RICHARD HÄRTEL.]—A mixture of the four acids is obtained by condensing cuminaldehyde with ethyl succinate in the presence of pure sodium ethoxide and anhydrous ether.

The yellow *aδ-dicumylfulgenic acid*,

$$C_6H_4Pr^\beta\cdot CH{:}C(CO_2H)\cdot C(CO_2H){:}CH\cdot C_6H_4Pr^\beta,$$

separates from light petroleum in sulphur-yellow crystals, or from chloroform in whitish-grey crystals containing chloroform of crystallisation. It has m. p. 220° (decomp.).

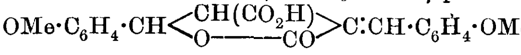
The corresponding *fulgide*, $C_{24}H_{24}O_3$, separates from light petroleum in orange-red, triangular plates or long needles, m. p. 112—113°. The colourless *aδ-dicumyl*iso*fulgenic acid* is found as its methyl hydrogen salt in the light petroleum mother liquors of the yellow acid. It crystallises from chloroform with solvent of crystallisation, and has m. p. 225° (decomp.). The corresponding *fulgide* is not so readily prepared as the isomeride, and crystallises in lemon-yellow plates or needles, m. p. 112—113°. Both the fulgenic acids, on reduction with sodium amalgam in the presence of carbon dioxide, yield *aδ-dicumylbutane-βγ-dicarboxylic acid*, $C_6H_4Pr^\beta\cdot CH_2\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_4Pr^\beta$, which crystallises from benzene, and has m. p. 220°. The colourless *iso*-acid is not so readily oxidised by permanganate as the yellow acid, and both fulgides react with bromine, yielding amorphous products.

Cumylparaconic acid,  $C_6H_4Pr^\beta\cdot CH{<}\begin{matrix}CH(CO_2H)\cdot CH_2\\ O\text{———————}CO\end{matrix}$, is isolated as an oil, which solidifies after several months, crystallises from water or chloroform, and has m. p. 158°.

Cumylitaconic acid, $C_6H_4Pr^\beta\cdot CH{:}C(CO_2H)\cdot CH_2\cdot CO_2H$, crystallises from a mixture of ether and light petroleum, has m. p. 200°, and gives a bluish-green coloration with concentrated sulphuric acid. The *anhydride*, $C_{14}H_{14}O_3$, crystallises from light petroleum in colourless, glistening prisms, m. p. 138°. Both paraconic and itaconic acids yield *cumyl*iso*paraconic acid* when boiled with 50% sulphuric acid. This acid crystallises from water in colourless needles, m. p. 131°, and, when moistened with concentrated sulphuric acid, gives no coloration for the first moment, but gradually develops a yellow colour.

VIII. *aδ-Dianisylfulgenic Acid and an Isomeric Lactonic Acid.*—[With ERICH BENARY.]—*aδ-Dianisylfulgenic acid*,

$$OMe\cdot C_6H_4\cdot CH{:}C(CO_2H)\cdot C(CO_2H){:}CH\cdot C_6H_4\cdot OMe,$$

and the isomeric lactonic acid, *a-anisylidene-γ-*p*-methoxyphenylparaconic acid*,  $OMe\cdot C_6H_4\cdot CH{<}\begin{matrix}CH(CO_2H)\\ O\text{———}CO\end{matrix}{>}C{:}CH\cdot C_6H_4\cdot OMe$, are obtained by the condensation of anisaldehyde with ethyl succinate in the presence of sodium ethoxide, and can be separated by means of benzene, in which the fulgenic acid is insoluble. This acid crystallises from glacial acetic acid or alcohol in lemon-yellow prisms, m. p. 242—243° (decomp.), after softening at 220°. The corresponding *fulgide*,

$$C_{20}H_{16}O_5,$$

crystallises from carbon disulphide in chrome-yellow needles, m. p

170—171°. The lactonic acid crystallises from benzene, is colourless, and has m. p. 108—109°. It is transformed into the fulgenic acid when boiled for twelve hours with potassium ethoxide solution.

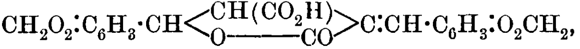
IX. *aδ-Diveratrylfulgenic Acid.*—[With KARL LEUNER.]—aδ-Diveratrylfulgenic acid and γ-veratrylitaconic acid are formed by the condensation of veratraldehyde with ethyl succinate, and the yield of the former is greater when an excess of aldehyde is used, but, as much resin is also formed under these conditions, the purification of the acids is rendered more tedious. A modification of Tiemann's method (this Journ., 1876, i, 76) for the preparation of veratraldehyde from vanillin is described. *Diveratrylfulgenic acid,*

$$C_6H_3(OMe)_2\cdot CH{:}C(CO_2H)\cdot C(CO_2H){:}CH\cdot C_6H_3(OMe)_2,$$

is insoluble in chloroform, crystallises from dilute alcohol, and has m. p. 220° (decomp.). The *fulgide*, $C_{22}H_{20}O_7$, crystallises from benzene in brilliant red, monoclinic plates, or large, double pyramids, m. p. 172—173°. *γ-Veratrylitaconic acid,*

$$C_6H_3(OMe)_2\cdot CH{:}C(CO_2H)\cdot CH_2\cdot CO_2H,$$

crystallises from water or chloroform in slender, colourless needles, m. p. 175°, and yields an insoluble *barium* salt. The *anhydride*, $C_{13}H_{12}O_5$, crystallises from benzene in orange-red needles containing benzene, or in crusts of yellow prisms free from benzene. The hydrocarbon is removed at 80°, and then both forms melt at 167°.

X. *aδ-Piperonylfulgenic Acid and an Isomeric Lactonic Acid.*—[With WALTER VIEWEG, RICHARD ECKERT, and GUSTAV REDDELIEN.]—The lactonic acid, *a-piperonylidene-γ-methylenedioxyphenylparaconic acid,*  $CH_2O_2{:}C_6H_3\cdot CH\left\langle\begin{matrix}CH(CO_2H)\\ O\text{———}CO\end{matrix}\right\rangle C{:}CH\cdot C_6H_3{:}O_2CH_2$, is the chief product formed when ethyl succinate and piperonaldehyde are left in contact with dry ether and sodium ethoxide for a short time at low temperatures. The product formed is the sodium salt of the corresponding hydroxy-acid, but when acidified this yields the colourless lactonic acid, which crystallises from acetic acid and has m. p. 182°. The acid is not affected by acetyl chloride, but with acetic anhydride yields a compound, $C_{24}H_{16}O_9$, with m. p. 265°. *aδ-Dipiperonylfulgenic acid,*

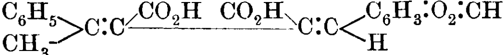
$$CH_2{:}O_2{:}C_6H_3\cdot CH{:}C(CO_2H)\cdot C(CO_2H){:}CH\cdot C_6H_3{:}O_2{:}CH_2,$$

is formed when the reaction mixture is kept for eight days at low temperatures, or when the lactonic acid is boiled for twelve hours with potassium ethoxide solution. It crystallises from glacial acetic acid in yellow prisms containing 2 molecules of acetic acid, which it loses at the ordinary temperature. The acid has then an orange-yellow colour, and m. p. 210° (decomp.). The *potassium* salt, $C_{20}H_{12}O_8K_2$, crystallises from 80% ethyl alcohol in yellow needles; the *ethyl* ester, $C_{24}H_{22}O_8$, in greenish-yellow, felted needles, m. p. 133°, and the *fulgide*, $C_{20}H_{12}O_7$, separates from chloroform in orange-coloured crystals, m. p. 210°. When reduced with sodium amalgam in the presence of carbon dioxide, the fulgenic acid yields colourless *aδ-dipiperonylbutane-βγ-dicarboxylic acid,*

$$CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot CH_2\cdot C_6H_3{:}O_2{:}CH_2,$$

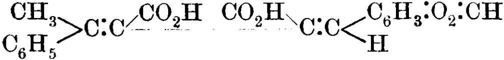
m. p. 228° (decomp.) after turning yellow at 210° and softening at 220°. With concentrated sulphuric acid it yields a pale red, and ultimately a purple-red, coloration. A comparison is made between the colours of various acids containing phenyl and piperonyl groups.

XI. *Two Stereoisomeric α-Piperonyl-δ-phenyl-δ-methylfulgenic Acids.* —[With FERDINAND GADEMANN and ROBERT ROSE.]—Piperonaldehyde condenses with the ester of phenylmethyl*iso*itaconic acid in the presence of dry ether and sodium ethoxide at low temperatures, yielding as the only product *α-piperonyl-δ-phenyl-δ-methylfulgenic acid*,



$\begin{matrix}C_6H_5\\CH_3\end{matrix}{>}C{:}C\begin{matrix}\diagup CO_2H & CO_2H\diagdown\end{matrix}C{:}C{<}\begin{matrix}C_6H_3{:}O_2{:}CH_2\\H\end{matrix}$

, which crystallises from glacial acetic acid or water, has m. p. 196—198° (decomp.), and gives a malachite-green coloration with concentrated sulphuric acid. The corresponding *fulgide*, $C_{20}H_{14}O_5$, crystallises from glacial acetic acid in greenish-yellow needles, m. p. 159—161°. The ester of phenylmethylitaconic acid does not condense with piperonaldehyde so readily as its isomeride, and yields *α-piperonyl-δ-phenyl-δ-methyl*allo*fulgenic acid*,



$\begin{matrix}CH_3\\C_6H_5\end{matrix}{>}C{:}C\begin{matrix}\diagup CO_2H & CO_2H\diagdown\end{matrix}C{:}C{<}\begin{matrix}C_6H_3{:}O_2{:}CH_2\\H\end{matrix}$

, which crystallises from 50% acetic acid in colourless plates, m. p. 201—202° (decomp.). Its solution in concentrated sulphuric acid has a reddish-yellow colour. The corresponding *fulgide*, $C_{20}H_{14}O_5$, crystallises from glacial acetic acid in pale orange-coloured needles, m. p. 201—202°. In the preparation of the *allo*-acid, it is advisable to isolate the barium salt, and to extract this with alcohol before decomposing with hydrochloric acid, as small amounts of impurity interfere with the crystallisation of the acid.

XII. *α-Piperonyl-δ-naphthyl-δ-methylfulgide.* — [With ALFRED LENZNER.]—The α- and β-naphthyl methyl ketones condense with ethyl succinate in the presence of dry ether and sodium ethoxide at low temperatures, yielding the acid esters of γ-(α- or β-)*naphthyl-γ-methylitaconic acid*, $C_{10}H_7\cdot CMe{:}C(CO_2Et)\cdot CH_2\cdot CO_2H$. The α-naphthyl compound crystallises from carbon disulphide in colourless prisms, m. p. 132°, and the corresponding dibasic *acid* has m. p. 168° (decomp.). The β-naphthyl derivative crystallises from a mixture of benzene and light petroleum, and has m. p. 103—104°; the corresponding dibasic *acid* has m. p. 165° (decomp.), and the *diethyl* ester, $C_{20}H_{22}O_4$, has b. p. 280—282°/64 mm. This ethyl ester condenses with piperonaldehyde at low temperatures in the presence of dry ether and sodium ethoxide, yielding the crude fulgenic acid, which, on treatment with acetyl chloride, yields *α-piperonyl-δ-2-naphthyl-δ-methylfulgide*,

$$C_{24}H_{16}O_5,$$

in the form of a dark orange-coloured powder.

XIII. *Triarylated Fulgenic Acids and Their Fulgides. Dyeing Experiments* (compare Abstr., 1904, i, 672; 1906, i, 91).—Good yields (80%) of triarylated fulgenic acids can be obtained by condensing aromatic aldehydes with ethyl diphenylitaconate in the presence of sodium ethoxide. The acids isolated are homogeneous, and do not consist of mixtures of stereoisomerides. The acids are yellow or orange-coloured, and the corresponding salts and esters are colourless or only slightly coloured. The corresponding fulgides are readily prepared, and are coloured red; they show pleochroism, and are strongly phototropic. The product, obtained by the condensation of ethyl phenylitaconate and benzophenone, is a lactonic acid, and is only slowly transformed into the triphenylfulgenic acid when boiled with sodium ethoxide solution.

The di-, tri-, and tetra-arylated fulgides in the form of extremely fine suspensions in water are capable of dyeing wool, and in this respect resemble the dyes described by Vignon (Abstr., 1910, ii, 272, 273).

[With ERICH BENARY.]—$\alpha\delta\delta$-Triphenylfulgide yields a *dibromide*, $C_{24}H_{16}O_3Br_2$, which separates from carbon disulphide in yellow plates containing solvent of crystallisation; it loses the solvent on exposure to the air, turns a paler colour, and then has m. p. 129° (decomp.).

[With CURT KOHLMANN.]—*$\delta\delta$-Diphenyl-α-p-chlorophenylfulgenic acid*, $C_6H_4Cl\cdot CH:C(CO_2H)\cdot C(CO_2H):CPh_2$, crystallises from 60% acetic acid in pale yellow needles, m. p. 242° (decomp.). The *sodium* salt crystallises in colourless plates containing alcohol, the *barium* salt is insoluble, and the *fulgide*, $C_{24}H_{15}O_3Cl$, crystallises in orange-red, triclinic prisms, m. p. 197°, and is strongly pleochroic.

[With GUSTAV REDDELIEN.]—The *methyl* ester of $\delta\delta$-diphenyl-α-o-methoxyphenylfulgenic acid separates from methyl alcohol in colourless crystals, m. p. 137°.

[With CURT KOHLMANN and GUSTAV REDDELIEN.]—*$\delta\delta$-Diphenyl-α-veratrylfulgenic acid*, $C_{26}H_{22}O_6$, crystallises from 60% acetic acid, has a very pale yellow colour, and melts at 154° (decomp.). The *sodium* salt is sparingly soluble in water, and crystallises from 80% alcohol; the *dimethyl* ester has m. p. 112°, and the *fulgide*, $C_{26}H_{20}O_5$, forms monoclinic plates, m. p. 164·5°.

[With CURT KOHLMANN, THEODOR BADENHAUSEN, and HARALD KALNING.]—*$\delta\delta$-Diphenyl-α-piperonylfulgenic acid*, $C_{25}H_{18}O_6$, crystallises from chloroform or benzene in pale yellow needles, m. p. 221° (decomp.), and the *fulgide*, $C_{25}H_{16}O_5$, forms red, monoclinic, pleochroic crystals, m. p. 201°. *$\delta\delta$-Diphenyl-α-piperonylbutane-$\beta\gamma$-dicarboxylic acid*, $CH_2O_2:C_6H_3\cdot CH_2\cdot CH(CO_2H)\cdot CH(CO_2H)\cdot CHPh_2$, crystallises from light petroleum in well-developed prisms, m. p. 182° (decomp.). The *anhydride* forms colourless, flat needles, m. p. 170—172°.

XIV. *Styrylfulgenic Acids and Fulgides.*—[With ERICH BENARY and SIEGFRIED SEYDEL.]—The styrylfulgenic acids are best prepared by the condensation of cinnamaldehyde with esters of substituted itaconic acids, and can be isolated in the anhydrous form or as compounds containing $1H_2O$, which is readily removed on gently heating.

$\delta\delta$-Diphenyl-α-styrylfulgenic acid,

$$CHPh:CH\cdot CH:C(CO_2H)\cdot C(CO_2H):CPh_2,$$

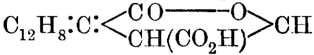
has m. p. 212—214° (decomp.). It absorbs water readily, yielding the *acid*, $C_{26}H_{22}O_5$, m. p. 200°, after sintering at 150—160° when rapidly heated.

$\delta\delta$-Diphenyl-α-styrylfulgide, $C_{26}H_{18}O_3$, crystallises in ruby-red needles, m. p. 186—189°, and yields a *dibromide*, m. p. 167—168° (decomp.).

δ-Phenyl-α-styrylfulgide, $C_{20}H_{14}O_3$, separates from benzene in orange-coloured crystals, m. p. 126°, and *α-styryl-$\delta\delta$-dimethylfulgide*, $C_{16}H_{14}O_3$, forms large, golden-yellow crystals, m. p. 203°. The corresponding

fulgenic acid exists in two forms, melting respectively at 170—173 and 223°.

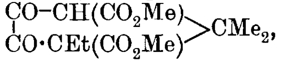
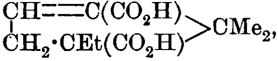
XV. *Diphenylenefulgenic Acids, the Isomeric Lactonic Acids, an Diphenylenefulgides.* — [With Theodor Badenhausen, Rudol Hennicke, and Emil Wahl.]—The diphenylenefulgenic acids ar formed by the condensation of fluorenone with esters of substitute itaconic acids, but the conditions vary in the different condensations.

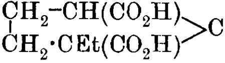
α-Phenyl-δ-diphenylenefulgenic acid is orange-coloured, has m. p 206—208° (decomp.), and yields a *fulgide*, $C_{24}H_{14}O_3$, which crystallise from light petroleum in dark red needles, m. p. 182—183°. *γ-Phenyl α-fluorenylparaconic acid*,  $C_{12}H_8{:}C{:}<\begin{matrix}CO\text{——}O\\CH(CO_2H)\end{matrix}>CHPh$, crystallise in yellowish-green cubes, m. p. 193°.

αα-Diphenyl-δ-diphenylenefulgenic acid crystallises from benzene, ha m. p. 201°, and yields a *fulgide*, $C_{30}H_{18}O_3$, with m. p. 269°.

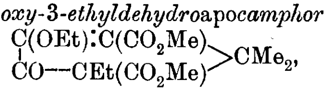
δ-Diphenylene-αα-dimethylfulgenic acid, $C_{20}H_{16}O_4$, crystallises fro dilute acetone in yellow plates, m. p. 208°. The *fulgide*, $C_{20}H_{14}O_3$ crystallises from ethyl acetate in orange-coloured needles, m. p. 180° and when reduced yields a *dihydrofulgide*, $C_{20}H_{16}O_3$, in the form o colourless rods, m. p. 218°. J. J. S.

Complete Synthesis of Ethyl*apo*camphoric Acid. Gusta Komppa and O. Routala (*Ber.*, 1911, **44**, 858—863).—If Blanc an Thorpe's contention that the methylation product of methyl diketo*apo*camphorate is an *O*-methyl derivative is correct (Trans., 1910, **97** 836), it is immaterial what alkyl group is introduced, because, bein attached to oxygen, it will be eliminated by hydriodic acid. It wil be seen, therefore, that the following synthesis of ethyl*apo*camphori acid, in the course of which the ethyl group withstands the attac of hydriodic acid, renders Blanc and Thorpe's position still les tenable.

A methyl-alcoholic solution of methyl diketo*apo*camphorate i treated with cold methyl-alcoholic sodium methoxide; ethyl iodid is then added, and the mixture is boiled for twenty hours. Th resulting ethyl and diethyl derivatives are separated by sodiu carbonate, the former, after being liberated from the alkaline solutio by dilute hydrochloric acid, being freed from unchanged methy diketo*apo*camphorate by means of ethereal copper acetate, in whic the copper derivative of methyl diketo*apo*camphorate is insoluble *Methyl diketoethyl*apo*camphorate*,  $\begin{matrix}CO\text{–}CH(CO_2Me)\\CO\cdot CEt(CO_2Me)\end{matrix}>CMe_2$, m. p 69—70·5°, obtained in this way, forms brilliant rhombohedra, an develops a reddish-brown coloration with aqueous alcoholic ferri chloride. Its solution in sodium hydrogen carbonate and a littl sodium carbonate is reduced by 2·5% sodium amalgam in a atmosphere of carbon dioxide, yielding ultimately an amorphou glassy mass of *dihydroxyethyl*apo*camphoric acid*, which withou further examination is heated on the water-bath for thirty hours wit hydriodic acid, D 1·7, and red phosphorus, whereby *ethyldehydro*apo*camphoric acid*,  $\begin{matrix}CH{=\!=}C(CO_2H)\\CH_2\cdot CEt(CO_2H)\end{matrix}>CMe_2$, m. p. 190—191°, is obtained

By heating this acid with hydrogen bromide in glacial acetic acid for twelve hours at 125°, and reducing the product with zinc dust and glacial acetic acid, the two stereoisomeric forms of ethyl*apo*camphoric acid are obtained. These are separated by treating them with acetyl chloride, dissolving the product in ether, and shaking the ethereal solution with aqueous sodium carbonate. trans-*Ethyl*apo*camphoric acid*, obtained from the sodium carbonate solution, is an oil. The ethereal solution contains the *anhydride*, m. p. 93° (corr.), of *cis*-ethyl*apo*camphoric acid; the cis-*acid* itself,  $\begin{matrix}CH_2\text{—}CH(CO_2H)\\ CH_2\cdot CEt(CO_2H)\end{matrix}\!\!>CMe_2$, has m. p. 183·5—184°.

Methyl 4-*keto*-5-*ethoxy*-3-*ethyldehydro*apo*camphorate*,

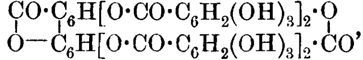


$$\begin{matrix}C(OEt)\text{:}C(CO_2Me)\\ CO\text{—}CEt(CO_2Me)\end{matrix}\!\!>CMe_2,$$

the diethyl derivative obtained in the ethylation of methyl diketo*apo*camphorate, has b. p. 166—167°/9 mm., $D_{17·5}^{17·5}$ 1·1270, and $n_D^{17·5}$ 1·48990, and does not give a coloration with ferric chloride.

C. S.

Tannins. IV. Galloyl-ellagic Acid. MAX NIERENSTEIN (*Ber.* 1911, **44**, 837—840).—*Tetragalloyl-ellagic acid*,

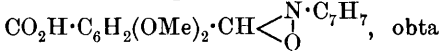


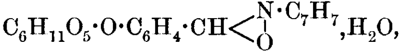
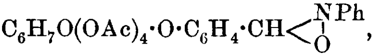
$$\begin{matrix}CO\cdot C_6H[O\cdot CO\cdot C_6H_2(OH)_3]_2\cdot O\\ O\text{—}C_6H[O\cdot CO\cdot C_6H_2(OH)_3]_2\cdot CO\end{matrix},$$

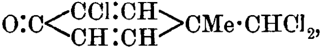
prepared by the interaction of ellagic acid in sodium hydroxide solution with tricarbomethoxygalloyl chloride, crystallises in small, yellow needles, m. p. 297—300°. It gives a bluish-green coloration with ferric chloride; on acetylation an amorphous powder is obtained. It is absorbed quantitatively by hide powder and casein, and precipitated by gelatin. Partial hydrolysis could not be effected.

E. F. A.

***N*-Alkylated Aldoximes.** JOHANNES SCHEIBER (*Ber.*, 1911, **44**, 761—769. Compare Mills and Bain, Trans., 1910, **98**, 1866).—All attempts to prepare *N*-alkylated aldoximes in optically active modifications have proved unsuccessful (compare Kipping and Salway, Trans., 1904, **85**, 438).

[With H. FLEISCHMANN.]—The N-*benzyl* derivative of opianic acid aldoxime,  $CO_2H\cdot C_6H_2(OMe)_2\cdot CH\!<\!\begin{matrix}N\cdot C_7H_7\\ O\end{matrix}$, obtained by condensing opianic acid with β-benzylhydroxylamine, crystallises from alcohol in colourless prisms, m. p. 153°. The *cinchonine* salt, $C_{36}H_{39}O_6N_3,3H_2O$, crystallises from water in long, brilliant, transparent needles, m. p. 97°; the anhydrous compound has m. p. 115—117°, and rapidly absorbs moisture on exposure to the air. The salt has $[\alpha]_D^{20}$ + 78·15° in alcoholic solution, and on treatment with ammonium hydroxide solution yields an inactive ammonium salt.

[With K. KLOPPE.]—It has not been found possible to obtain isomeric alkylated oximes by condensing β-benzyl- or β-phenyl-hydroxylamine with an optically active aldehyde, for example, helicin. N-*Benzylhelicinaldoxime*,  $C_6H_{11}O_5\cdot O\cdot C_6H_4\cdot CH\!<\!\begin{matrix}N\cdot C_7H_7\\ O\end{matrix},H_2O$, crystallises in small, felted needles, m. p. 165°, and has $[\alpha]_D^{20}$ $-56{\cdot}82°$ in alcoholic solution. The corresponding *phenyl* derivative, $C_{19}H_{21}O_7N,H_2O$, forms small, colourless needles, m. p. 180°, and has $[\alpha]_D^{20}$ $-59{\cdot}27°$; it rapidly absorbs water, yielding a *trihydrate*, m. p. 125°. When hydrolysed by emulsin, the phenyl derivative yields inactive *N*-phenylsalicylaldoxime (Plancher and Piccinini, Abstr., 1905, i, 705). N-*Phenyltetra-acetylhelicinaldoxime*,  $C_6H_7O(OAc)_4{\cdot}O{\cdot}C_6H_4{\cdot}CH\left<\begin{matrix}NPh\\ | \\ O\end{matrix}\right.$, H_2O, obtained by condensing tetra-acetylhelicin with β-phenylhydroxylamine, and also by the action of β-acetobromoglucose on the sodium derivative of phenylsalicylaldoxime, separates from benzene in colourless crystals, with m. p. 166°, and $[\alpha]_D^{20}$ $-29{\cdot}68°$. J. J. S.

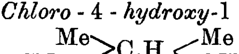
Hydroaromatic Compounds. Chloro-derivatives of Hydroaromatic Ketones and Semibenzenes. KARL AUWERS (*Ber.*, 1911, **44**, 788—809. Compare Abstr., 1907, *i*, 399—403).—Doubly unsaturated ketones of the type of 1-methyl-1-dichloromethyl*cyclo*hexadien-4-one form additive compounds with two or four atoms of chlorine, and these compounds react with alkalis, losing hydrogen chloride, and yielding chloro-derivatives of the original ketones. From these chlorinated ketones, for example,  $O{:}C\left<\begin{matrix}CCl{:}CH\\ CH{:}CH\end{matrix}\right>CMe{\cdot}CHCl_2$, tertiary alcohols can be synthesised by means of magnesium alkyl iodides, and from the alcohols, alkylidenechloro*cyclo*hexadienes (semibenzenes) are obtained by the action of anhydrous formic acid. When heated, the alkylidene derivatives readily undergo molecular rearrangement, and by the wandering of the $\cdot CHCl_2$ group yield benzene derivatives of the type 3-chloro-4-ββ-dichloroethyltoluene. The position of the ring chlorine atom has been proved by the elimination of hydrogen chloride from this compound, and the oxidation of the resulting styrene derivative to 2-chloro-*p*-toluic acid.

5 : 6-*Dichloro*-1-*methyl*-1-*dichloromethyl*-Δ^2-cyclo*hexen*-4-*one*,

$$CO\left<\begin{matrix}CH{=\!=\!=}CH\\ CHCl{\cdot}CHCl\end{matrix}\right>CMe{\cdot}CHCl_2,$$

obtained by the action of dry chlorine gas or of a carbon tetrachloride solution on the corresponding hexadiene, forms glistening, regular crystals, m. p. 118—120° (decomp.). It is volatile with steam, and decomposes when kept for some time.

5-*Chloro*-1-*methyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadien*-4-*one*, $C_8H_7OCl_3$, crystallises from dilute methyl alcohol in small needles, m. p. 67°, b. p. 189·5—190°/22 mm., and yields a *semicarbazone*, $C_9H_{10}ON_3Cl_3$, in the form of compact, colourless needles, m. p. 181—182°, which are hydrolysed by 30% sulphuric acid.

3-*Chloro*-4-*hydroxy*-1 : 4-*dimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*,  $\begin{matrix}Me\\ CHCl_2\end{matrix}\!>C_6H_4<\!\begin{matrix}Me\\ OH\end{matrix}$, crystallises from light petroleum in colourless needles, m. p. 104°, and when shaken for ten minutes with eight to ten times its weight of concentrated formic acid yields 3-*chloro*-1-*methyl*-1-*dichloromethyl*-4-*methylene*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_9H_9Cl_3$; this is transformed at 85° into 5-*chloro*-1-*methyl*-4-ββ-*dichloroethylbenzene*,

$C_9H_9Cl_3$, which is a colourless oil, b. p. 147·8—148·6°/19 mm., D_4^{20} 1·2873, n_α 1·54528, n_D 1·55012, n_β 1·56130, n_γ 1·57143.

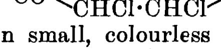
2 : 3 : 5 : 6-*Tetrachloro*-1-*methyl*-1-*dichloromethyl*cyclo*hexan*-4-*one*, $C_8H_8OCl_6$, exists in two stereoisomeric modifications. The *trans*-compound is formed when the ketone is treated with a carbon tetrachloride solution of chlorine (3 mols.) in the presence of a little iron powder; it separates from light petroleum in regular crystals, m. p. 135—136° (decomp.), and is more stable than the dichloride. The *cis*-compound is formed when carbon disulphide is used as a solvent, and the solution exposed to light. It crystallises in brilliant cubes, has m. p. 176° (decomp.), and is not so soluble as the isomeride.

3 : 5 - *Dichloro*-1-*methyl* - 1 - *dichloromethyl* - $\Delta^{2:5}$- cyclo*hexadiene*-4-*one*, $C_8H_6OCl_4$, obtained by warming gently either the *cis*- or *trans*-compound with alcoholic potassium hydroxide, or with an acetic acid solution of potassium acetate, crystallises from light petroleum in colourless, flat needles, m. p. 97°, and does not yield a semicarbazone. When reduced with zinc dust and acetic acid, it yields *o*-dichloro-*p*-cresol (Claus and Riemann, Abstr., 1883, 1111). 3 : 5-*Dichloro*-4-*hydroxy*-1 : 4-*dimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_9H_{10}OCl_4$, exists in two stereoisomeric forms. The one crystallises from light petroleum in short, glistening, brittle needles, m. p. 104°, or with $\frac{1}{2}C_6H_6$ in glistening needles, m. p. 97—98°, the other crystallises from light petroleum, and has m. p. 60—70°. 3 : 5-*Dichloro*-1-*methyl*-1-*dichloromethyl*-4-*methylene*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_9H_8Cl_4$, obtained by heating the hydroxy-compound with formic acid, has $D_4^{16\cdot7}$ 1·4084, n_α 1·57462, n_D 1·58005, and n_β 1·59387 at 16·7°.

3 : 5-*Dichloro*-4-*ββ*-*dichloroethyltoluene*, $C_6H_2Cl_2Me{\cdot}CH_2{\cdot}CHCl_2$, is a colourless oil, b. p. 158·5—159·5°/15 mm., and has D_4^{19} 1·3976, n_α 1·56306, n_D 1·56784, n_β 1·57991, and n_γ 1·59033 at 19°.

Ice-cold concentrated sulphuric acid transforms the alcohol (m. p. 104°) into 3 : 5-*dichloro*-2 : 4-*dimethylbenzylidene chloride*, $C_6HCl_2Me_2{\cdot}CHCl_2$, which crystallises from light petroleum in glistening needles, m. p. 44—45°.

The corresponding *aldehyde*, $C_6HCl_2Me_2{\cdot}CHO$, crystallises in long, opaque needles, m. p. 108—112°, and yields a *semicarbazone*, $C_{10}H_{11}ON_3Cl_3$, m. p. 231—232°. 3 : 5-*Dichloro*-2 : 4-*dimethylbenzoic acid*, $C_6HCl_2Me_2{\cdot}CO_2H$, crystallises in colourless, glistening plates, m. p. 191°, and its *methyl* ester in slender needles, m. p. 49°.

1 : 3-Dimethyl-1-dichloromethyl-$\Delta^{2:5}$-*cyclo*hexadiene-4-one yields a *dichloride* only, namely, 5 : 6-*dichloro*-1 : 3-*dimethyl*-1-*dichloromethyl*-Δ^2-cyclo*hexen*-4-*one*,  $CO<\begin{matrix}CMe{=}CH\\CHCl{\cdot}CHCl\end{matrix}>CMe{\cdot}CHCl_2$, which crystallises from hot alcohol in small, colourless needles, m. p. 100°. 5-*Chloro*-1 : 3-*dimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*-4-*one*, $C_9H_9OCl_3$, crystallises from dilute alcohol in nacreous plates, m. p. 56°, and reacts with magnesium methyl iodide, yielding 5-*chloro*-4-*hydroxy*-1 : 3 : 4-*trimethyl*-1-*dichloromethyl*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_{10}H_{13}OCl_3$, which crystallises from light petroleum in needles, m. p. 80°. When shaken with formic acid for half an hour, the alcohol yields 5-*chloro*-1 : 3-

dimethyl-1-*dichloromethyl*-4-*methylene*-$\Delta^{2:5}$-cyclo*hexadiene*, $C_{10}H_{11}Cl_3$, as a pale yellow oil, $D_4^{17\cdot3}$ 1·2693, n_α 1·56255, n_D 1·56812, and n_β 1·58230 at 17·3°.

5-*Chloro*-1 : 3-*dimethyl*-4-$\beta\beta$-*dichloroethylbenzene*,

$$C_6H_2ClMe_2\cdot CH_2\cdot CHCl_2,$$

is a yellow oil, b. p. 155°/17 mm., $D_4^{16\cdot1}$ 1·2622, n_α 1·54788, n_D 1·55278, n_β 1·56427, and n_γ 1·57091 at 16·1°, and reacts with alcoholic potassium hydroxide, yielding 6-ω-*dichloro*-2 : 4-*dimethylstyrene*,

$$C_6H_2Me_2Cl\cdot CH{:}CHCl,$$

which crystallises from methyl alcohol in slender needles, m. p. 38—38·5°. When oxidised it yields an aldehyde, and from the aldoxime, by the elimination of water, 6-*chloro*-2 : 4-*dimethylbenzonitrile*, C_9H_8NCl, is obtained. This forms brittle, glistening needles, m. p. 54°, and is identical with the nitrile obtained from 6-chloro-2 : 4-dimethylaniline. The corresponding *amide* has m. p. 167°. J. J. S.

Catalytic Hydrogenation of *cyclo*Pentanone. MARCEL GODCHOT and FELIX TABOURY (*Compt. rend.*, 1911, **152**, 881—883).—On hydrogenating *cyclo*pentanone in presence of reduced nickel at 125°, water is formed with *cyclo*pentane, *cyclo*pentanol (50%), and a ketone (40%) having an odour of menthol. The latter is probably α-cyclo*pentyl*cyclo*pentanone*, $C_{10}H_{16}O$, arising by hydrogenation of an intermediate unsaturated ketone. It has m. p. −13°, b. p. 115—117°/12 mm., D^{16} 0·9801; the *oxime* has m. p. 75°; the *semicarbazone*, m. p. 210°. W. O. W.

Action of Light on Cinnamylideneacetophenone. HANS STOBBE and CONRAD RÜCKER (*Ber.*, 1911, **44**, 869—872. Compare Stobbe and Wilson, Trans., 1910, **97**, 1722).—When a saturated solution of cinnamylideneacetophenone in benzene or chloroform is exposed to sunlight, a white precipitate consisting of a bimolecular ketone and a resin is obtained after two to three days; the same result is obtained by using a quartz mercury lamp, the precipitate in this case containing a larger proportion of the resin. The precipitate is recrystallised from a mixture of alcohol and chloroform, and is then repeatedly extracted with acetone, whereby the pure ketone, $(C_{17}H_{14}O)_2$, m. p. 192°, is obtained. By distillation in a vacuum, or by heating its solution in phenetole or phenylcarbimide at 140—180°, the bimolecular ketone is depolymerised, and yields, not the original ketone, but an isomeric iso*cinnamylideneacetophenone*, $C_{17}H_{14}O$, m. p. 235°.

The question whether the three ketones are interconvertible has not yet been satisfactorily answered. Chloroform solutions of the *iso*ketone and of the bimolecular ketone are more or less resinified by exposure to sunlight. When, however, a saturated solution of cinnamylideneacetophenone in chloroform is exposed to sunlight for about a month and the precipitate is removed, the mother liquor, after exposure to diffuse daylight for a year and a-half, contains the yellow *iso*cinnamylideneacetophenone, together with the bimolecular ketone. C. S.

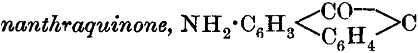
Preparation of Alkylanthraquinones from Alkylbenzoyl Chlorides and Aluminium Chloride. I. CHR. SEER (*Monatsh.*, 1911, **32**, 143—166).—When *m*-toluoyl chloride and aluminium chloride are heated at 130° for two hours, and finally at 130—140° for sixteen hours, the product is a mixture of, probably three, dimethylanthraquinones, the least soluble of which, m. p. 235—236°, is obtained in 19% yield by crystallisation from acetic acid and from nitrobenzene. This compound, which is identical with the substance obtained by Lavaux by the interaction of methylene chloride, toluene, and aluminium chloride, is also produced in the following manner: *m*-Toluoyl chloride and *m*-xylene in carbon disulphide yield with aluminium chloride *m-tolyl m-4-xylyl ketone*, $C_6H_4Me{\cdot}CO{\cdot}C_6H_3Me_2$, b. p. 315—320, which is converted, after being boiled for five days, into 2 : 6-dimethylanthracene, m. p. 243°; the latter is oxidised by chromic and acetic acids to the dimethylanthraquinone, m. p. 235—236°. A consideration of the author's and of Lavaux's methods of preparing the substance leads by the process of exclusion to the conclusion that the compound must be 2 : 6-dimethylanthraquinone; Dewar and Jones' supposed 2 : 6-dimethylanthraquinone (Trans., 1904, **85**, 212) is probably the 2 : 7-isomeride.

By nitration with concentrated sulphuric acid and potassium nitrate, 2 : 6-dimethylanthraquinone yields (?) 1 : 5-*dinitro*-2 : 6-*dimethylanthraquinone*, colourless needles, which is converted into the *diamino*-compound, m. p. 255—256°, dark red needles, by reduction with alkaline sodium hydrosulphide. 1 : 5-*Di-iodo*-2 : 6-*dimethylanthraquinone*, obtained in the usual way, forms orange-yellow needles, m. p. 273°.

Anthraquinone-2 : 6-dicarboxylic acid, conveniently obtained by boiling 2 : 6-dimethylanthraquinone with chromic and glacial acetic acids for sixty hours, forms a *chloride*, $C_{16}H_6O_4Cl_2$, m. p. 197—198°, from which the *amide*, $C_{16}H_{10}O_4N_2$, m. p. above 370°, is produced by alcoholic ammonia, and 2 : 6-*di-α-naphthoylanthraquinone*, $C_{36}H_{20}O_4$, m. p. 183—185°, by naphthalene and aluminium chloride in nitrobenzene at 75—80° after twenty hours. C. S.

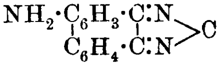
Phenanthrene Series. XXX. Preparation of 4-Hydroxy- from 4-Nitro-phenanthraquinone. JULIUS SCHMIDT and OTTO SCHAIRER (*Ber.*, 1911, **44**, 740—745).—4-Hydroxyphenanthraquinone has been prepared from the corresponding nitro-compound (Schmidt and Austin, Abstr., 1904, i, 69) by reduction with tin and hydrochloric acid, diazotising, and warming with water.

4-*Nitrophenanthraquinonedioxime*, $C_{14}H_9O_4N_3$, separates from alcohol in pale yellowish-green crystals, m. p. 210° (decomp.).



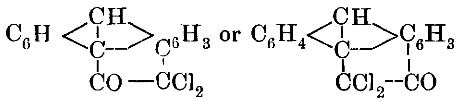
4-*Aminophenanthraquinone*, $NH_2{\cdot}C_6H_3{<}\begin{matrix}CO-\\C_6H_4\end{matrix}{>}CO$, is a black powder with a red lustre, has no definite m. p., and irritates the nasal mucous membrane. The *hydrochloride* of 4-*aminophenanthraquinol*,

$C_{12}H_{12}O_2NCl$,

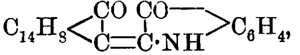
obtained by the reduction of the nitroquinone, crystallises in colourless plates, and turns brown during the process of drying. The most characteristic derivative of the aminoquinone is the 4-*aminophenanthraphenazine*,  $\begin{matrix}NH_2\cdot C_6H_3\cdot C:N \\ C_6H_4\cdot C:N\end{matrix}\!>C_6H_4$, the hydrochloride of which separates from water as a pale greyish-green, crystalline powder, m. p. 274—275° (decomp.). The *base* forms an olive-green, crystalline powder, m. p. 190° (not sharp).

4-*Hydroxyphenanthraquinone* forms a red powder, m. p. 285°. The *acetyl* derivative, $C_{16}H_{10}O_4$, separates from alcohol in pale brown, nodular masses, m. p. 188—189°. 4-*Hydroxyphenanthraquinonesemicarbazone*, $C_{15}H_{11}O_3N_3$, forms brownish-red crystals, m. p. 258° (decomp.), and 4-*hydroxyphenanthraphenazine*, $C_{20}H_{12}ON_2$, dark red, microscopic crystals, m. p. 233° (decomp.). J. J. S.

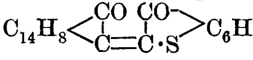
Derivatives of Aceanthrenequinone. Carl Liebermann and Milan Zsuffa (*Ber.*, 1911, **44**, 852—858. Compare this vol., i, 202).—The following compounds show that an extensive parallelism exists between aceanthrenequinone and acenaphthenequinone. Aceanthrenequinone, which is purified best by means of its compound with sodium hydrogen sulphite, is oxidised by chromic acid to anthraquinone-1-carboxylic acid, m. p. 293—294° (corr.). By distillation with zinc dust it yields impure aceanthrene, m. p. 115—140°. By treatment with phosphoryl chloride and phosphorus pentachloride it yields *dichloroaceanthrenone* (annexed formula), yellow needles, m. p. 182—184°.

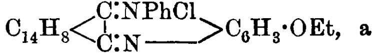


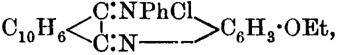
"*Aceanthren-2-indole-indigotin*" [*Indoxylaceanthrenone*],



$$C_{14}H_8<\begin{matrix}CO\ CO— \\ C{=}C\cdot NH\end{matrix}>C_6H_4,$$

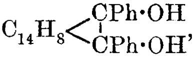
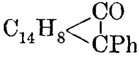
m. p. 266°, brown needles, obtained by heating aceanthrenequinone and indoxyl in glacial acetic acid containing a little hydrochloric acid, gives a brown coloration with concentrated sulphuric acid, which changes to grey and then to blue. "*Aceanthren-2-thionaphthen-indigotin*" [*Oxythionaphthenylaceanthrenone*],  $C_{14}H_8<\begin{matrix}CO\ CO \\ C{=}C\cdot S\end{matrix}>C_6H_4$, is prepared in a similar manner from hydroxythionaphthen (compare Friedländer and Bezdzik, Abstr., 1908, i, 673).

Azonium bases are readily obtained by the interaction of aceanthrenequinone and semidine bases. Thus, the quinone and 5-ethoxy-2-aminodiphenylamine hydrochloride in boiling glacial acetic acid yield, by the addition of a little hydrochloric acid, *ethoxyphenylaceanthraphenazonium chloride*,  $C_{14}H_8<\begin{matrix}C:NPhCl \\ C:N\text{———}\end{matrix}>C_6H_3\cdot OEt$, a dark green, metallic mass; the corresponding *nitrate* forms reddish-brown needles. *Ethoxyphenylacenaphthaphenazonium chloride*,



$$C_{10}H_6<\begin{matrix}C:NPhCl \\ C:N\text{———}\end{matrix}>C_6H_3\cdot OEt,$$

prepared in a similar manner from acenaphthenequinone for the purpose of comparison, forms brownish-yellow needles, and dyes wool yellow; the preceding anthracene derivative dyes wool a dirty ponceau-red.

Diphenylaceanthrene glycol,  $C_{14}H_8<\begin{array}{l}CPh\cdot OH\\ |\\ CPh\cdot OH\end{array}$, m. p. 160—162°, pale yellow needles, obtained from aceanthrenequinone and magnesium phenyl bromide, is converted by concentrated hydrochloric and glacial acetic acids into *diphenylaceanthrenone*,  $C_{14}H_8<\begin{array}{l}CO\\ |\\ CPh_2\end{array}$, m. p. 215—217°, yellow needles (compare Beschke and Kitaj, Abstr., 1909, i, 917).

Diphenyl-4-carboxylic acid, $CO_2H\cdot C_6H_4\cdot C_6H_5$, m. p. 224°, obtained by heating diphenyl, oxalyl chloride, and aluminium chloride in carbon disulphide, is best purified by means of its sparingly soluble *sodium* salt. *Retenecarboxylic acid*, $C_{18}H_{17}\cdot CO_2H$, prepared and purified in a similar manner, has m. p. 121—123°. Xanthone yields a *dicarboxylic acid*, $C_{13}H_8O(CO_2H)_2$, m. p. above 265°, under similar conditions.

C. S.

Oxidation of Camphene. Gustav Komppa (*Ber.*, 1911, **44**, 863—865).—When preparing *apo*camphoric acid by the oxidation of camphene by nitric acid, the author has always obtained an acid which does not yield an anhydride by treatment with acetyl chloride, and which he has always regarded as *trans-apo*camphoric acid. By further examination, however, the acid, which has the composition $C_{10}H_{14}O_3$, and m. p. 233·5—234·5°, and forms a phenylhydrazone, m. p. 146°, proves to be ketopinic acid.

This discovery is of interest, because now all of the compounds—campheneglycol, hydroxycamphenylanic acid, tricyclenic acid, hydroxy*apo*camphanecarboxylic acid, ketopinic acid, carboxy*apo*camphoric acid—which represent the successive steps in the oxidation of camphene to *apo*camphoric acid, have, with the exception of hydroxy*apo*camphancarboxylic acid, been isolated from the products of oxidation of camphene.

C. S.

Components of Essential Oils. "False Camphor Wood Oil" (faux camphrier). Natural Occurrence of Myrtenal and *d*-Perilla Aldehyde. Friedrich W. Semmler and B. Zaar (*Ber.*, 1911, **44**, 815—819).—False camphor wood oil, in addition to *d*-limonene and cineol, consists mainly of an aldehyde, $C_{10}H_{14}O$, b. p. 99—104°/9 mm., D^{18} 0·965, n_D 1·50803, $[\alpha]_D$ + 135·6°, which is the optical isomeride of *l*-perilla aldehyde. In addition the oil contains a dicyclic aldehyde, $C_{10}H_{14}O$, identical with the synthetical myrtenal (Semmler and Bartelt, Abstr., 1907, i, 429). This is the first occurrence of myrtenal in an essential oil. Myrtenal and perilla aldehyde are related in the same manner as pinene and limonene, and the occurrence of both in the same oil is remarkable.

E. F. A.

Oil of Thea Sasanqua. H. Kimura (*Ber. Deut. Pharm. Ges.*, 1911, **21**, 209—212).—The young leaves of the Japanese *Thea Sasanqua* are steeped in water for twenty-four hours and then distilled with steam. The oil, the yield of which varies from 0·4—1·0%, according to the period elapsing between the gathering of the leaves and their treatment (no oil is obtained after three months' keeping), is optically inactive, has a sweet, pleasant odour, and D^{21} 1·061. It contains about 97% of eugenol, a very small amount of an aldehydic or ketonic substance, and an ester. By hydrolysis with 2% alcoholic potassium hydroxide, the ester yields an alcohol with the odour of geraniol and a malodorous acid; these are being further examined. C. S.

Hydrogenation of Turpentine Oil. GUSTAVE VAVON (*Bull. Soc. chim.*, 1911, [iv], **9**, 256—261. Compare Darmois, Abstr. 1908, ii, 747; 1910, i, 52).—The hydrogenation of French, German, and American turpentine oils has been studied, and it is shown that (1) these all consist of α- and β-pinenes; (2) the two pinenes yield the same hydrocarbon on reduction; (3) sophistication of turpentine oil may be detected by (*a*) fractionation and (*b*) reduction and examination of the resulting products.

One hundred and thirty-six grams of the fraction of turpentine oil boiling at 155—165°, on reduction with platinum-black in presence of hydrogen, absorbs 1 gram-mol. of hydrogen, giving a *hydrocarbon*, $C_{10}H_{18}$, b. p. 166°, m. p. $-50°$, D_{15}^{15} 0·861, and $[\alpha]$ $+23·8°$ to $-23·8°$ for $\lambda = 578$, depending on the source of the oil used.

The relationship between the rotations of fractions of the same turpentine oil and those of the same fractions after reduction, indicates that the three oils examined consist essentially of α-pinene and β-pinene. The latter has b. p. 164°, m. p. $-50°$, $\alpha_J = 39·6°$, and on reduction gives a hydrocarbon having $\alpha_J = -40·6°$. α-Pinene on reduction gives a hydrocarbon having $\alpha_J = +41°$. French, German, and American turpentine oils contain respectively 63, 23, and 72% of α-pinene, consisting of the two optically inverse forms in varying proportions.

A pure turpentine oil should consist of at least 80%, boiling below 164°, and that portion boiling from 155—158° on hydrogenation by platinum-black should give a hydrocarbon boiling constantly at 166°. The platinum-black may be used several times without losing its activity if it is washed with ether after each operation and heated for a few minutes at 200°. T. A. H.

Caoutchouc Nitrosites and their Application in Analysis. PAUL ALEXANDER (*Zeitsch. angew. Chem.*, 1911, **24**, 680—687. Compare Abstr., 1907, i, 433).—This paper is devoted mainly to a criticism of a communication on this subject by Gottlob (Abstr., 1908, i, 95). The author brings forward fresh evidence in support of his contention that a nitrosite having the composition

$$C_{10}H_{15}O_7N_3$$

cannot be obtained directly from caoutchouc, as stated by Gottlob (*loc. cit.*) and Harries (compare Abstr., 1905, i, 223). The nitrosite formed directly from the interaction of nitrous fumes and caoutchouc approximates to the formula $C_9H_{12}O_6N_2$, but is not to be regarded as a simple substance. The production of carbon dioxide during the reaction has been verified, and it has been demonstrated also that the same gas is liberated when the crude nitrosite is heated at 40—80°; in fact, it has been possible to absorb about 87% of the one molecular proportion of carbon dioxide evolved from one molecular proportion of caoutchouc. In conclusion, the author states that this reaction may be employed for the analysis of crude caoutchoucs, and, in many cases, also for the estimation of caoutchouc in vulcanised rubber products. W. H. G.

Cold Vulcanisation. B. V. BYSOFF (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 209. Compare Abstr., 1910, i, 865; this vol., i, 314).—Comparative measurements have been made of the amount of sulphur which is fixed when dry caoutchouc is vulcanised by means of dry and moist benzene solutions of sulphur chloride. In two pairs of experiments with benzene solutions containing 0·5 and 1·0 gram of sulphur chloride per 100 c.c., it was found that the amount of fixed sulphur in the vulcanisation with the moist solution was only 76 (77) % of that fixed when the dry solution was employed. With undried caoutchouc and a dry benzene solution a similar reduction of the amount of fixed sulphur was observed. H. M. D.

Behaviour of Colloidal Metals (Platinum, Gold, Silver, and Palladium) Prepared by Bredig's Method on Solutions of Guaiaconic Acid. GEORGE A. BUCKMASTER (*7th Intern. Congr. Appl. Chem.*, Sect. IV A 2, 29).—Guaiaconic acid in oxygen-free alcohol is oxidised to guaiacum-blue by colloidal metals prepared by Bredig's method, for the particles of metal contain occluded or adsorbed oxygen. A given weight of any of these colloidal metals oxidises a definite amount of guaiaconic acid. The metallic sol is then inactive, but may be reactivated by air or oxygen. Gold sol, when first prepared, is active for a few hours, but rapidly loses the property, which is preserved for weeks and months by the sols of platinum, palladium, and silver. The occluded oxygen of platinum sols can be driven out by boiling, or by the passage of pure hydrogen or carbon dioxide, and the inactive sols obtained can be reactivated by oxygen. The oxidation of guaiaconic acid is therefore due, not to the colloidal metal as such, but to the occluded oxygen. The action of platinum-black on guaiaconic acid is similarly due to occluded oxygen.
R. V. S.

The Pseudo-Peroxydase Reaction between Hæmoglobin its Derivatives, and Guaiaconic Acid (Guaiacum Reaction for Blood Pigment). GEORGE A. BUCKMASTER (*7th Intern. Congr. Appl. Chem.*, Sect. IV A 2, 30).—The oxidation of guaiaconic acid, aloin, or leucomalachite-green in the presence of traces of hydrogen peroxide is effected by minute amounts of hæmoglobin or any of its derivatives which contain iron. Pure hæmatoporphyrin or hæmatoidin (that is, iron-free derivatives) are incapable of causing the oxidation of these substances. Blood solutions which have been heated in a sealed tube at 200° for three hours still give the reaction. The reaction is therefore not due to a peroxydase, but is connected with the presence of the iron contained in the hæmoglobin. R. V. S.

The Sugar in Sophorin. HENRI TER MEULEN (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 411—415).—A sugar has been isolated from sophorin, a glucoside present in the flower-buds of the Chinese yellow currant (*Sophora japonica*), and proved to be identical with rhamninose, although it was not obtained pure. Sophorin was treated with rhamninase solution for a day at 60°, the mixture filtered, and, after concentration at reduced pressure, the filtrate boiled with alcohol to destroy the enzyme. Fractional precipitation with ether yielded a light yellow syrup. With the polarimeter a rotation of $-3°29'$ was observed, the theoretical value for the same quantity of rhamninose being $3°36'$. Sophorin is probably identical with rutin. A. J. W.

Balanophorin. I. M. SIMON (*Monatsh.*, 1911, **32**, 89—104).—Brief references are given to previous investigations of balanophorin, the waxy substance obtained from the *Balanophorae*. It is extracted by ether from the dried Javanese tubers, and purified by successive treatment with alcohol and acetone. The purified substance, $C_{12}H_{20}O$(?), is a white, amorphous powder, has m. p. 56—57°, and is not decomposed by aqueous or alcoholic alkalis even at 140°. By distillation under 19 mm., or by fusion with potassium hydroxide at 150—210°, it yields palmitic acid and other products as yet unexamined. C. S.

Dye in the Root of Azafran. CARL LIEBERMANN (*Ber.*, 1911, **44**, 850—851).—The root of a plant obtained from Paraguay, and belonging to the family of the Scrophulariaceæ, is used under the name azafran or azafranillo to colour fats. It contains about 1% of a dye, called *azafrin*, which is easily extracted by boiling benzene. From the solution the dye is obtained in orange-red crusts, which form microscopic needles, m. p. 214°, after recrystallisation. It does not contain nitrogen or methoxy- or ethoxy-groups, but the presence of one hydroxyl group is shown by Zerewitinoff's method. It dyes wool yellow, and forms yellow to orange lakes with Scheurer's mordants, but not with the usual mordants; wool extracts the whole of the dye from a hyposulphite vat. The dye gives a fine blue solution in concentrated sulphuric acid, which becomes violet by the addition of alcohol. The examination of the dye is being continued.
C. S.

Chlorophyll. XIII. Decomposition and Formation of Chlorophyll. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1911, **380**, 148—154).—In continuation of the previous work (this vol., i, 141), it is shown that chlorophyllase has synthesising properties, and can build up chlorophyll from phytol and chlorophyllide.

The method consists in hydrolysing chlorophyll, for example, by digesting the meal from leaves of *Gallopsis* with moist ether for several days, then adding phytol, and in the course of several days one-third to three-fourths of the original chlorophyll is regenerated. This confirms the view that the enzyme plays an important function in the formation of chlorophyll in plant tissues. The chlorophyll obtained yields the same phytochlorin-*e* and phytorhodin-*g* as are obtained from natural chlorophyll.

It is also shown that chlorophyllase can esterify chlorophyllide in the presence of ethyl alcohol, yielding ethyl chlorophyllide. J. J. S.

Chlorophyll. XIV. Comparative Experiments with Chlorophyll from Different Plants. III. RICHARD WILLSTÄTTER and MAX ISLER (*Annalen*, 1911, **380**, 154—176. Compare Willstätter, Hocheder, and Hug, Abstr., 1910, ii, 150; Willstätter and Oppe, this vol., i, 140).—The solution of the question as to the identity of the chlorophyll obtained from different plants has been attempted by an examination of the phytochlorins and phytorhodins obtained by their decomposition. Previous experiments have indicated that in the great majority of cases the products obtained from dried leaves are phytochlorin-*e* and phytorhodin-*g*, although several exceptions had been met with. It is shown in the present communication that these exceptions are due, not to differences in the natural phytochromin, but to the methods of treatment of the material producing alterations in the chlorophyll. All these exceptions disappear when the dried material is extracted, the chlorophyll solution immediately treated with acid, and the resulting phæophytin hydrolysed in the cold with alkali. Under these conditions the dried leaves of all varieties of plants yield only phytochlorin-*e* and phytorhodin-*g*.

If the filtered chlorophyll extract is kept, the phytochromin undergoes change, especially in the case of the extract from stinging nettles, and the final products of decomposition are phytochlorin-*f*, which is soluble in 11% hydrochloric acid, and a phytorhodin with feebler basic properties than phytorhodin-*g*. Of extreme importance is the sensitiveness of phytorhodin towards alkali, the longer the product is left in contact with warm alkali the smaller is the yield of phytorhodin. If, however, this source of error is avoided, the relative molecular proportions of phytorhodin to phytochlorin are approximately 1 : 2·5.

Experiments have been made with fresh vegetable tissues as well as with dried, and the investigation is complicated by the fact that during the processes of dividing and extracting large quantities of the material fermentative changes of a complex nature can take place. For example, in the case of grass, phytochlorin-*f* is obtained, whereas dry grass gives the normal product, phytochlorin-*e*.

The best method of treating the fresh tissue is the addition of aqueous methyl alcohol, by means of which the division and extraction of the material is greatly facilitated. Under these conditions, provided the extraction is made immediately after the addition of the alcohol, the phæophytin obtained yields in all cases the normal products of decomposition, namely, phytochlorin-*e* and phytorhodin-*g*, and in practically the same proportion as obtained from dry leaves.

The question as to whether the phytochlorin and phytorhodin are derived from the same molecule of chlorophyll and phæophytin is discussed, and the conclusion is drawn that in all probability they are derived from different molecules, so that chlorophyll consists of two components, one of which gives rise to phytochlorin and the other to phytorhodin (compare Tsvett, Abstr., 1907, i, 787). The amounts of phytochlorin-*e* and phytorhodin-*g* obtained from a given quantity of phæophytin by the action of alcoholic potassium hydroxide were estimated colorimetrically by comparison with known quantities of the pure substances.

The fresh material examined included leaves of the following: *Hyloconium*, *Aspidium*, *Equisetum* *Pinus*, *Salix*, *Urtica*, *Platanus*, *Rubus*, *Buxus*, *Aesculus*, *Petroselinum*, *Heracleum*, *Galeopsis*, *Solanum*, and *Sambucus*. J. J. S.

Chlorophyll. XV. Isolation of Chlorophyll. RICHARD WILLSTÄTTER and ERNST HUG (*Annalen*, 1911, **380**, 177—211).—The object of the investigation has been the isolation of pure chlorophyll. It occurs in plant tissues mixed with yellow pigments, for example, carotin and xanthophyll, and with fats, waxes, and salts of aliphatic acids. Many of these distribute themselves between solvents in much the same manner as chlorophyll itself, and their removal is tedious. The presence of these impurities always reduces the magnesium contents of the colouring matter, and is indicated by the presence of calcium compounds in the ash derived from the specimen.

The chlorophyll was always extracted from dried leaves, and estimated colorimetrically by Willstätter, Hocheder, and Hug's method (Abstr., 1910, ii, 151) by comparison with ethylchlorophyllide solutions of known concentration. The expression, degree of purity, is used to express the percentage of chlorophyll in 100 grams of dried extract when heated for a half to three-quarters of an hour under reduced pressure.

Although the amount of chlorophyll extracted is greater the longer the extraction is carried out, it is inadvisable to prolong the period of extraction, as the chlorophyll can undergo alteration during this time (compare Willstätter and Oppe, this vol., i, 141, and Willstätter and Isler, preceding abstract). To obtain unaltered chlorophyll it is essential that the extraction should be rapid, although the amount extracted is not so large. The method used is a modification of that of Willstätter and Stoll (this vol., i, 142), and consists in spreading the dried meal on the thimble before the addition of the solvent. With a charge of 2 kilos. the extraction requires two to three hours, and the volume of solvent is about 1·5 litres per kilo. of meal. Using ethyl alcohol, the degree of purity of the extract is about 14—16, as the chlorophyll contains about six times its own weight of impurities. Before treatment with alcohol it is an advantage to subject the meal to a preliminary extraction with benzene (3 litres) and then light petroleum (1·5 litres per kilo.). The light petroleum is essential in order to remove the benzene, and it is not necessary to dry the meal after extraction with the different solvents. This preliminary extraction increases appreciably the degree of purity of the subsequent crude solution in light petroleum.

To obtain such a solution, the alcoholic extract is shaken with two-thirds its volume of light petroleum and one-third its volume of water. Fractional extraction offers no advantages, and the degree of purity of the solution is usually 33—40, provided the preliminary extraction with benzene and light petroleum is carried out. By twice washing the light petroleum solution with aqueous methyl alcohol (90%) it is possible to increase the degree of purity to 50—60. It is essential that the alcohol should not be too concentrated, as considerable amounts of chlorophyll are then removed. The degree of purity can be increased to 70 by extracting the washed light petroleum solution twice with 95% methyl alcohol saturated with light petroleum (b. p. 30—50°), when about half the chlorophyll is dissolved by the alcohol. The alcoholic solution is finally shaken with light petroleum, and to obtain the chlorophyll from this final light petroleum solution (purity 70), it is washed with water until free from methyl alcohol, when the pigment is precipitated in a very fine state of division which cannot be filtered. The addition of large amounts of anhydrous sodium sulphate, or of smaller amounts and a little calcium carbonate, renders the precipitation complete, and also deposits the precipitate in such a form that it can be filtered with ease. To purify the chlorophyll it is dissolved in 96% alcohol, precipitated with dilute sodium chloride solution, and finally dissolved in ether and precipitated with light petroleum. The yield is 0·75 to 1 gram from 2 kilos. of stinging nettle meal containing 14—16 grams of chlorophyll.

A pure specimen should possess the following characteristics:

1. The ash must correspond with the theoretical, and consist of pure magnesium oxide.
2. The phytol content must be 33%, and the phytol must be free from solid impurities.
3. During the hydrolysis with alkalis the temporary formation of the brown coloration must be given.
4. By the decomposition of the phæophytin, the normal products, phytochlorin-*e* and phytorhodin-*g*, must be formed.
5. The specimen must contain no yellow pigments.
6. The spectrum must correspond with that of the chlorophyll in the leaf extract.

The pure compound is a bluish-black, glistening powder with a metallic lustre, and when finely divided gives a greenish- or bluish-black powder. It appears crystalline under the microscope, and has no definite m. p.; for example, different specimens melt at 93—96° or 103—106° when heated in ordinary m.-p. tubes. Its ethereal solution has a brilliant greenish-blue colour, and is strongly fluorescent. It is practically insoluble in cold light petroleum, but dissolves readily on the addition of a few drops of methyl or ethyl alcohol. It is also soluble in benzene and pyridine, and its alcoholic solution gives Kraus's reaction. The pigment has neither acid nor basic properties, but is readily decomposed by both acids and alkalis. Analyses agree with the formula $C_{55}H_{72}O_6N_4Mg$. Its absorption spectrum is analogous to that of ethyl chlorophyllide, and it undergoes alcoholysis or hydrolysis in the presence of chlorophyllase (compare this vol., i, 141).

The chlorophyll thus obtained is a mixture of two components (compare Willstatter and Isler, preceding abstract), which have been isolated and will be described later. J. J. S.

The Existence of Two Chlorophyllans. M. TSVETT (*Biochem. Zeitsch.*, 1911, **31**, 505—506).—The author maintains as a result of his adsorption-spectroscopic analytical researches that two chlorophyllans exist, as also two chlorophyllins. S. B. S.

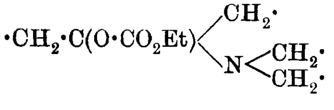
A New Vegetable Colouring Matter: Thujorhodin. M. TSVETT (*Compt. rend.*, 1911, **152**, 788—789).—The leaves of *Thuja orientalis*, as well as of other Coniferæ (*Cryptomeria japonica, Juniperus virginiaca, Taxus baccata,* etc.), after grinding with sand and calcium carbonate, yield a new colouring matter on extraction with carbon disulphide or light petroleum. This substance, for which the name *thujorhodin* is proposed, gives the lipochrome blue coloration with concentrated sulphuric acid. The solution in carbon disulphide is red, and shows four absorption bands, λ 570—560, 530—515, 470—475 [? 455], 450—440. The alcoholic solution is rose-coloured, and shows less distinct bands, whilst three bands are visible in the light petroleum solution, which is yellow. W. O. W.

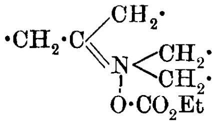
Separation of Urobilin from its Chromogen. LÉON GRIMBERT (*Compt. rend.*, 1911, **152**, 727—728).—The fresh urine is extracted with chloroform. After filtering the chloroform through cotton wool, an alcoholic solution of zinc acetate is added until the turbidity first formed disappears; the appearance of a green fluorescence indicates the presence of free urobilin. In this case the chloroform is shaken with a few c.c. of aqueous sodium phosphate neutral to phenolphthalein. This removes only the chromogen of urobilin (Saillet's urobilinogen). The chloroform layer now gives the fluorescence only after treatment with a trace of iodine or other oxidising agent. The chromogen cannot be extracted by chloroform from solutions which are alkaline to phenolphthalein. W. O. W.

Isomeric Disulphoxides from Thianthren. KARL FRIES and WILHELM VOGT (*Ber.*, 1911, **44**, 756—761).—The products described by Krafft and Lyons (Abstr., 1896, i, 297) as thianthren dioxide and thianthrenmonosulphone are shown to be isomeric disulphoxides. Both are readily reduced to thianthren by hydrogen bromide at the ordinary temperature, or by warming with zinc dust and acetic acid, whereas sulphones are not attacked by hydrobromic acid. The compounds possess basic properties, and are not oxidised by nitric acid, whereas thianthrenmonosulphone is not basic, and is readily oxidised to a trioxide.

*iso*Thianthren disulphoxide crystallises readily from benzene in slender needles, and from water or glacial acetic acid in prisms, m. p. 249°. It dissolves in concentrated nitric or hydrochloric acid, yielding colourless solutions, and is transformed into the isomeric disulphoxide when heated for some time at 250° or more readily at 280°. The same transformation occurs when the *iso*-compound is dissolved in concentrated sulphuric acid, kept for two days, and then poured into water. Thianthren disulphoxide is most easily prepared by the action of chlorine on a benzene solution of thianthren, and has m. p. 284° (Krafft and Lyons: 278—279°). It is less soluble than the *iso*-compound in glacial acetic acid and in hydrochloric or nitric acids. Its solution in concentrated sulphuric acid has a reddish-violet colour, and when this solution is kept for two days and then diluted with water, a mixture of the two isomeric disulphoxides is obtained. J. J. S.

Quinine and Euquinine. A. Astruc and L. Courtin (*J. Pharm. Chim.*, 1911, [vii], **3**, 292—294. Compare Astruc, *Bull. Soc. chim.*, 1907, [iv], **1**, 192).—The authors briefly recapitulate the points of similarity and difference between quinine aud euquinine; the most important difference is the fact that euquinine behaves as a mono-acidic base. The formation of euquinine by the attack of ethyl chloroformate on the hydroxyl group in the quinine molecule leads to a constitution containing the group (I). This constitution is not in harmony with the stability of euquinine, or with its monobasic nature. The authors suggest that a constitution containing the group (II) is in better agreement with the facts. C. S.


(I.)


(II.)

Ephedrine and ψ-Ephedrine. Paul Rabe (*Ber.*, 1911, **44**, 824—827).—Ephedrine and ψ-ephedrine are optically isomeric β-methylamino-α-phenylpropane-α-ols of the formula

OH·CHPh·CHMe·NHMe.

The ammonium base of ephedrine decomposes into water, methylamine, and α-phenylpropylene αβ-oxide, b. p. 204°, $[\alpha]_D^{16}$ +65·84°.

This oxide, when heated with aqueous methylamine in sealed tubes on the water-bath, forms the hydrochloride, $C_{10}H_{15}ON,HCl$, which melts partly at 148—149°, the rest at 165°, and has $[\alpha]_D^{19}$ +24·2°. It is a mixture of methylated αβ-hydramines. E. F. A.

New Leucomaine. J. Ubeda y Correal (*7th Intern. Congr. Appl. Chem.*, Sect. IV A 2, 112—113).—On treating 29 kilograms of fresh beef with water containing hydrochloric acid, a solution is obtained from which, by evaporation to dryness, extraction with alcohol, precipitation with mercuric chloride, and subsequent decomposition with hydrogen sulphide, a substance can be prepared which yields a platinichloride crystallising in red, acicular prisms (angles 48°49′ and 131°16′ respectively), and containing 47·22—47·31% of platinum. When the platinichloride is decomposed with hydrogen sulphide, a solution is obtained which reacts with gold chloride, picric acid, potassium and cadmium iodides, and other reagents. The hydrochloride forms colourless crystals (angles 31°33′ and 148°27′ respectively). R. V. S.

Luciferesceine, the Fluorescent Material Present in Certain Luminous Insects. F. Alex. McDermott (*J. Amer. Chem. Soc.*, 1911, **33**, 410—416).—Coblentz (*Physikal. Zeitsch.*, 1909, **10**, 955) has discovered that the firefly (*Photinus pyralis*) contains a substance which gives solutions with a bright blue fluorescence. More recently, he has found that *Photinus corruscus* and *Photuris pennsylvanica* also contain this substance.

The author has detected it in *Photinus pyralis*, *P. corruscus*, and also in *P. scintillans*, but has been unable to confirm its presence in *Photuris pennsylvanica*. It is particularly abundant in a sticky fluid which the insects emit when irritated. This substance, *luciferesceine*, can be obtained in an impure condition from an alcoholic extract of the insects, or, in a purer form, by dissolving in alcohol the sticky liquid on the walls of the vessels in which the insects have been confined. The alcoholic solution thus obtained is clear, colourless, has a bright blue fluorescence, and, on evaporation, yields a pale yellow, amorphous residue of luciferesceine. The compound gives a red coloration with concentrated sulphuric acid, and a dense, cream-coloured precipitate with potassium ferrocyanide. In general, its reactions indicate that it is probably of an alkaloidal nature. It seems likely that luciferesceine is contained in a defensive secretion of the insect, but that its fluorescence does not bear any relation to the vital processes or to the defensive function. E. G.

Preparation of ψ-Morphine by Mineral Catalysis. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1911, [iv], **9**, 264—266).—Ten c.c. of a 4% solution of copper sulphate, just decolorised with potassium cyanide, is poured into a solution containing 5 grams of morphine hydrochloride and 20 c.c. of hydrogen peroxide (10 to 12 vols.) in 200 c.c. of water. After a few minutes, oxygen is evolved and a precipitate of ψ-morphine, which soon becomes crystalline, is formed. The alkaloid may be purified by dissolving it in ammonia solution (22° B), decolorising with animal charcoal, and finally evaporating to a small bulk. The yield is from 20 to 25% of the theoretical.

T. A. H.

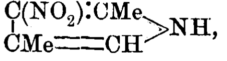
Guaninepentoside from Molasses Residues. KARL ANDRLÍK (*7th Intern. Congr. Appl. Chem.* 1909, Sect. V., 331—337).—Molasses residues when boiled with copper sulphate and sodium hydroxide yield about 0·04% of guanine pentoside, $C_5H_8O_4,C_5H_5N_5O,2H_2O$, which crystallises in slender, colourless, sparingly soluble needles. When boiled with dilute mineral acids, it is hydrolysed to a pentose, $[\alpha]_D - 16·7°$ (41·9%), and guanine (40%), and the pentoside becomes brown at 234—241°, m. p. (decomp.) above 300°; in dilute sulphuric acid it has $[\alpha]_D - 13·95°$. E. F. A.

Nitropyrrole. ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 311—314).—Pyrrole can be nitrated by the method previously suggested (*ibid.*, 1902, **11**, ii, 16) using ethyl nitrate in the presence of sodium ethoxide or metallic sodium, and if the isolation of the sodium compound of nitropyrrole is avoided (for it was found to be spontaneously inflammable, *loc. cit.*), nitropyrrole can be prepared. Pyrrole diluted with ether is treated with sodium wire (1 mol.) and ethyl nitrate (1 mol.); the reaction is commenced by

f f 2

slightly warming, and, after some days at the ordinary temperature (protected from moisture and carbon dioxide), the sodium will have disappeared. Ice is then added, and from the mixture of nitrite and *sodium* salt obtained, the former is removed by taking advantage of the insolubility of the *silver* salt of nitropyrrole. The sodium salt is then again obtained, and from it by the action of carbon dioxide free *nitropyrrole* is prepared. It forms pale yellow, glistening scales or prisms, or rhombohedra, m. p. 63·5°. Of the two possible constitutions, that of 3-nitropyrrole is considered the more probable.

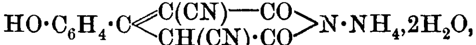
Nitro-2 : 4-*dimethylpyrrole*, of the probable formula



$$\left.\begin{array}{l}\mathrm{C(NO_2){:}CMe}\\ \mathrm{CMe{=}{=}CH}\end{array}\right>\mathrm{NH},$$

is prepared similarly, but more easily, because the slighter solubility of its *sodium* compound renders purification by means of the silver compound unnecessary. It crystallises in prisms, m. p. 111°. Both these nitro-compounds are unaffected by permanganate in alcoholic solution. R. V. S.

Action of Cyanacetic Ester on *o*- and *p*-Hydroxybenzaldehydes in the Presence of Ammonia. MARIO SCLAVI (*Atti R. Accad. Sci. Torino*, 1911, **46**, 181—194).—By the interaction of *p*-hydroxybenzaldehyde (1 mol.) with cyanoacetic ester (2 mols.) and ammonia (3 mols.) at the ordinary temperature, the author has obtained the ammonium salt of *p*-hydroxybenzaldicyanoglutaconimide [2 : 6-diketo-3 : 5-dicyano-4-*p*-hydroxyphenyltetrahydropyridine],



$$\mathrm{HO{\cdot}C_6H_4{\cdot}C}\left<\begin{array}{l}\mathrm{C(CN){-}{-}CO}\\ \mathrm{CH(CN){\cdot}CO}\end{array}\right>\mathrm{N{\cdot}NH_4,2H_2O},$$

and as secondary products the two corresponding (saturated and unsaturated) amides. From salicylaldehyde, *o*-hydroxybenzylidenedicyanodiacetic ester was chiefly formed, along with an *ammonium* salt which could not be identified.

The *ammonium* salt of 2 : 6-diketo-3 : 5-dicyano-4-*p*-hydroxyphenyltetrahydropyridine is a white substance, which does not melt below 300°, and does not lose ammonia even at 100°. By double decomposition in aqueous solution a number of crystalline salts were prepared from it, including those of iron (*ferric* and *ferrous*), *copper*, and *potassium*. The last is sparingly soluble in the cold, solutions containing only one part in three thousand of potassium chloride being precipitated after some hours. The *magnesium* salt,

$$(C_{13}H_6O_3N_3)_2Mg,6H_2O,$$

forms long, colourless crystals. The *barium* salt,

$$(C_{13}H_6O_3N_3)_2Ba,6H_2O,$$

crystallises similarly. The *silver* salt, $C_{13}H_6O_3N_3Ag,H_2O$, forms yellowish-white crystals, which change in the light. 2 : 6-*Diketo*-3 : 5-*dicyano*-4-p-*hydroxyphenyltetrahydropyridine*, $C_{13}H_7O_3N_3$, obtained from the barium or silver salt, forms lustrous, white crystals. a-*Cyano*-p-*hydroxyphenylacrylamide*, $OH{\cdot}C_6H_4{\cdot}CH{:}C(CN){\cdot}CO{\cdot}NH_2$, forms bright yellow crystals, m. p. 245° (with evolution of ammonia). a-*Cyano*-β-p-*hydroxyphenylpropionamide*,

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(CN){\cdot}CO{\cdot}NH_2,$$

forms long, colourless crystals, m. p. 156°. R. V. S.

Rupture of the Pyridine Ring. WILHELM KÖNIG and R. BAYER (*J. pr. Chem.*, 1911, [ii], **83**, 325—328).—In this preliminary note the authors mention a number of substances, inorganic and organic, the additive compounds of which with pyridine are decomposed by primary or secondary amines, preferably aniline or 2-methyldihydroindole, yielding, by rupture of the pyridine ring, the so-called "pyridine dyes" (compare Reitzenstein and Breuning, this vol., i, 225).

C. S.

The New Series of Leuco-bases and Colouring Matters from Diphenylethylene. PAUL LEMOULT (*Compt. rend.*, 1911, **152**, 962—964. Compare Abstr., 1909, i, 836; Busignies, Abstr., 1909, i, 736).—Wahl and Meyer (Abstr., 1910, i, 134) having called in question the author's view that the presence of hydrogen attached to the ethylenic carbon atom in alkyl derivatives of di-*p*-aminodiphenylethylene is essential for the production of blue dyes from these leuco-bases, a further series of the compounds has been examined.

Michler's ketone was treated with a magnesium alkyl iodide, using the methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, *n*-sec.-butyl, *iso*amyl, and *cyclo*hexyl compounds. Two series of derivatives were thus obtained: compounds of the type $CHR\!:\!C(C_6H_4\cdot NMe_2)_2$, giving intense green or blue colorations with nitrous acid, and compounds of the type $CRR'\!:\!C(C_6H_4\cdot NMe_2)_2$, which gave extremely pale colorations when oxidised in this way. Corresponding colours were obtained on satinette mordanted with tannin.

n-*Propylidenetetramethyldiaminodiphenylmethane*,

$$CHEt\!:\!C(C_6H_4\cdot NMe_2)_2,$$

has m. p. 47·5°; the iso*propylidene* compound, m. p. 89°; the corresponding n-*butylidene* compound, m. p. 50·5°; the n-sec.-*butylidene* derivative, $CMeEt\!:\!C(C_6H_4\cdot NMe_2)_2$, m. p. 79°. W. O. W.

Tautomerism of Amidines. RUDOLF PUMMERER (*Ber.*, 1911, **44**, 810. Compare this vol., i, 231).—O. Fischer (Abstr., 1907, i, 353) has already shown that Meldola's amidines derived from naphthalene (Trans., 1903, **83**, 1185) are not tautomerides. J. J. S.

Compounds of Antipyrine with the Chlorides of Tin. CHARLES ASTRE and J. VIDAL (*Bull. Soc. chim.*, 1911, [iv], **9**, 309—312. Compare Abstr., 1900, i, 362—411).—When a solution of 10 grams of stannous chloride in 100 c.c. of concentrated hydrochloric acid diluted with its own volume of water is added drop by drop to a solution of 10 grams of antipyrine in 100 c.c. of the same acid, a white precipitate is obtained having the composition

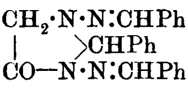
$$4C_{11}H_{12}ON_2,SnCl_4,4HCl.$$

This precipitate is not formed at 100°, but, on cooling the solution, the compound separates in large, tabular, clinorhombic crystals, which can also be obtained by immersing strips of tin in a hydrochloric acid solution of antipyrine. The crystals become pasty at 80°, but the melting point is not definite. The change from stannous to stannic chloride in the presence of antipyrine is not an isolated fact, since ferrous chloride is similarly oxidised to ferric chloride.

When the stannous chloride is replaced by stannic chloride, microscopic, white, clinorhombic crystals are obtained, having the composition: $3C_{11}H_{12}ON_2,SnCl_4,3HCl$, which also possess no definite melting point. They can be distinguished from the former compound by the fact that their solution in hydrochloric acid does not give precipitates with solutions of mercuric chloride and potassium ferricyanide. With the former compound the precipitates are white and green in colour respectively. T. S. P.

Action of Hydrazine Hydrate on Ethyl Chloroacetate. THEODOR CURTIUS and LUDWIG HUSSONG (*J. pr. Chem.*, 1911, [ii], 83, 249—278).—The authors mention the complex reactions by which hydrazino-fatty acids have been prepared, and also refer to the unsuccessful attempts of Schöfer (*Diss.*, Kiel, 1892) and of Foersterling (Abstr., 1895, i, 3 4) to obtain hydrazinoacetic acid by the action of hydrazine hydrate and phthalylhydrazide respectively on ethyl chloroacetate. They find that the addition of ethyl chloroacetate to hydrazine hydrate results in the formation chiefly of hydrazinoacethydrazide, whilst by reversing the order of the addition hydrazinodiacethydrazide is the main product; in both cases, however, about 50% of the ester is reduced to ethyl acetate, an equivalent amount of nitrogen being evolved.

For example, ethyl chloroacetate is added slowly to hydrazine hydrate below 70° (the nitrogen evolved is collected and measured), and the product is diluted with water and shaken for a long time with successive small quantities of benzaldehyde. The resulting benzylidene compounds (except that which is obviously pure benzaldazine) are treated successively with 95% alcohol, light petroleum, and benzene. The residue obtained by evaporating the last solution is purified by alcohol, whereby *tribenzylidenehydrazinoacethydrazide* (annexed formula), m. p 176° (decomp.), is obtained in white needles. This substance, like tribenzylidenehydrazinodiacethydrazide (see below), dissolves in concentrated hydrochloric acid at 60°, but is not reprecipitated by dilution; by treating the diluted solution with sodium acetate, *dibenzylidenehydrazinoacethydrazide*,



$$\begin{array}{l} CH_2\cdot N\cdot N{:}CHPh \\ | \qquad\quad >CHPh \\ CO{-}N\cdot N{:}CHPh \end{array}$$

$$CHPh{:}N\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot N{:}CHPh,$$

m. p. 161° (decomp.), is obtained. By prolonged boiling with hydrochloric acid, tribenzylidenehydrazinoacethydrazide is decomposed completely into its constituents.

Conversely, when hydrazine hydrate (3 mols.) is added to ethyl chloroacetate, and the product diluted with water and shaken repeatedly with benzaldehyde, the characteristic benzylidene compound obtained is *tribenzylidenehydrazinodiacethydrazide*,

$$CHPh{:}N\cdot N(CH_2\cdot CO\cdot NH\cdot N{:}CHPh)_2,$$

m. p. 219° (decomp.), in 15—20% yield. The substance dissolves in concentrated hydrochloric acid at 35—40°, and is recovered for the most part by diluting the solution with water; by keeping the undiluted solution at the ordinary temperature in contact with benzene, *hydrazinodiacethydrazide hydrochloride*,

$$NH_2\cdot N(CH_2\cdot CO\cdot NH\cdot NH_2)_2,3HCl,H_2O,$$

separates in yellowish-white crystals, which darken at 150°, and become greyish-black at 180°, without melting. By shaking a slightly acidified aqueous solution of the hydrochloride with benzaldehyde, hydrated tribenzylidenehydrazinodiacethydrazide, $C_{25}H_{24}O_2N_6,H_2O$, is obtained as a white powder, which sinters at 92°, partly melts at about 120°, and is fused completely at 190°; by treatment with absolute alcohol, the hydrated compound is converted into the anhydrous form mentioned above. In a similar manner, hydrazinodiacethydrazide hydrochloride can be converted into hydrated *tri*-m-*nitrobenzylidenehydrazinodiacethydrazide*, $C_{25}H_{21}O_8N_9,H_2O$, m. p. 222—223° (decomp.), and *tri*-m-*chlorobenzylidenehydrazinodiacethydrazide*, $C_{25}H_{21}O_2N_6Cl_3,H_2O$, which sinters at 100°, and melts between 110—180°; neither of these two compounds loses H_2O by boiling with alcohol or by prolonged heating at 60—70°.

Hydrazinodiacetic acid, $NH_2{\cdot}N(CH_2{\cdot}CO_2H)_2$, m. p. 166—167° (decomp.), is obtained by keeping tribenzylidenehydrazinodiacethydrazide in contact with concentrated hydrochloric acid and benzene for fifteen to twenty hours, separating the benzene layer, and distilling the acid solution with steam for twenty to twenty-five minutes. The acid is more conveniently obtained by adding hydrazine hydrate (about 5 mols.) to an alcoholic solution of chloroacetic acid, whereby nitrogen is not evolved, and a syrup is obtained which is diluted with water and shaken with benzaldehyde; the hydrazinodiacetic acid, which does not react with benzaldehyde, is thus obtained mixed with benzaldazine, and the two substances are easily separated by dissolving the latter in hot alcohol. From its method of formation, hydrazinodiacetic acid might have the symmetrical constitution

$$CO_2H{\cdot}CH_2{\cdot}NH{\cdot}NH{\cdot}CH_2{\cdot}CO_2H,$$

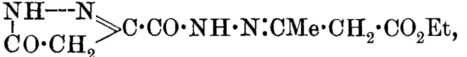
but this is rejected, because, although the acid itself does not react with benzaldehyde, its hydrazide does, yielding the tribenzylidenehydrazinodiacethydrazide described above. Moreover, the ease with which hydrazinodiacetic acid reduces ammoniacal silver solutions in the cold, Fehling's solution at the ordinary temperature, and mercuric oxide and potassium permanganate by warming, indicates the presence of the group $NH_2{\cdot}N{:}$ rather than $\cdot NH{\cdot}NH\cdot$. Ammonia, not hydrazine, is obtained when hydrazinodiacetic acid is heated with concentrated hydrochloric or sulphuric acid; the other product of hydrolysis could not be isolated.

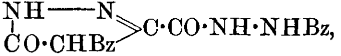
By the action of hydrazine hydrate on ethyl bromoacetate, ethyl iodoacetate, ethyl di-iodoacetate, chloroacetamide, or di-iodoacetamide (all of which are prepared from ethyl diazoacetate), nitrogen is evolved, and the whole of the halogen is obtained in an ionic condition.

C. S.

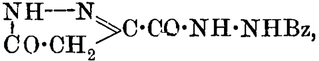
Action of Hydrazine Hydrate on Ethyl Bromosuccinate.

THEODOR CURTIUS and HEINRICH GOCKEL (*J. pr. Chem.*, 1911, [ii], **83**, 279—311. Compare preceding abstract).—When hydrazine hydrate (4—5 mols.) is added to ethyl bromosuccinate and the mixture is heated for eight and a-half hours, the product is not a derivative of hydrazinosuccinic acid, but a mixture of 5-pyrazolone-3-carboxylohydrazide and its hydrazine salt; the same substance is obtained more conveniently by von Rothenburg's method (Abstr., 1895, i, 302). The substance, which contains $\frac{3}{4}H_2O$, and has m. p. 253—254°, not 238—239°, forms a yellow *dihydrochloride*, $C_4H_6O_2N_4,2HCl$, which easily changes to a white *hydrochloride*, $C_4H_6O_2N_4,HCl$, and a *hydrazine* salt, $C_4H_6O_2N_4,N_2H_4$, m. p. 199—200° (decomp.). When heated with concentrated hydrochloric acid it yields 5-pyrazolone-3-carboxylic acid, which is converted by alcoholic hydrogen chloride into its ethyl ester and by nitrous acid into 4-oximino-5-pyrazolone-3-carboxylic acid; these compounds have been described by von Rothenburg (*loc. cit.*) and Ruhemann (Trans., 1896, **69**, 1395).

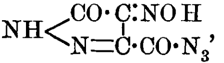
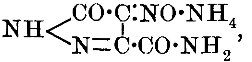
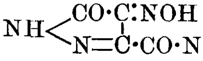
5-Pyrazolone-3-carboxylohydrazide reacts with benzaldehyde in very dilute hydrochloric acid to form the *benzylidene* derivative, $C_{11}H_{10}O_2N_4$, m. p. 252—253° (decomp.), with ethyl acetoacetate to form the substance,  $\begin{matrix}NH\text{---}N\\ \mid\quad\quad\\ CO\cdot CH_2\end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et$, m. p. 182° (decomp.), and with alcoholic benzoyl chloride ($1\frac{1}{2}$ mols.) in alkaline solution to form *4-benzoyl-5-pyrazolone-3-carboxylobenzoylhydrazide*,

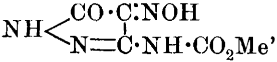

$$\begin{matrix}NH\text{——}N\\ \mid\quad\quad\\ CO\cdot CHBz\end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot NHBz,$$

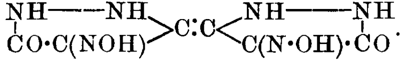
m. p. 214° (decomp.), and *5-pyrazolone-3-carboxylobenzoylhydrazide*,


$$\begin{matrix}NH\text{---}N\\ \mid\quad\quad\\ CO\cdot CH_2\end{matrix}\!\!>\!C\cdot CO\cdot NH\cdot NHBz,$$

m. p. 269° (decomp.), the former being insoluble, the latter soluble, in sodium hydroxide.

4-Oximino-5-pyrazolone-3-carboxyloazoimide,  $NH\!<\!\begin{matrix}CO\cdot C{:}NOH\\ \quad\;\mid\\ N{=}C\cdot CO\cdot N_3\end{matrix}$, obtained by the action of sodium nitrite ($2\frac{1}{2}$ mols.) on 5-pyrazolone-3-carboxylohydrazide in dilute hydrochloric acid cooled by a freezing mixture, explodes at 100—105°. Its yellow ethereal solution reacts with ammonia, forming a flesh-coloured *ammonium* salt of 4-oximino-5-pyrazolone-3-carboxylamide,  $NH\!<\!\begin{matrix}CO\cdot C{:}NO\cdot NH_4\\ \quad\;\mid\\ N{=}C\cdot CO\cdot NH_2\end{matrix}$, darkening at 220—290°, an alkaline solution of which, by acidification, yields *4-oximino-5-pyrazolone-3-carboxylamide*, a greenish-yellow powder darkening at 240°. The ethereal solution of the azoimide reacts with aniline to form a mixture of the *anilide*,  $NH\!<\!\begin{matrix}CO\cdot C{:}NOH\\ \quad\;\mid\\ N{=}C\cdot CO\cdot NHPh\end{matrix}$, m. p. 211—216° (decomp.), and its *aniline* salt, $C_{10}H_8O_3N_4,PhNH_2$ (which exists in two forms: yellow, m. p. 161—164°, and red, m. p. 158—162°), and with *p*-toluidine yielding the *p-toluidide*, $C_{11}H_{10}O_3N_4$, m. p. 222—223° (decomp.), and its *p-toluidine* salt.

Methyl 4-oximino-5-pyrazolone-3-carbamate,  $NH\!<\!\begin{matrix}CO\cdot C{:}NOH\\ \quad\;\mid\\ N{=}C\cdot NH\cdot CO_2Me\end{matrix}$, m. p. 218° (decomp.), is obtained by boiling the pure dry azoimide with an excess of methyl alcohol, and separates from methyl alcohol in small, red needles containing $\frac{3}{4}$MeOH. The corresponding *ethyl* ester, prepared in a similar manner, has m. p. 174° (decomp.), and also separates from methyl alcohol in red needles containing $\frac{3}{4}$MeOH. The methyl ester is decomposed by boiling 20% hydrochloric acid, yielding carbon dioxide, hydrogen cyanide, hydrazine, hydroxylamine, ammonia, oxalic acid, and a yellow substance, $C_8H_8O_2N_8$, which darkens on heating, but does not melt below 300°, dissolves easily in sodium hydroxide or carbonate, develops a dark red coloration with ferric chloride, and does not react with benzaldehyde or phenylhydrazine; possibly it is *bis-4-oximino-5-pyrazolidone*,



$$\begin{array}{l}\mathrm{NH{-}{-}NH}\\ \mathrm{CO{\cdot}C(NOH)}\end{array}\!\!>\mathrm{C{:}C}<\!\!\begin{array}{l}\mathrm{NH{-}{-}NH}\\ \mathrm{C(N{\cdot}OH){\cdot}CO}\end{array}.$$

C. S.

Decomposition of Uric Acid by Organic Alkaline Solvents. HANNAH STEVENS and CLARENCE B. MAY (*J. Amer. Chem. Soc.*, 1911, **33**, 434—447).—It is well known that uric acid is decomposed by solutions of alkali hydroxides and carbonates. Experiments have now been made to ascertain the behaviour of uric acid in solutions of certain organic bases, namely, piperazine, urotropine, and lycetol (piperazine tartrate). The action of piperazine is of special interest, since this substance is used medicinally as a uric acid solvent.

Uric acid dissolves readily in piperazine at the ordinary temperature, but only slightly in urotropine, lycetol, or ammonium hydroxide. Piperazine, ammonium sulphide, and ammonium hydroxide effect the decomposition of uric acid in the absence of neutral salts, but the decomposition by piperazine takes place more slowly in presence of ammonium sulphate, disodium hydrogen phosphate, or sodium chloride. Urotropine exerts but little action on uric acid.

When uric acid is boiled with ammonium sulphide solution, it is decomposed to almost the same extent as it is by sodium sulphide solution, but thiouranil does not seem to be produced. E. G.

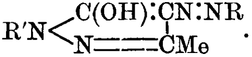
Quadriurates. OTTO ROSENHEIM (*Zeitsch. physiol. Chem.*, 1911, **71**, 272).—The conclusion arrived at by Kohler (this vol., i, 243) that quadriurates are mixtures of biurates and uric acid was reached experimentally by the author in conjunction with Tunnicliffe some years ago (*Lancet*, June 16th, 1900). W. D. H.

Recovery of Adenine. GEORGE DE F. BARNETT and WALTER JONES (*J. Biol. Chem.*, 1911, **9**, 93—96).—To free adenine from hypoxanthine, the base must be converted into the picrate, which as such is useless, and can be changed into a non-toxic salt only by the use of an excessive amount of ether. When, however, the picrate is dissolved in ammonia and the solution treated with ammoniacal silver nitrate, the adenine is precipitated quantitatively, whilst more than 90% of the picric acid remains dissolved. This forms the basis of a method of recovering adenine and of dealing with filtrates from adenine picrate, which contain other purine bases as well as picric acid. W. D. H.

Conversion of Arylamineazo*iso*oxazolones into Azopyrazolones. CARL BÜLOW and ARNULF HECKING (*Ber.*, 1911, **44**, 467—480).—A third method of preparing pyrazolone dyes is based on the observation of Knorr and Reuter (Abstr., 1894, i, 372), that by the action of phenylhydrazine on the phenylhydrazone of ketomethyl-

*iso*oxazolone in acetic acid solution the phenylhydrazine of ketophenylmethylpyrazolone is obtained. This method is now extended to a number of substituted *iso*oxazoles (Bülow and Hecking, this vol., i, 244), both hydrazine, phenylhydrazine, and dinitrophenylhydrazine being used. The conversion depends on the strength of the base used, and is a function of the solubility of the reaction product.

The azopyrazolones possess all the tinctorial properties of the true *o*-hydroxyazo-dyes, in particular the fastness to alkali. Their properties also depend on the nature of the arylamine azo-residue, and on the group attached to the nitrogen of the heterocyclic ring,



$$\mathrm{R'N}\Big<\begin{array}{l}\mathrm{C(OH){:}\overset{}{C}N{:}NR}\\ \mathrm{N{=\!=\!=}\underset{}{C}Me}\end{array}.$$

When R is a purely aromatic radicle and R′ is hydrogen, the acidity of the compound increases, and it dissolves easily in a very small quantity of piperidine. It is not precipitated from the solution by the continued addition of water; the yellow colour is not altered by the addition of alkali hydroxide. The dissolved salt is decomposed, however, by carbon dioxide.

When R′ is a purely aromatic radicle, the compound also readily dissolves in piperidine, but the salt is hydrolysed on the addition of a certain quantity of water. The very finely-divided precipitate dissolves again in alkali hydroxide.

The solutions of the monoazopyrazolone dyes in concentrated sulphuric acid are yellow so long as only benzene residues are present. Derivatives of α-naphthylamine are deep bluish-red or reddish-violet; those of β-naphthylamine are brownish-red.

4-Benzeneazo-5-hydroxy-3-methylpyrazole, prepared from the corresponding *iso*oxazole and hydrazine hydrate, forms reddish-yellow platelets, m. p. 199°.

4-p-*Nitrobenzeneazo*-5-*hydroxy*-3-*methylpyrazole* crystallises in slender, yellow needles, m. p. 264—265°. It behaves towards potassium hydroxide as a very weak dibasic acid; in dilute alkali it dissolves with a brown colour; in 50% alkali this changes to bluish-red, and after a time reddish-violet needles separate; on dilution the bluish-red solution becomes brown again. Carbon dioxide precipitates the unaltered azo-dye. Many of the other azopyrazoles described behave similarly.

4-p-*Nitrobenzeneazo*-5-*hydroxy*-1-*phenyl*-3-*methylpyrazole* forms red needles, m. p. 198°; the phenolic *potassium* salt crystallises in slender, matted, brown needles.

4-op-*Dinitrobenzeneazo*-5-*hydroxy*-3-*methylpyrazole* crystallises in yellowish-red, flat needles, m. p. 277—278°. The *di*(?)*potassium* salt separates in brownish-blue flakes.

4-op-*Dinitrobenzeneazo*-5-*hydroxy*-1-*phenyl*-3-*methylpyrazole* is obtained in violet-red needles, m. p. above 300°.

4-*Benzeneazo*-5-*hydroxy*-1-op-*dinitrophenyl*-3-*methylpyrazole* crystallises in short, thick, dirty violet needles, m. p. 216—217°.

4-o-*Tolueneazo*-5-*hydroxy*-3-*methylpyrazole* separates in rhombic aggregates of tiny, reddish-yellow plates, m. p. 221—223°. The isomeric 4-p-*Tolueneazo*-5-*hydroxy*-3-*methylpyrazole* is obtained in smaller yield; it crystallises in lustrous, orange needles, m. p. 195—196°. The two isomerides show similar shades in the same solvent, the para-derivative being more soluble.

4-o-*Tolueneazo-5-hydroxy-1-phenyl-3-methylpyrazole* crystallises in yellowish-red needles, m. p. 181—182°. The same compound is obtained by the combination of 1-phenyl-3-methyl-5-pyrazolone with the diazo-compound of *o*-toluidine (D.R.-P. 153861). The isomeric 4-*p*-tolueneazo-5-hydroxy-1-phenyl-3-methylpyrazole separates in red needles, m. p. 137° (compare Lapworth, Trans., 1903, **83**, 1124).

4-m-*Xyleneazo-5-hydroxy-4-methylpyrazole* forms very slender, matted, silky, glistening, orange needles, m. p. 190—191°.

4-m-*Xyleneazo-5-hydroxy-1-phenyl-3-methylpyrazole* is obtained in aggregates of lustrous, yellowish-red, rhombic plates, or slender, orange needles, m. p. 167°.

4-a-*Naphthaleneazo-5-hydroxy-3-methylpyrazole* separates in orange-red plates, m. p. 247°. The corresponding 4-a-*naphthaleneazo-5-hydroxy-1-phenyl-3-methylpyrazole* crystallises in lustrous, yellowish-red needles, m. p. 202—203°.

4-β-*Naphthaleneazo-5-hydroxy-3-methylpyrazole* is a bright red, crystalline powder, m. p. 238—239°. 4-β-*Naphthaleneazo-5-hydroxy-1-phenyl-3-methylpyrazole* forms short needles, m. p. 186—187°. The yellow solution in piperidine becomes milky when considerably diluted

4-o-*Carboxybenzeneazo-5-hydroxy-3-methylpyrazolone*, prepared by boiling hydrazine hydrate with the oxime of ethyl *o*-carboxybenzeneazoacetoacetate, forms microscopic aggregates of brownish-yellow plates, m. p. 280°.

4-o-*Carboxybenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole* crystallises in very beautiful orange-red, stunted needles with a blue surface reflex, m. p. 269—270°.

4-*Nitro*-o-*carboxybenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole* separates in reddish-violet needles with a lustrous, blue reflex, m. p. 285°. E. F. A.

The Heat Coagulation of Proteins. I. Is the Hydrogen Ion Concentration Altered on Coagulation? SÖREN P. L. SÖRENSEN and E. JÜRGENSEN (*Biochem. Zeitsch.*, 1911, **31**, 397—442).—The authors in an extensive series of experiments with different acids have determined the optimal conditions of coagulation, generally by estimating the amount of nitrogen in the uncoagulated portion of the solution. In these experiments they have also made numerous measurements of the hydrogen ion concentration in the mixtures, both before and after coagulation by means of concentration cells. The optimal concentration for coagulation is about $p_H = 4{\cdot}6$, but varies slightly with the concentration of the protein (blood-serum or egg-white), and is somewhat lower than the isoelectric point, $p_H = 5{\cdot}52$, as determined by Michaelis and Rona. After coagulation the hydrogen ion concentration becomes smaller, and this the authors ascribe to the separation of the protein from solution, the protein itself having acidic functions, to which the hydrogen ion concentration of the solution are due. This explains the slight variability in the hydrogen ion concentration which affords the optimal conditions of coagulation in proteins of varying strengths of solution. (It is higher for stronger than weaker solutions.) No carbon dioxide is evolved during coagulation. Certain peculiarities in the case of egg-white solutions were observed. The maximal separation under optimal conditions of the coagulum is in this case only reached after several hours, after which, owing to the action of the liquid, some of the coagulum passes again into solution. S. B. S.

The Fixing of Acids by Egg-albumin and Viscosity. WILHELM E. RINGER (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 243—260).—The nature of acid protein solutions has been investigated by measurements of the *E.M.F.* of hydrogen concentration cells, of electrical conductivity, and of viscosity. Solutions containing egg-albumin and variable amounts of hydrochloric acid or sodium hydroxide, and, in addition, solutions of egg-albumin, serum-albumin, and serum-globulin with varying amounts of acetic acid, were examined in detail. The results of these measurements indicate that considerable amounts of acid and alkali are fixed by the proteins, and the process is considered to be in the nature of chemical combination rather than adsorption. H. M. D.

Electrochemistry of Proteins. IV. Dissociation in Solutions of the Globulinates of the Alkaline Earths. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1911, **15**, 166—177. Compare Abstr., 1910, ii, 679, 939; Hardy, Abstr., 1906, i, 121).—The conductivity at 30° of solutions of potassium, calcium, barium, and strontium hydroxides neutralised to phenolphthalein with globulin show that the salts obey Ostwald's dilution law. The same conclusion may be drawn for sodium globulinate at 18° from Hardy's measurements.

As in the case of the caseinogenates, the value of $\rho(v_1+v_2)$ is about twice as great for the alkalis as the alkaline earths, where v_1,v_2 are the ionic mobilities, and ρ the number of equivalents of salt formed from one equivalent of alkali.

It is assumed that ρ equals 2 for the alkali salts, so that (v_1+v_2) is about the same (26×10^{-5} cm. per sec.) for all the globulinates, a result in accord with Hardy's measurements of the velocity of the globulin ion.

At neutrality to phenolphthalein the globulinates dissociate into two protein ions, each possessed of twice as many valencies as there are molecules of base bound up in one molecule of globulinate. The simplest formula of potassium globulinate, $KX^{\cdot\cdot}+X(OH)_n''$, does not explain the fact that the alkali globulinates take up a second equivalent of globulin, becoming neutral to litmus. These are represented: $KHX^{\cdot\cdot\cdot\cdot}+X(OH)_n''''$, so that the salt neutral to phenolphthalein is $K_2X^{\cdot\cdot\cdot\cdot}+X(OH)_n''''$, and the corresponding alkaline earth salt, which is saturated with globulin, although neutral to phenolphthalein only, is represented: $Ca_2(X)_2^{\cdot\cdot\cdot\cdot}+X_2(OH)_{2n}''''$.

On this assumption the ions are quadrivalent, and the dissociation constants for the globulinates are: K, 0·01470; Ca, 0·00360; Ba, 0·00493; Sr, 0·00211. R. J. C.

Histidine in Pig's Thyreoglobulin. FRED C. KOCH (*J. Biol. Chem.*, 1911, 9, 121—122).—Nürnberg failed to obtain enough histidine from thyreoglobulin (from ox-thyroids) to definitely establish its presence. In the present research, sufficient was obtained for the purpose. The material was prepared from pig's thyroids.

W. D. H.

Swelling of Casein Under the Influence of Sodium Chloride and Lactic Acid. W. VAN DAM (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 102—107. Compare this vol., i, 91).—The structure of cheese is sometimes dough-like and sometimes granular, and the author has endeavoured to trace the cause of this difference by determining the amount of casein dissolved by solutions containing 5%, 3%, and 1% of sodium chloride and various amounts of lactic acid. Curves showing the relation between the dissolved casein and the concentration of the hydrogen ions are given. A. J. W.

Electrochemistry of Proteins. V. The Electrochemical Equivalent of Caseinogen and its Relation to the Combining and Molecular Weights of Caseinogen. T. BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1911, 15, 178—196. Compare preceding page).—Electrolysis of potassium caseinogenate with a current of 0·001 ampere liberates gas at both electrodes, and on the anode a firm, white, spongy precipitate is deposited, the cellular texture of which is apparently due to gaseous oxygen. The deposit consists of normal caseinogen containing less than 0·2% of ash.

The amount of caseinogen removed from the solution was determined by the refractometer, and a correction was applied to the experimental data to compensate for loss of caseinogen from the anode by dissolution in the electrolyte, the amount of this correction depending on the alkalinity of the solution and the duration of electrolysis.

The electrochemical equivalent of caseinogen in solutions containing 50×10^{-5} to 100×10^{-5} equivalents of potassium hydroxide per gram is $0·0242 \pm 0·0019$ gram of caseinogen per coulomb as a mean of fourteen determinations. This must be the equivalent of caseinogen at its minimum, since, whatever the proportion of potassium hydroxide to caseinogen in the electrolyte, no caseinogen will be deposited until the potassium hydroxide in the anode film is saturated.

The equivalent of caseinogen is therefore 2336 ± 183 at saturation. Since 1 gram of caseinogen saturates $11·4 \times 10^{-5}$ equivalents of potassium hydroxide, the molecular weight of caseinogen is $(8772)_n$, and the basicity, $(8772)_n \div (2336 \pm 183)$, that is, 4, or some multiple of 4.

The formula of potassium caseinogenate in solutions neutral to phenolphthalein was deduced from cryoscopic determinations to be $K_2X^{\cdot\cdot\cdot\cdot} + X(OH)_n{}^{''''}$, molecular weight 2200, admixed with a small proportion of $(KHX)_2{}^{\cdot\cdot\cdot\cdot} + X_2(OH)_{2n}{}^{''''}$, molecular weight 4400, the latter being the main constituent in solutions neutral to litmus. At saturation the formula is: $KH_7X_4{}^{\cdot\cdot\cdot\cdot} + X_4(OH)_{4n}{}^{''''}$, molecular weight 8800.

The conductivity of calcium hydroxide solution in presence of caseinogen indicates that the alkalis and alkaline earths dissolve caseinogen in equivalent proportions. The author discusses the formula and dissociation of the alkaline-earth caseinogenates in view of the difference between caseinogen and globulin in this repect.

The percentage of glutamic acid in caseinogen indicates a minimum molecular weight of 1336 (4008/3), whereas the tyrosine indicates 4022. The sulphur and phosphorus also indicate a minimum molecular weight of about 4000. R. J. C.

Inosic Acid. IV. Phœbus A. Levene and Walter A. Jacobs (*Ber.*, 1911, **44**, 746—753. Compare Abstr., 1908, i, 931 ; 1909, i, 164, 540).—The phosphoric acid residue in *d*-ribosephosphoric acid is attached to the δ-carbon atom of the ribose molecule, since, on oxidation with nitric acid (D = 1·2) at 40° and subsequent rapid evaporation and treatment with calcium hydroxide, calcium phospho-ribonate and calcium phosphate are obtained. The calcium salt is identical with that obtained from the oxidation product of *d*-ribosephosphoric acid. By the hydrolysis of phospho-*d*-ribonic acid at 130° in neutral solution (ammonium acetate), *d*-ribonic acid is obtained, which is identical with the acid formed when *d*-ribose is oxidised with bromine water.

Details for the preparation of *d*-ribosephosphoric acid are given. J. J. S.

Inosic Acid. Walter A. Jacobs and Phœbus A. Levene (*Proc. Amer. Soc. Biol. Chem.*, 1910, xxv ; *J. Biol. Chem.*, 9).—Inosic acid is hypoxanthine phosphoriboside. The phosphoric acid group is bound to the ω-carbon atom of the ribose. W. D. H.

Oxyprotosulphonic Acid. Jozef Buraczewski and L. Krauze (*Zeitsch. physiol. Chem.*, 1911, **71**, 153—156).—The oxyprotosulphonic acids (compare Maly, Abstr., 1885, 824) of egg-albumin, serum-albumin, and casein are differentiated on treatment with boiling glacial acetic acid into acid compounds (*a*) insoluble in acetic acid, termed α-oxyprotosulphonic acid, and (*b*) soluble in acetic acid, but precipitated by ether or by water, termed β-oxyprotosulphonic acid. On cooling the acetic acid solution, an acid substance separates in the case of egg- and serum-albumin, which has not been further investigated. The relation of carbon to nitrogen in both α- and β-oxyprotosulphonic acids indicates that the protein molecule has not been hydrolysed in their formation. E. F. A.

Some Physico-chemical Properties of Lecithin Emulsions and of Lecithin–Protein Mixtures. Hans Handovsky and Richard Wagner (*Biochem. Zeitsch.*, 1911, **31**, 32—45).—Lecithin emulsions show an increased viscosity as compared with water, which is diminished on the addition of electrolytes. The lecithin precipitation by hydrochloric acid can be inhibited by salts in concentrations in which they themselves do not precipitate it. Indifferent narcotics have no effect on the viscosity Globulin can be precipitated by lecithins from sera which are poor in electrolytes (that is, have just sufficient salts to hold the globulin in solution). The precipitation is inhibited by neutral salts. Neither precipitation nor viscosity phenomena give any indication of a colloid complex between lecithin and neutral serum albumin when lecithin is added in the form of an emulsion. S. B. S.

The Valency of Iron in Blood Pigment. WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1911, **71**, 100—104).—Polemical. Reasons are given why the author disagrees with Manchot's conclusion that the iron of hæmoglobin cannot be in ferrous, but must be in ferric combination. W. D. H.

The Theory of Enzyme Action. OSCAR LOEW (*Biochem. Zeitsch.*, 1911, **31**, 159—167).—The author claims that his views on enzyme action have been misrepresented in recent text-books on enzymes, in that it has been stated that the labile enzymatic substances decompose explosively. He distinguishes between two kinds of substances with chemical lability, the "potentially-labile," which on small stimulus decompose explosively, and the "kinetically-labile," where the energy is exerted in a continuously active form. The differences are illustrated by various examples. S. B. S.

Reversibility of Enzyme Action. ADOLF WELTER (*Zeitsch. angew. Chem.*, 1911, **24**, 385—387).—A brief résumé is given of the more important cases in which the reversibility of enzyme action has been demonstrated (compare Croft Hill, Trans., 1898, **73**, 634; Proc., 1901, **17**, 184; Kastle and Loevenhart, Abstr., 1901, i, 178; Visser, *ibid.*, 1905, ii, 577; Hanriot, *ibid.*, 1901, ii, 175; Pottevin, *ibid.*, 1903, ii, 494). Details are given for the production of fatty acids on the large scale by the hydrolysis of natural fats by means of the lipatic enzyme present in seeds. Experiments are also described which prove that in the absence of large quantities of water these enzymes are capable of synthesising appreciable amounts of esters from glycerol and the acids derived from certain natural fats. J. J. S.

Composition of Invertase. ALBERT P. MATHEWS and T. H. GLENN (*J. Biol. Chem.*, 1911, **9**, 29—56).—As ordinarily prepared, invertase is probably a combination of a protein and a mannosan. All attempts to free the protein from the gum and retain enzymic activity were failures. Acid alcohol destroys the activity. The parallelism between activity and nitrogen content is believed to indicate that the active substance is a protein. W. D. H.

Temperature-coefficient of the Decomposition of Invertase. HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, **71**, 134—142. Compare Euler and Ugglas, Abstr., 1910, i, 345, 796).—The influence of heating for half an hour at various temperatures on invertase prepared by autolysis has been determined. Half of the invertase is destroyed under these conditions at 63° ± 0·2°. In an extract of dried yeast the presence of proteins and carbohydrates has no influence on the heat stability of invertase. Lactose has no protective influence; phosphate has also no influence. There is no difference in the heat stability of invertase from top and bottom fermentation yeasts, contrary to statements on this point in the textbooks of Effront and Oppenheimer. E. F. A.

Nucleases. PHŒBUS A. LEVENE and FLORENTIN MEDIGRECEANU (*J. Biol. Chem.*, 1911, 9, 65—83).—Plasma of heart muscle, liver, kidney, and intestinal mucosa hydrolyse inosin, giving rise to the free base and *d*-ribose; plasma of pancreas and blood serum have no effect. Inosic acid is hydrolysed into phosphoric acid, *d*-ribose, and hypoxanthine by the same materials. The same plasmata hydrolyse guanylic acid, with the addition of that of the pancreas (one experiment); the tendency to gelatinise causes difficulties in the investigation of guanylic acid. Cytidin is regarded as a complex of pentose and cytosine, although not in glycosidic linking; no cleavage occurred with any plasma. The cleavage of yeast nucleic acid by the plasmata into phosphoric acid, purine bases, *d*-ribose, cytidin, and uridin was incomplete. No definite regularity in the velocity of the reactions was noticed. W. D. H.

Nucleases. WALTER JONES (*J. Biol. Chem.*, 1911, 9, 129—138). —A nuclease is generally understood to be an enzyme which liberates purine bases from nucleic acid in a form in which they are directly precipitable by the reagents usually employed for that purpose. The definition is, however, unsatisfactory. There is, further, no assurance that the enzyme of one gland can decompose the nucleic acid of another organ. The nucleic acids are constituted on one type; according to Levene and Jacobs, a phosphoric acid group is linked to a nitrogenous ring by *d*-ribose. This "nucleotide" structure is common to all nucleic acids, but differences occur in the nitrogenous rings and in re-duplication of molecules; it would therefore be surprising to find one enzyme which can decompose them all. The present investigation deals with guanylic acid, a mononucleotide, that is, a nucleic acid which yields only one purine base, guanine. Extract of ox-spleen readily effects its decomposition, giving rise to xanthine and uric acid by oxidation of the guanine. Pig's pancreas cannot do this, although it is rich in nuclease. W. D. H.

The Physiological Agents Concerned in Nuclein Fermentation, with Special Reference to Four Independent Deamidases. WALTER JONES (*J. Biol. Chem.*, 1911, 9, 169—180).— Although pig's pancreas will not liberate the purine base from guanylic acid, it nevertheless liberates phosphoric acid, and thus converts guanylic acid into guanosine. Extracts of pig's spleen and liver have the same action, and also liberate phosphoric acid from thymus-nucleic acid. The nucleosides (such as guanosine) which remain are compounds of *d*-ribose and the purine base; the amino-nucleosides, guanosine and adenosine, can further be converted into xanthosine and inosine (or hypoxanthosine), the corresponding hydroxy-compounds, as Levene and Jacobs showed. Such deamidations are quite analogous to those which occur when guanine and adenine are converted into xanthine and hypoxanthine respectively. Nevertheless, the deamidation is accomplished by different enzymes; thus guanase and guanosine-deamidase are separate enzymes; one is present, for instance, in pig's liver and the other is not. Similarly, adenosine-deamidase and adenase are not identical enzymes. W. D. H.

Pancreatic Lipase. ANT. HAMSIK (*Zeitsch. physiol. Chem.*, 1911, 71, 238—251).—Previous authors have noticed that filtration of a glycerol extract of pancreas removes its lipoclastic action. In the present research it is shown that clear glycerol extracts can be prepared from the dried pancreas of the pig, and that these retain their fat-splitting properties after filtration through a Chamberland filter. Pancreatic lipase is reversible in its action, and synthesises fat from palmitic and stearic acids and glycerol. Neutral salts inhibit both fat-splitting and fat-synthesis, but soaps act favourably on both.
W. D. H.

Significance of Colloidal Manganese Oxide Solutions in Biochemical Oxidations. BOUWE SJOLLEMA (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 399—406. Compare Abstr., 1909, ii, 484, and Marck, *Diss.*, Heidelberg, 1907).—By agitating samples of quinol solution with Marck's manganese solution, some in presence of peroxydase from horse-radish (*Cochlearia armoracia*) and some without it, the author found that the oxidation of the quinol and its transformation into quinhydrone by the manganese peroxide is facilitated by the presence of the peroxydase. In the oxidation of quinol, a mixture of colloidal manganese peroxide and a peroxydase behaves like the system peroxydase + oxygenase, so that the manganese plays the part of oxygenase. A. J. W.

Relation of Hæmoglobin Derivatives and Peroxydases to Inorganic Catalysts. W. MADELUNG (*Zeitsch. physiol. Chem.*, 1911, 71, 204—237).—It is probable that the mechanism of the action of oxydases, peroxydases, and catalases rests on an inorganic basis. Such ferment action is to be expected in all cases where compounds are present which are able to exist in several stages of oxidation, which are capable of forming unstable molecular compounds with molecules of oxygen or hydrogen peroxide, and in which the higher oxides can be converted into the lower and vice versâ. It is shown in the case of the blood-colouring matter that complex iron compounds fulfil these conditions, and it is probable that the greater part, if not all, such ferments owe their activity to complex iron compounds.

When neutral aqueous solutions of benzidine are oxidised in presence of traces of a neutral mineral salt, benzidine-blue is precipitated in the form of microscopic matted needles. On separating the dye, and adding hydrochloric acid to it, brown flakes of the dichloroimide are formed, which dissolve in potassium iodide, liberating iodine. The free iodine is titrated with thiosulphate, and a convenient measure of the oxidising activity is obtained. The benzidine is used in 0·04% solution containing 1% of sodium chloride, a considerable excess being employed.

With blood the amount of oxidising action is proportional to the amount taken. Small quantities of mineral acids prevent the formation of the blue, but the amount formed is doubled on the addition of sodium acetate to the acid, or on saturating the neutral solution with carbon dioxide. The optimum amount of sodium chloride necessary for precipitation of the blue is about 1%. The activity of blood is roughly proportional to the hæmoglobin present.

E. F. A.

New Method for the Preparation of a Catalase from Blood and its Properties. Jules Wolff and Eloi de Stœcklin (*Compt. rend.*, 1911, **152**, 729—731).—The following process gives a catalase free from hæmoglobin, and oxyhæmoglobin free from catalase. Unlike Senter's method (Abstr., 1903, ii, 661) it does not diminish the activity of the enzyme. The corpuscles of defibrinated blood are washed with physiological salt solution and removed by centrifugation. The paste of corpuscles is made up to the original volume of blood with distilled water, laked with ether, and the liquid decanted and filtered. The filtrate is kept for twenty hours at −10°, after the addition of one-fifth its volume of alcohol. Oxyhæmoglobin crystallises out, and a further crop separates on addition of more alcohol. The liquid is now covered with a layer of toluene 0·5 cm. deep, which, after some days, precipitates proteins with the last traces of oxyhæmoglobin. The clear, yellow filtrate contains a stable and very active catalase.

It has been shown that pure oxyhæmoglobin is decomposed by hydrogen peroxide, whereas this is without action on the crude product. In the latter case the catalase present exerts a protective influence on the oxyhæmoglobin by facilitating the combination of oxyhæmoglobin with molecular oxygen. W. O. W.

The Reduction Ferments. I. The Schardinger Enzyme (Perhydridase). Alexis Bach (*Biochem. Zeitsch.*, 1911, **31**, 443—449).—The enzyme acts in the system ferment–methylene blue–aldehyde–water. According to the author's theory, scission of water by the oxidisable substance (aldehyde) takes place under the influence of the catalyst, which forms with the hydrogen of the water a strongly reducing substance. He draws attention to the analogy of the reducing enzymes (for which he suggests the name reducase instead of the etymologically incorrect reductase) with the oxydases and peroxydases.

The Schardinger enzyme (that is, the enzyme acting in the methylene blue–aldehyde system) can be prepared from calf's liver by extracting the organ with 1% sodium hydrogen carbonate solution and neutralising the extract with acetic acid. From this extract the enzyme can be precipitated by alcohol, and from the precipitate it can be re-extracted in purer form by ½% sodium hydrogen carbonate, which extract acts readily after neutralisation with acetic acid. S. B. S.

Organic Chemistry.

Preparation of Methyl Bromide. Artur Bygdén (*J. pr. Chem.*, 1911, [ii], **83**, 421—424).—Methyl bromide is obtained in 83—84% yield (as against 44·5% by the bromine and phosphorus method) by adding carefully 450 grams of methyl alcohol to 600 grams of concentrated sulphuric acid, adding gradually 230 grams of water and 300 grams of powdered potassium bromide to the cold mixture, and heating until gas ceases to be evolved.

In some cases methyl bromide is a more suitable substance than methyl iodide for the preparation of the magnesium methyl halides; the gas in slight excess is passed into the mixture of ether and magnesium. C. S.

Equilibrium between *iso*Butyl and *tert.*-Butyl Bromides at Elevated Temperatures. Roger F. Brunel (*Ber.*, 1911, **44**, 1000—1009).—*iso*Butyl bromide usually contains traces of *n*-propyl bromide; attempts to purify *iso*butyl alcohol by means of the urethane were not successful, and finally very careful fractional distillation was resorted to for the preparation of the pure alcohol. This has b. p. 107·19—107·43°/760 mm., D_{25}^{25} 0·8002—0·80032, D_4^{25} 0·7979—0·79802, and gives *iso*butyl bromide, b. p. 91·1—91·5°, D_{25}^{25} 1·2624—1·2616, D_4^{25} 1·2588—1·2580.

Estimation of the *tert.*-butyl bromide present after heating either the *iso*- or *tert.*-butyl bromide at 280° until equilibrium is attained indicates the presence of 90·7% of the tertiary derivative in the equilibrated mixture. E. F. A.

Aliphatic Halogen Compounds from α-Pipecoline. Julius von Braun and W. Sobecki (*Ber.*, 1911, **44**, 1039—1048).—By the action of phosphorus pentachloride on benzoyl-α-pipecoline the ring is opened and αε-dichlorohexane formed. With phosphorus pentabromide the chief product is αε-dibromohexane; in addition, an unsaturated bromide and considerable quantities of a *tribromide*, $C_6H_{11}Br_3$, are formed. This is due to part of the dibromohexane losing hydrogen bromide and forming an unsaturated compound of the constitution $CH_2Br\cdot[CH_2]_2\cdot CH{:}CHMe$ or $CH_2Br\cdot[CH_2]_2\cdot CH_2\cdot CH{:}CH_2$, which is immediately brominated by the phosphorus pentabromide at the double bond. The structure of the tribromide was determined by treatment with magnesium in ethereal solution, when either

$$MgBr\cdot[CH_2]_3\cdot CH{:}CHMe$$

or $MgBr\cdot[CH_2]_3\cdot CH_2\cdot CH{:}CH_2$ is formed. The action of carbon dioxide causes the formation of an unsaturated acid, $C_6H_{11}\cdot CO_2H$, which yields glutaric and acetic acids on oxidation, and therefore has the composition of a δε-heptenoic acid, $CO_2H\cdot[CH_2]_3\cdot CH{:}CH\cdot CH_3$.

The tribromide is accordingly αδε-tribromohexane. These products are all optically inactive.

$\alpha\epsilon$-Dibromohexane is a liquid of aromatic odour, b. p. 101—105°/9 mm., D_4^{20} 1·5989. Proof that the product does not contain also $\alpha\delta$-dibromohexane is afforded by the conversion into pure 1-benzyl-2-pipecoline by boiling with benzylamine in alcoholic solution. With aniline in a similar manner 1-phenyl-2-pipecoline is obtained; this is colourless, and has an agreeable odour resembling phenylpiperidine, b. p. 143°/20 mm. The picrate has m. p. 162°; the methiodide is a colourless, crystalline powder, m. p. 145°.

$\alpha\delta\epsilon$-*Tribromohexane* is a heavy, colourless liquid, b. p. 152—154°/16 mm, D_4^{20} 1·9613. Δ^{δ}-Heptenoic acid (compare Fichter and Gully, Abstr., 1897, i, 590) has b. p. 117°/11 mm., D_4^{20} 0·9496, n_D 1·4444.

F. F. A.

Chloroacetylene. José Rodriguez Mourelo and A. García Banús (*Anal. Fis. Quim.*, 1911, **9**, 84—87).

—Chloroacetylene may be prepared by the action of alcoholic sodium hydroxide on acetylene dichloride at 40° in a current of nitrogen, the operation being suitable for lecture demonstration.

G. D. L.

Fusibility Curves of Gaseous Mixtures; Compounds of Hydrogen Chloride and of Sulphur Dioxide with Methyl Alcohol. Georges Baume and Georges Pamfil (*Compt. rend.*, 1911, **152**, 1095—1097. Compare Abstr., 1909, ii, 545; 1910, ii, 825).

—Vitrification at low temperatures prevents complete examination of the freezing-point curve for mixtures of methyl alcohol and hydrogen chloride. It has been followed, however, for mixtures containing 0—10, 35—55, and 90—100% of the alcohol, and shows a sharply defined maximum corresponding with a compound MeOH,HCl. Mixtures of methyl alcohol and sulphur dioxide are very viscous at low temperatures; the curve reveals the existence of two compounds, $MeOH,SO_2$ and $2MeOH,SO_2$. The system $HCl+SO_2$ shows a single eutectic and no maximum.

W. O. W.

Certain Properties of Aqueous Solutions of Trimethylcarbinol. Antony G. Doroschewsky (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 66—73).

—From the values obtained by previous investigators and by himself, the author deduces the following constants for trimethylcarbinol: m. p. 25—25·5°, b. p. 82·55°, D_4^{25} 0·7806.

Examination of the values of D_4^{20} and of D_4^{25} obtained by Young and Fortey (Trans., 1902, **81**, 717) for various aqueous solutions of trimethylcarbinol shows that the rate at which the sp. gr. varies with the composition (ds/dp) changes irregularly at both temperatures, so that the fourth decimal figures of the values given are probably inaccurate.

A corrected table is given, showing for solutions containing from 0 to 100% of trimethylcarbinol the values of D_4^{25}, D_4^{20}, ds/dp at each of these temperatures, and ds/dt. The extent of the contraction occurring on mixing water and trimethylcarbinol increases with rise of temperature for concentrated solutions, and diminishes for solutions containing less than 70% of the alcohol. With rise of temperature, the maximum of contraction moves appreciably in the direction of the more concentrated solutions. With aqueous solutions of ethyl alcohol a totally different behaviour is observed; increases of the amount of contraction with temperature occurs with dilute solutions (10%), and the position of the contraction does not change even at very high temperatures.

For pure trimethylcarbinol, the author finds n_D^{25} 1·38548. With aqueous solutions of trimethylcarbinol, the index of refraction does not exhibit a maximum, and the values are in good agreement with those calculated by means of Gladstone's formula corrected according to Pulfrich. The indices of refraction are greater than the values calculated from the compositions of the solutions. T. H. P.

Synthesis of Methylethylnonylcarbinol. MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 351).—[With UNANOFF.]—*Methylethylnonylcarbinol*, $C_{13}H_{28}O$, prepared by the action of magnesium and ethyl bromide on methyl nonyl ketone in ethereal solution, is a faintly yellow liquid, b. p. 135—137°/15 mm. T. H. P.

Principal Properties of Oxonium Dibromides of Simple Ethers. WLADIMIR W. TSCHELINZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 219—225).—The author criticises McIntosh's views (Trans., 1905, **87**, 784; Abstr., 1910, i, 808) on the constitution of the compounds formed by bromine with ethyl and other ethers (compare Tschelinzeff and Konowaloff, Abstr., 1909, i, 353). T. H. P.

Synthesis of Secondary α-Keto-alcohols. D. GAUTHIER (*Compt. rend.*, 1911, **152**, 1100—1102).—α-Keto-alcohols cannot be obtained by the hydrolysis of the corresponding alkyloxy-ketones (Abstr., 1909, i, 353), but are readily prepared by the action of an organo-magnesium halide (2 mols.) on a cyanohydrin (1 mol.).

Pentan-γ-one-β-ol, OH·CHMe·COEt, formed by the action of ethyl magnesium bromide on acetaldehyde cyanohydrin, has b. p. 63°/20 mm.; it reduces Fehling's solution, and gives a *semicarbazone*, m. p. 201°, and a *cyanohydrin*, b. p. about 130°/20 mm. On treatment with magnesium ethyl bromide (2 mols.) it forms *γ-ethylpentane-βγ-diol*, $OH\cdot CHMe\cdot CEt_2\cdot OH$, b. p. 105°/17 mm.

β-Methylhexan-δ-one-γ-ol, $OH\cdot CHPr^{\beta}\cdot COEt$, b. p. 85°/45 mm., forms a *semicarbazone*, m. p. 90°. W. O. W.

Preparation of Diacetone Alcohol from Acetone. ALFRED HOFFMAN (D.R.-P. 229678).—Diacetone alcohol (b. p. 150°) can be readily prepared by passing acetone through powder or nodules of a catalyst, such as calcium hydroxide; the unchanged acetone is subsequently separated from the product by distillation.

F. M. G. M.

Mixed Organo-metallic Derivatives of Zinc and their Use in Organic Syntheses. EDMOND E. BLAISE (*Bull. Soc. chim.*, 1911, [iv], **9**, i—xxvi).—A lecture delivered before the Chemical Society of France on the 18th March, 1911. T. A. H

Catalytic Esterification of Alcohols by Fatty Acids: Case of Formic Acid. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **152**, 1044—1047. Compare this vol., i, 258).—The esterification of formic acid previously stated to be unrealisable by the catalytic method can be effected by employing as catalyst titanium oxide at 150°, or thorium oxide at 200—220°. In the former case, 65% of the acid is esterified when mixed with the vapour of alcohol in equimolecular proportions, but the proportion diminishes as the molecular weight of the alcohol increases. At higher temperatures, the acid decomposes. Methyl, ethyl, propyl, butyl, *iso*butyl, *iso*amyl, and benzyl formates have been prepared by this process, using excess of the alcohol.

Esters may be obtained from secondary and tertiary alcohols by working at temperatures below that at which the hydrocarbon is formed. Equimolecular proportions of *iso*butyric acid and *iso*propyl alcohol with titanium oxide gave 16·5% of the ester at 235° and 37% at 292°; *tert.*-butyl alcohol gave 6% of ester at 235°. W. O. W.

Action of Alkyl Halides on Anhydrides of Monobasic Acids in Presence of Magnesium and Zinc. IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 352—353).—The action of *iso*butyl iodide and magnesium (or zinc) on acetic anhydride yields, not a tertiary alcohol (compare Saytzeff, Abstr., 1907, i, 815), but the secondary methyl*iso*butylcarbinol.

Among the products obtained by the action of *iso*amyl iodide on acetic anhydride in presence of magnesium is a *hydrocarbon*, $C_{12}H_{24}$, b. p. 189—194°. T. H. P.

Direct Synthesis of the Glycerides. II. ITALO BELLUCCI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 235—238. Compare Bellucci and Manzetti, this vol., i, 259; also Gianoli, *ibid.*, i, 349).—Continuing his experiments the author finds that it is unnecessary to employ a vacuum, as previously recommended. When a mixture of the theoretical quantities of oleic acid and glycerol is heated for three hours at 200—250° in a current of carbon dioxide (which does not pass through the liquid), an almost quantitative yield of triolein is obtained. The reaction is much hastened by vigorous stirring. It takes place also in the presence of air, but some discoloration occurs, which necessitates purification of the product. Similar results were obtained with palmitic and stearic acids. R. V. S.

Elaidin and Elaidic Acid. A. GAWALOWSKI (*Chem. Zentr.*, 1911, i, 383; from *Pharm. Post.*, 1910, **43**, 1033).—By decomposing purified lead plaster with hydrochloric acid, the author has obtained stearoelaidic acid, $C_{18}H_{30}O_2$, colourless, pearly crystals, m. p. 38·4°, D^{15} 0·942, and oleoelaidic acid, $C_{18}H_{25}O_2$ (?), in a pure condition. The latter acid is oily, and has m. p. 20·2°, D 0·955. F. B.

Lauronolic and *allo*Campholytic Acids. JULIUS BREDT (*J. pr. Chem.*, 1911, [ii], **83**, 395—400).—[With PAUL MARRES.]—Hitherto two important criteria for the identification of lauronolic acid have been the facts that its calcium salt forms characteristic crystals and contains $3H_2O$. The authors now show that only $2H_2O$ are present in the calcium salt of lauronolic acid obtained by the dry distillation of camphanic acid, or by the decomposition of chlorocamphoric anhydride by sodium carbonate.

Walker and Henderson's *allo*campholytic acid (Trans., 1895, **67**, 340) forms a calcium salt containing $2H_2O$, and exhibiting the characteristic crystalline form of calcium lauronolate. Formerly *allo*campholytic acid was regarded as identical with γ-lauronolic acid, until Noyes and Taveau showed that the latter is a mixture (Abstr., 1906, i, 397). The preceding analytical result indicates that lauronolic and *allo*campholytic acids are identical, the more so that Walker and Henderson have shown that they yield identical campholactones and bromocampholactones; against this view, however, should be mentioned the different rotations of the two acids, and the different m. p.'s of their amides. Perkin regards *allo*campholytic acid as stereoisomeric with lauronolic acid (Trans., 1898, **73**, 815), whilst Noyes has recently stated that it is a mixture (Abstr., 1910, i, 754).

C. S.

Constitutions of Woringer's Lauronolic Acid, Dihydrolaurolactone (Campholactone), and Laurolene. JULIUS BREDT (*J. pr. Chem.*, 1911, [ii], **83**, 400—405).—A theoretical discussion. Lapworth and Lenton have suggested that during the decomposition of camphanic acid into carbon dioxide, dihydrolaurolactone (campholactone), and lauronolic acid, one of the *gem*-methyl groups wanders to the neighbouring non-methylated carbon atom (Trans., 1900, **77**, 1057 ; 1901, **79**, 1289). The acceptance of this theory, and of the constitutions of lauronolic acid and dihydrolaurolactone arising therefrom, renders explicable (1) the formation of laurenone from lauronolic acid (Tiemann and Tigges, Abstr., 1901, i, 5), and the conversion of its hydroxylamino-oxime into a nitroso-compound conforming with Piloty's rule; (ii) the production of nitrocampholactone (nitrodihydrolaurolactone) from campholactone by direct nitration (Schryver, Trans., 1898, **73**, 559), and its reduction to a hydroxylaminocampholactone, which can be oxidised to a nitrosocampholactone also conforming to Piloty's rule; (iii) the formation of a nitro*iso*campholactone (nitrodihydro*iso*laurolactone) by the nitration of *iso*campholactone (Noyes and Homberger, this vol., i, 110). Nitrocampholactone and nitro*iso*campholactone are probably stereoisomeric, the isomerism being caused by an interchange in the positions of the nitro- and the methyl groups attached to the same carbon atom.

Lapworth and Lenton's theory gains in probability from the fact that campholactone and *iso*campholactone do not yield a trace of camphoronic acid by oxidation (and therefore no longer retain the *gem*-dimethylated *cyclo*pentane ring of camphoric acid), whereas the lactone, m. p. 161°, obtained by the electrolytic reduction of camphononic acid, behaves quite differently from the two campholactones and is readily converted into camphoronic acid by warming with dilute nitric acid (Bredt, Abstr., 1909, i, 498).

The constitution ascribed to laurolene (obtained as a by-product in the formation of lauronolic acid) by Eykmann (Abstr., 1907, i, 378), and confirmed by Noyes and Derick (Abstr., 1910, i, 753), is also in harmony with Lapworth and Lenton's theory. C. S.

The Walden Inversion and Substitution Processes. EMIL FISCHER (*Annalen*, 1911, **381**, 123—141).—The author gives a brief résumé of the more important examples of the Walden inversion (compare Walden, Abstr., 1896, i, 139, 205; 1898, i, 127, 178; 1899, ii, 538; E. Fischer, *ibid.*, 1907, i, 192, 381; 1908, i, 324, 387; 1909, i, 359; 1910, i, 622; McKenzie and Wren, Trans., 1910, **97**, 1356; McKenzie and Clough, *ibid.*, 1909, **95**, 777; 1910, **97**, 2564; McKenzie and Humphreys, *ibid.*, 1910, **97**, 121).

Most of the examples are met with in the case of α-substituted aliphatic acids and their derivatives. The inversion is not met with in the reactions with *l*-β-hydroxybutyric acid, but is apparently met with in the reaction of nitrous acid on β-aminobutyric acid.

On the whole, the author agrees with the views put forward by Werner (this vol., i, 424). In processes of substitution, it is not necessary that the new group should occupy the same position as the old; it is just as likely that it will take up another position. Whether the configuration of the compound undergoes change during the reaction depends on the nature of the reaction, and, secondly, on the nature of the groups already attached to the asymmetric carbon atom.

Such changes are difficult to represent by means of the usual stereochemical models, and a somewhat modified form of model is recommended, in which the spheres representing the atoms are attached to one another by surfaces covered with stiff bristle.

The author agrees with Michael's view that many, if not all, cases of substitution are preceded by the formation of Kekulé complex molecules. If during the decomposition of such a complex the new substituent enters into a position different from that occupied by the original group, Walden's inversion has taken place. It is extremely difficult in any particular case to say whether inversion has taken place or not. If the inversion is not complete, the result is partial racemisation.

The phenomena met with in the addition of halogens and halogen hydracids to stereoisomeric unsaturated compounds are probably of a similar type, and hence the difficulties met with in attempting to deduce the configurations of unsaturated compounds by means of such reactions. Even in certain cases of the addition of hydroxyl groups to unsaturated compounds, molecular rearrangement may occur; this occurs in the terpene series, although the addition of hydroxyl groups by oxidation to fumaric and malic acids proceeds normally.

In the case of substitution in compounds with several asymmetric carbon atoms, if the product is homogeneous the conclusion can be drawn that the substitution is normal, or complete inversion has occurred. If, on the other hand, a mixture of products is obtained which are not optical antipodes, this indicates partial or complete racemisation of the asymmetric carbon atom affected. Examples from the sugar and terpene series are mentioned. J. J. S.

Action of Zinc on a Mixture of the Haloid Ester and Anhydride of Saturated Monobasic Acids. MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 350—351).—The action of zinc on a mixture of ethyl α-bromo*iso*butyrate and acetic anhydride in ethereal solution yields *β-hydroxy-ααβγγ-pentamethylglutaric acid*, $CO_2H\cdot CMe_2\cdot CMe(OH)\cdot CMe_2\cdot CO_2H$, m. p. 152—161°, the *silver* salt of which was analysed. T. H. P.

Dissociation Constants of Oxalic Acid. JOHANNES E. ENKLAAR (*Chem. Weekblad*, 1911, **8**, 375—382. Compare Jellinek, this vol., ii, 362).—For solutions of oxalic acid and sodium hydroxide of various concentrations at 18°, the dissociation constant ($100K$) is 3·4—3·6. From these results the author draws the conclusion that at the concentrations and temperature of the experiments, oxalic acid has the character of a binary electrolyte, and shows no tendency to form complex or acid salts. A. J. W.

Preparation of Normal Oxalic Acid Esters of Lower Aliphatic Alcohols. RUDOLF SCHEUBLE (D.R.-P. 229679).—Methyl or ethyl oxalates can be readily prepared by heating together anhydrous oxalic acid (120 parts) and ethyl alcohol (200 parts) during six hours at 120°, and subsequently removing the excess of alcohol by distillation under diminished pressure; 160 parts of pure ester were thus obtained. F. M. G. M.

Preparation of Oxalates from Alkali Formates. C. F. BOEHRINGER & SÖHNE (D.R.-P. 229853).—Pure colourless sodium oxalate (in 88% yield) can be obtained by heating sodium formate (300 parts) with boric acid or borax (3 parts) in a vessel fitted with an agitator during thirty to forty minutes at a temperature of 360—410°. F. M. G. M.

Reactions of Metallic Oxalates with Some Salts. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1911, 332—334).—Chlorides in general when heated with calcium oxalate give rise to a reaction of the type: $CaC_2O_4 + MCl_2 = CaCl_2 + MO + CO + CO_2$, but if 2 mols. of cupric chloride are used, the following reaction occurs: $CaC_2O_4 + 2CuCl_2 = CaCl_2 + Cu_2Cl_2 + 2CO_2$. With bromides two kinds of reaction may occur: (1) $CaC_2O_4 + MBr_2 = CaBr_2 + MO + CO + CO_2$; (2) $CaC_2O_4 + MBr_2 + O = CaBr_2 + MO + 2CO_2$. Both occur with mercurous bromide, depending on which salt is in excess. The second takes place with lead, cupric, and nickel bromides, and the first with tin and cuprous bromides. With iodides the first type of reaction, referred to under bromides, takes place, whilst with nitrates carbon dioxide only is evolved. The residue from the action of uranyl nitrate contains uranium dioxide, due to the reduction of the trioxide by the carbon formed by decomposition of the oxalate. Sodium hydrogen sulphate heated with calcium oxalate produces carbon monoxide and dioxide. Potassium and sodium sulphates decompose the oxalate only at a high temperature and with difficulty.

T A H

Condensation of Ethyl ββ-Dimethylglycidate with Ethyl Bromoacetate. Georges Darzens and J. Sejourné (*Compt. rend.*, 1911, **152**, 1105—1107. Compare this vol., i, 259).—A mixture of ethyl ββ-dimethylglycidate and ethyl bromoacetate in benzene solution, on the addition of zinc, yields an organo-zinc compound, which treated in the usual way forms *ethyl* α-*hydroxy*-α-iso*propylsuccinate*, $CO_2Et{\cdot}CPr^{\beta}(OH){\cdot}CH_2{\cdot}CO_2Et$, b. p. 120—121°/3 mm., 254° under ordinary pressure; the corresponding *acid* has m. p. 139°. The molecular transposition involved in the formation of this ester is accounted for by the preliminary change of the glycidic ester into ethyl dimethylpyruvate, which then condenses normally with the alkyl compound (compare Haller, Abstr., 1906, i, 625). W. O. W.

Preparation of Mesoxalic Esters. André Meyer (*Bull. Soc. chim.*, 1911, [iv], **9**, 423—425).—In applying the process of Bouveault and Wahl (Abstr., 1904, i, 556) as modified by Schmitt (Abstr., 1905, i, 508), and subsequently by Curtiss (Abstr., 1906, i, 480; 1908, i, 760), the author finds that the yield of ethyl mesoxalate obtained from ethyl malonate varies within wide limits. The explanation of this is that in the action of nitrogen trioxide on ethyl malonate an oximino-compound is first formed, which by the further action of the trioxide is converted into an unstable substance (compare Curtiss and Tarnowski, Abstr., 1908, i, 760; Lemaire, Abstr., 1909, i, 199), the decomposition of which gives rise to the mesoxalate. In cases where a small yield of the diketonic ester is obtained, the unstable compound remains in the residues from the reaction, and such residues on the application of heat decompose violently, giving a further yield of ethyl mesoxalate.

To obtain good yields the nitrogen trioxide must be dry, and to prevent the deleterious action of moisture a little acetic anhydride may be added to the ethyl malonate. T. A. H.

Destruction of Tartrates by Fermentation. Charles Ordonneau (*Bull. Soc. chim.*, 1911, [iv], **9**, 398—402).—Crude tartrates undergo bacterial anaerobic fermentation with production of salts of acetic acid and of smaller quantities of formic, butyric, and higher acids, but not of propionic acid. Aerobic fermentation also occurs with ultimate formation of carbonates, and not of salts of volatile acids. W. O. W.

Condensations with Ultra-violet Light. Richard Pribram and Adolf Franke (*Ber.*, 1911, **44**, 1035—1039).—Purified formaldehyde in aqueous solution when exposed to ultra-violet light in a quartz vessel undergoes condensation, forming a product which is partly volatile in steam and reduces Fehling's solution in the cold. A colourless residue remains in the vessel after distillation, which dissolves in water and behaves as glycollaldehyde. No such change takes place in formaldehyde which is not exposed to ultra-violet light. E. F. A.

Formation of Acetaldehyde by the Pyrogenic Decomposition of Some Oxalates. DOMENICO GANASSINI and EVERARDO SCANDOLA (*Chem. Zentr.*, 1911, i, 63; from *Boll. Soc. Med.-Chirurg., Pavia*, 1910).—Some oxalates, particularly those of barium, strontium, calcium, magnesium, and tin, and the normal oxalates of the alkali metals, yield, when heated in the moist condition, small quantities of acetaldehyde. Oxalic acid itself does not give aldehyde.

The formation of acetaldehyde by heating calcium oxalate may be used for the detection of oxalic acid. The moist precipitate, obtained by the addition of calcium chloride in the presence of acetic acid, is heated in a tube, and the aldehyde detected in the issuing vapours by means of the blue coloration which it gives with paper, moistened with sodium nitroprusside and piperazine. F. B.

Acetaldehyde-hydrazine. ROBERT STOLLÉ (*Ber.*, 1911, **44**, 1134—1135).—*Acetaldehyde-hydrazine*, $C_8H_{18}N_6,6H_2O$, the hydrazine analogue of aldehyde-ammonia, is prepared by the interaction of hydrazine hydrate and acetaldehyde in alcoholic solution. It forms small, colourless crystals, m. p. 60°, which lose water when kept for a long time in a vacuum. It is stable towards alkalis, but is decomposed into its constituents when warmed with dilute acids. Its aqueous solutions on being acidified and shaken with benzaldehyde, yield benzalazine. With silver nitrate, it forms an *additive* compound, $C_6H_{18}N_6,3AgNO_3$, and is converted by amyl nitrite and sodium ethoxide in alcoholic solution into an unstable *sodium* salt, the constitution of which has not yet been determined. F. B.

Chloraloxime. F. CARLO PALAZZO and F. FAZIO (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 244—246).—Chloraloxime was found by Meyer (Abstr., 1891, 1181) to yield, on decomposition with alkali hydroxide, the theoretical quantity of hydrogen chloride required by the equation: $CCl_3\cdot CH{:}NOH + H_2O = CO_2 + HCN + 3HCl$, but only one-half of the theoretical quantities of carbon dioxide and hydrogen cyanide. It is now found that the white substance formed in this process has the formula $C_2H_3O_2NCl_2$, and reacts with hydroxylamine, chlorine being eliminated. An odour resembling that of a nitrile oxide is also observed in the decomposition of chloraloxime with alkali, and it is probable that the first products of the action are chloroform, hydroxylamine, and formic acid, the chloroform and hydroxylamine then reacting to form hydrogen chloride and formonitrile oxide. C. H. D.

The Action of Ammonia and Sodium Carbonate on Different Varieties of Sugar in Dilute Aqueous Solutions. ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, **32**, 97—100).—*N*/100 ammonia solution exerts but little action on dilute solutions (0·2 to 1%) of arabinose, dextrose, lævulose, galactose, and maltose at 37° when allowed to remain for twenty-four hours. This is in marked contrast to the action of *N*/100-sodium hydroxide, which, under the same conditions, causes the polarisation to sink to 0°. *N*/10-ammonia acts even less energetically than *N*/100-sodium hydroxide. The action of sodium carbonate solutions is also considerably weaker than those of sodium hydroxide. S. B. S.

The Composition of the Hexosephosphoric Acid formed by Yeast-juice. I. ARTHUR HARDEN and WILLIAM J. YOUNG (*Biochem. Zeitsch.*, 1911, 32, 173—176).—In reply to Lebedeff (Abstr., 1910, i, 716) it is pointed out that the equation proposed by the authors for the reaction between phosphate and a hexose in the presence of yeast-juice: $2C_6H_{12}O_6 + 2R_2HPO_4 = 2CO_2 + 2C_2H_6O + C_6H_{10}O_4(PO_4R_2)_2 + 2H_2O$ is founded, apart from the composition of the hexosephosphoric acid (following abstract), on the ratios determined between (1) the phosphate added and the carbon dioxide and alcohol produced as a consequence of this addition in the presence of excess of sugar, (2) the sugar used and the carbon dioxide produced in the presence of excess of phosphate.

During the initial period of the fermentation these ratios were found to be $R_2HPO_4 : CO_2$ and $C_6H_{12}O_6 : CO_2$.

The only equation which is compatible with these ratios and with the production of a phosphoric acid derivative containing 6 carbon atoms is that given above. W. J. Y.

The Composition of the Hexosephosphoric Acid formed by Yeast-juice. II. WILLIAM J. YOUNG (*Biochem. Zeitsch.*, 1911, 32, 177—188).—The hexosephosphoric acid was filtered through a Martin gelatin filter in order to ensure its freedom from any colloidal matter, which, according to Lebedeff (Abstr., 1910, i, 716), vitiated the analysis of the salts previously quoted (Abstr., 1909, i, 863). In spite of this treatment the barium salt still corresponded with the formula previously given, $C_6H_{10}O_4(PO_4H_2)_2$.

When hexosephosphoric acid is heated with phenylhydrazine, one phosphoric acid group is split off and a phenylhydrazine salt of a phosphoric acid derivative of a hexosazone formed, which has the composition ascribed to it by von Lebedeff,

$$C_6H_8N_2,H_2PO_4,C_6H_6(OH)_3(N_2HPh)_2.$$

The hexosephosphoric acids derived from dextrose, lævulose, and mannose all yield the same osazone, m. p. 150—152°, thus affording further evidence that the same hexosephosphoric acid is obtained from all these sugars.

The osazone dissolves in sodium hydroxide solution with liberation of one molecule of phenylhydrazine, and, on adding excess of the reagent, the sodium salt of the osazone, $Na_2PO_4\cdot C_6H_6(OH)_3(N_2HPh)_2$, is obtained in yellow needles. When an aqueous solution of this sodium salt is acidified with acetic acid and phenylhydrazine added, the original phenylhydrazine salt of the osazone is formed, whilst if aniline is added in place of phenylhydrazine the corresponding aniline salt is obtained, $C_6H_5\cdot NH_2,H_2PO_4\cdot C_6H_6(OH)_3(N_2HPh)_2$, yellow needles, m. p. 133—135°.

Hexosephosphoric acid forms with phenylhydrazine in the cold an unstable compound, which is a salt of the hydrazine with the hydrazone of hexosediphosphoric acid,

$$(C_6H_5N_2H_3,H_2PO_4)_2,C_6H_7(OH)_3\cdot N_2HPh,$$

white needles, m. p. 115—117°, whilst a similar crystalline compound is formed with *p*-bromophenylhydrazine, m. p. 127—128°. When these hydrazones are heated with more of the hydrazine, 1 molecule of phosphoric acid is liberated, and the corresponding osazone derivative formed.

Hexosephosphoric acid thus contains an active carbonyl group and two phosphoric acid groups, and one of the latter is probably attached to the carbon atom adjacent to the carbonyl group, since it is split off in the formation of the osazone. W. J. Y.

The Destruction of Dextrose by Light. Paul Mayer (*Biochem. Zeitsch.*, 1911, **32**, 1—9).—Under the influence of light (quartz lamp) in presence of traces of sodium carbonate, dextrose undergoes a characteristic change, which is different to that which it undergoes in the presence of the carbonate alone without exposure to rays. There are formed traces of volatile acids, aldehydes, and glucosone. A complete destruction of the sugar into carbon monoxide and dioxide, etc., under the conditions of the experiments (relatively low temperature) was not observed. S. B. S.

Action of Normal Barium Hydroxide on Dextrose and Galactose. Fred W. Upson (*Amer. Chem. J.*, 1911, **45**, 458—479).—It is claimed by Kiliani, that the formation of saccharinic acids from the hexoses cannot be effected by the hydroxide of sodium, potassium, or barium, but only by that of calcium, to which he attributes a specific action. It has been found, however, by Nef and also by the author that all alkali hydroxides give analogous results under similar conditions of concentration, but that the proportions of the various saccharinic acids produced vary greatly with the concentration of the reagent.

An investigation has now been made of the action of *N*-barium hydroxide on *d*-galactose and dextrose. Some of the saccharinic acids were isolated which were obtained by Nef (Abstr., 1910, i, 714) by the action of 8*N*-sodium hydroxide on these sugars, but whereas Nef isolated large quantities of α- and β-*meta*-saccharinic and α- and β-*iso*saccharinic acids with six carbon atoms, only small amounts of the first three of these acids were obtained in the present case, whilst relatively larger amounts of *dl*-lactic and *dl*-αγ-dihydroxybutyric acids were produced. The quantity of optically inactive C_5 and C_6 saccharinic acids, formed from inactive pentoses and hexoses produced by synthetic condensation, was also relatively larger and rendered the detection and isolation of the active C_6 saccharinic acids exceedingly difficult E. G.

Action of (1) Hydracids, (2) Formic and Acetic Acids, in Increasing Proportions, on Starch and Dextrin. William Oechsner de Coninck and A. Raynaud (*Bull. Acad. Roy. Belg.*, 1911, 213—215, 335—337. Compare Abstr., 1910, i, 655, and this vol., i, 181).—When equal quantities of starch or dextrin are heated with increasing quantities of hydrochloric or hydrobromic acid for the same length of time, the amount of hydrolysis is proportional to the concentration of acid employed, but the quantity of dextrin hydrolysed is always greater than that of starch hydrolysed.

With acetic and formic acids as hydrolytic agents, on the contrary, whilst the amount of hydrolysis is still proportional to the concentration of the acid, the quantities of dextrin and starch hydrolysed are practically equal, thus establishing a marked difference between hydrolysis as effected by mineral and organic acids. T. A. H.

Ethylene- and Propylene-diammonium Aurihalides. ALEXANDER GUTBIER and C. J. OBERMAIER (*Chem. Zentr.*, 1911, i, 540—541; from *Sitzungsber.*, *Physik.-med. Soz.*, *Erlangen*, 42).—A description of the preparation and properties of the aurichlorides and auribromides. *Ethylenediammonium aurichloride*, $C_2H_8N_2,2HAuCl_4,2H_2O$, yellow, tabular crystals of monoclinic habit; the *auribromide*,

$$C_2H_8N_2,2HAuBr_4,2H_2O,$$

red to brownish-red lamellæ, possibly monoclinic.

Propylenediammonium aurichloride, $C_3H_{10}N_2,2HAuCl_4,2H_2O$, and *propylenediammonium auribromide*, $C_3H_{10}N_2,2HAuBr_4,H_2O$, resemble the corresponding ethylenediamine compounds. F. B.

Spatial Change of Position During Reactions of Stereoisomeric Compounds. ALFRED WERNER (*Ber.*, 1911, **44**, 873—882).—The author has studied the reactions of a large number of stereoisomeric diethylenediaminecobalt salts of the general formula $[A_2Co\ en_2]X_n$, and finds that the replacement of an acid group in co-ordinative combination with the metallic atom by ammonia, water, etc., is frequently accompanied by a change in the spatial configuration, the new group taking up a different position to that originally occupied by the group which it has replaced.

Thus *trans*-dichloro- and *trans*-dibromo-diethylenediaminecobalt salts are almost quantitatively converted into *cis*-chloro- and *cis*-bromoamminediethylenediaminecobalt salts by the action of strong aqueous ammonia; *trans*-dichlorodiethylenediaminecobalt chloride when dissolved in water is transformed into *cis*-chloroaquodiethylenediaminecobalt chloride.

A similar change of configuration is also found to occur during substitution reactions. The following examples are given: *trans*-chloro*iso*thiocyanodiethylenediaminecobalt salts, when treated with strong aqueous ammonia, yield *cis*-hydroxylo*iso*thiocyanodiethylenediamine salts, which may be isolated in the form of aquo-salts, $\left[\begin{matrix}SCN\\H_2O\end{matrix}\ Co\ en_2\right]X_2$; *trans*-dibromodiethylenediaminecobalt bromide is quantitatively formed by dissolving *cis*-chlorobromodiethylenediaminecobalt bromide in hydrobromic acid; when *cis*-chloroamminediethylenediaminecobalt nitrite is treated with sodium nitrite, both *cis*- and *trans*-nitroamminediethylenediaminecobalt nitrites are obtained.

Change of configuration also takes place during reactions in which ammonia, water, etc., are expelled from combination with the metallic atom. Thus *trans*-chloronitrodiethylenediaminecobalt nitrite is obtained from *cis*-chloroamminediethylenediaminecobalt nitrite by heating in concentrated aqueous solution, whilst *trans*-diaquodiethylenediaminecobalt chloride when kept is transformed into *cis*-dichlorodiethylenediaminecobalt chloride.

That this change of configuration is not associated with the transformation of the less stable into the more stable form is proved by the fact that the changes lead as frequently from the cis- to the trans-group as in the reverse direction. This view is further supported by the following reactions: (1) Salts of the *trans*-dichlorodiethylenediamine group yield, with potassium hydroxide, *cis*-hydroxyloaquodiethylenediaminecobalt salts, whilst the stereoisomeric *cis*-dichloro-compounds are converted by ammonia into salts of the *trans*-hydroxyloaquodiethylenediamine group; (2) both *cis*- and *trans*-*iso*thiocyanoamminediethylenediaminecobalt salts when warmed with potassium thiocyanate give rise exclusively to salts of the *trans*-di*iso*thiocyanodiethylenediaminecobalt group; the stereoisomeric chloro*iso*thiocyanodiethylenediaminecobalt chlorides are converted by liquid ammonia into a mixture of *cis*- and *trans*-*iso*thiocyanoamminediethylenediaminecobalt chlorides, in approximately the same proportions.

An explanation of these strange transformations was found from a consideration of the difference in the behaviour exhibited by various salts belonging to the same group. When chloroamminediethylenediaminecobalt nitrite and thiocyanate are warmed in concentrated aqueous solution, loss of ammonia takes place, whilst with other salts of the same group no action occurs. Diaquotetramminecobalt sulphate undergoes no change on keeping, whereas the bromide and chloride are completely converted into $\left[\begin{matrix}Br\\H_2O\end{matrix}Co(NH_3)_4\right]Br_2$ and $\left[\begin{matrix}Cl\\H_2O\end{matrix}Co(NH_3)_4\right]Cl_2$ respectively.

Differences in the behaviour of acid groups attached to the metallic atom have also been observed. Whilst salts of the chloro*iso*thiocyanodiethylenediaminecobalt group are quantitatively transformed into *iso*thiocyanoamminediethylenediaminecobalt salts, and salts of the nitratonitrodiethylenediaminecobalt group when subjected to the same treatment yield nitroamminediethylenediamine salts, di*iso*thiocyano- and dinitro-diethylenediaminecobalt salts remain unchanged.

From the changes illustrated in the above examples, the author draws the following conclusions: (1) The central atom of a complex radicle exerts an attraction on groups not directly attached to it, tending to bring them into co-ordinative combination with the central atom. (2) The magnitude of this attraction depends on the nature of the groups. (3) The attraction will be exercised in a definite spatial direction, and this will therefore define the position taken up by the new group. (4) In the case of a co-ordinatively saturated compound, a new group can only enter into union with the central atom by the expulsion of another group, and that group will therefore be expelled which is least firmly attached.

Since the spatial position of the entering group is independent of that originally occupied by the group expelled, an explanation is thus afforded of the changes in the spatial configuration described above. The formation of a mixture of stereoisomerides in many reactions is explained on the assumption that the attraction exerted by the central atom is exercised in different spatial directions.

In the case of substitution reactions proceeding according to the scheme: $AX + BY = AY + BX$, an additive compound is first produced; the group X becomes, thereby, less firmly attached, and, owing to the attraction exerted on the group Y by the central atom, is finally expelled, the group Y then entering into co-ordinative union with the central atom.

Examples are given in which intermediate additive compounds have been isolated. The stereoisomeric *iso*thiocyanoaquodiethylenediaminecobalt salts, $\left[{}^{\mathrm{SCN}}_{\mathrm{H_2O}}\mathrm{Co\ en_2}\right]\mathrm{X_2}$, yield, with silver nitrate, stable crystalline *silver* salts, $\left[{}^{\mathrm{AgSCN}}_{\mathrm{H_2O}}\mathrm{Co\ en_2}\right]\mathrm{X_3}$, from which silver thiocyanate is removed only on boiling. *trans*-Chloro*iso*thiocyanodiethylenediaminecobalt nitrate, $\left[{}^{\mathrm{SCN}}_{\mathrm{Cl}}\mathrm{Co\ en_2}\right]\mathrm{NO_3}$, forms with silver nitrate an *additive* compound, $\left[{}^{\mathrm{SCN}}_{\mathrm{AgCl}}\mathrm{Co\ en_2}\right](\mathrm{NO_3})_2$, which is soluble in cold water, is precipitated on the addition of nitric acid, and loses silver chloride when heated in aqueous solution.

By treating chloroamminediethylenediaminecobalt nitrite with sodium nitrite, an *intermediate* product, $\left[{}^{\mathrm{NaCl}}_{\mathrm{NH_3}}\mathrm{Co\ en_2}\right](\mathrm{NO_2})_3$, is obtained; in concentrated solution this loses ammonia, forming chloronitrodiethylenediaminecobalt nitrite, whilst in dilute solution sodium chloride is removed with the formation of nitroamminediethylenediaminecobalt nitrite.

The author has extended these ideas on the process of substitution and the change of spatial configuration to the reactions of organic compounds, and, on the assumption of the intermediate formation of additive compounds, gives an explanation of the Walden inversion.

F. B.

New Synthesis of γ-Homocholine. Ernst Berlin (*Chem. Zentr.*, 1911, i, 475; from *Zentr. Physiol.*, 1910, **24**, 779—780).—γ-Homocholine may be prepared by methylating β-aminopropyl alcohol with methyl iodide; it is isolated by precipitating it with phosphotungstic acid and conversion into the *aurichloride*, $C_6H_{16}ONCl,AuCl_3$, m. p. 163°.

Morley's β-homocholine (Abstr., 1881, 151) is identical with that described by Malengreau and Lebailly (Abstr., 1910, i, 545). F. B.

Homocholine Ether. Ernst Berlin (*Chem. Zentr.*, 1911, i, 475; from *Zentr. Physiol.*, 1910, **24**, 929—930).—In the preparation of γ-homocholine by the interaction of trimethylamine and trimethylenechlorohydrin, and subsequent isolation by means of the aurichloride, a salt sparingly soluble in water was obtained. On converting this into the platinichloride it was separated into hexamethyltrimethylenediamine platinichloride and *homocholine ether platinichloride*,

$$O(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3Cl)_2,PtCl_4,$$

m. p. 258—260°. The *aurichloride*, $C_{12}H_{30}ON_2Cl_2,2AuCl_3$, has m. p. 230—232°. F. B.

The Action of Mercuric Chloride on Glycine. MAX SIEGFRIED (*Ber. K. Sachs. Ges. Wiss. Math.-phys. Klasse*, 1910, **62**, 57—68).

—An account of numerous experiments on the action of mercuric chloride on glycine under greatly varying conditions; the evolved ammonia was estimated and various organic products analysed.

Iminodiacetic acid was obtained and shown to be identical with that previously prepared from chloroacetic acid; it yields a *silver* salt, $C_4H_5O_4NAg_2$, and a blue *copper* salt. The action of mercuric chloride and mercury acetamide on glycine was also studied. F. M. G. M.

aa'-Ethylenedi-iminodi*iso*butyric Acid. N. SCHLESINGER (*Ber.*, 1911, **44**, 1135—1137).

—*aa'-Ethylenedi-iminodi*iso*butyronitrile hydrochloride*, $C_2H_4(NH\cdot CMe_2\cdot CN)_2,2HCl$, is precipitated in the form of a white, crystalline powder by passing hydrogen chloride into the ethereal solution of the product obtained by the interaction of potassium cyanide, ethylenediamine hydrochloride, and acetone in the presence of a small quantity of water. It has m. p. 93—96° (sintering at 93°), and is hydrolysed by hydrochloric acid to *aa'-ethylenedi-iminoisobutyric acid hydrochloride*, $C_{10}H_{20}O_4N_2,HCl,2H_2O$, which crystallises in lustrous needles, m. p. above 245°.

The *ethyl* ester, $C_{14}H_{28}O_4N_2$, prepared from the preceding compound by Fischer's method, has b. p. 171—172°/15 mm., D_4^{20} 0·9934, n_D^{20} 1·4432, and yields a crystalline *hydrochloride*.

*aa'-Ethylenedi-iminodi*iso*butyric acid*, $C_2H_4(NH\cdot CMe_2\cdot CO_2H)_2$, obtained from the ethyl ester by boiling with water, is a white, crystalline powder, and gives a blue *copper* salt, $C_{10}H_{18}O_4N_2Cu$.

Other ketones and also aldehydes react with potassium cyanide and ethylenediamine hydrochloride in a similar manner. F. B.

Action of *iso*Amyl Nitrite on Amines and Amides. S. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1—17).

—In order to throw light on the reaction taking place between amines (or amides) and nitrous acid or nitrosyl chloride, the author has replaced the latter by *iso*amyl nitrite, which has the advantage of reacting in absence of water or mineral acid.

With acetamide, *iso*amyl nitrite yields *iso*amyl alcohol, acetic acid, water, nitrogen, and *iso*amyl acetate. With carbamide, *iso*amyl alcohol, carbon dioxide, water, nitrogen, and *iso*amyl carbamate. With *iso*amylamine, *iso*amyl alcohol, nitrogen, and a large proportion of secondary products with high b. p. With dibenzylamine, dibenzylnitrosoamine and *iso*amyl alcohol; and with diphenylamine, diphenylnitrosoamine and *iso*amyl alcohol.

Comparison of these results with those obtained with (1) ammonia and esters (or anhydrides or chloroanhydrides) of organic acids; (2) amines and nitrous acid; (3) amines and nitrosyl chloride, and (4) hydrazine and ethyl nitrite, indicates the reactions in the above cases to be expressed by the following equations:

With acetamide:
$CH_3{\cdot}CO{\cdot}NH_2 + C_5H_{11}O{\cdot}NO = CH_3{\cdot}CO{\cdot}NH_2(NO){\cdot}O{\cdot}C_5H_{11} = CH_3{\cdot}CO{\cdot}NH{\cdot}NO + C_5H_{11}{\cdot}OH = CH_3{\cdot}CO_2H + N_2 + C_5H_{11}{\cdot}OH$; $CH_3{\cdot}CO_2H + C_5H_{11}{\cdot}OH = CH_3{\cdot}CO_2{\cdot}C_5H_{11} + H_2O$.

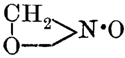
With carbamide:
(I) $NH_2{\cdot}CO{\cdot}NH_2 + 2C_5H_{11}O{\cdot}NO = CO[{\cdot}NH_2(NO){\cdot}O{\cdot}C_5H_{11}]_2 = CO({\cdot}NH{\cdot}NO)_2 + 2C_5H_{11}{\cdot}OH$; $CO({\cdot}NH{\cdot}NO)_2 = CO({\cdot}N{:}N{\cdot}OH)_2 = CO_2 + H_2O + 2N_2$.

(II) $NH_2{\cdot}CO{\cdot}NH_2 + C_5H_{11}O{\cdot}NO = NH_2{\cdot}CO{\cdot}NH_2(NO){\cdot}O{\cdot}C_5H_{11} = NH_2{\cdot}CO{\cdot}NH{\cdot}NO + C_5H_{11}{\cdot}OH$; $NH_2{\cdot}CO{\cdot}NH{\cdot}NO = NH_2{\cdot}CO_2H + N_2$, and $NH_2{\cdot}CO_2H + C_5H_{11}{\cdot}OH = NH_2{\cdot}CO_2{\cdot}C_5H_{11} + H_2O$.

With *iso*amylamine:
$C_5H_{11}{\cdot}NH_2 + C_5H_{11}O{\cdot}NO = C_5H_{11}{\cdot}NH_2(NO){\cdot}O{\cdot}C_5H_{11} = C_5H_{11}{\cdot}NH{\cdot}NO + C_5H_{11}{\cdot}OH = 2C_5H_{11}{\cdot}OH + N_2$.

With dibenzylamine or diphenylamine: $NR_2H + C_5H_{11}O{\cdot}NO = NO{\cdot}NR_2H{\cdot}O{\cdot}C_5H_{11} = NR_2{\cdot}NO + C_5H_{11}{\cdot}OH$, where $R = Ph$ or CH_2Ph.

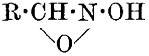
T. H. P.

The Constitution of the Hydroxamic Acids. F. Carlo Palazzo (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 249—252).—The conductivity of the hydroxamic acids shows that all have a similar constitution; it is therefore sufficient to examine one such acid in detail, and formohydroxamic acid has been chosen. The reactions are discussed in order to show that the formula  $\overset{CH_2}{\underset{O}{|}}\!>N{\cdot}OH$ best expresses its behaviour.

C. H. D.

Oxalo-monohydroxamic Acid. F. Carlo Palazzo and E. Oliveri-Mandala (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 247—248).—Compounds of the type $CHX{:}NOH$, where $X = Cl$, Br, I, NO_2 or SCN, decompose at about 0°. *Oxalo-monohydroxamic acid*, $CO_2H{\cdot}C(OH){:}NOH$, obtained by Dimroth and Dienstbach (Abstr., 1909, i, 63) only in the form of a salt, may be prepared by mixing concentrated aqueous solutions of hydroxylamine and sodium methyl oxalate. The pure sodium salt crystallises on cooling. After conversion into the copper salt and decomposition by hydrogen sulphide, the acid is obtained, m. p. 118°. The *silver* salt,

$$C_2HO_4NAg_2,$$

like the corresponding mercury salt, is not convertible into a fulminate, and the authors regard this as a further proof that hydroxamic acids have the constitution  $R{\cdot}\underbrace{CH{\cdot}N}_{O}{\cdot}OH$ (compare preceding abstract).

C. H. D

Some Hydroxamic Acids of the Pyrone Series. E. Oliveri-Mandala (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 303—304).—In view of the behaviour of pyrone derivatives with hydroxylamine (Azzarello, Abstr., 1905, i, 916) the action of hydroxylamine on the esters of chelidonic and triethylmeconic acids has been examined. It is found that both compounds yield hydroxamic acids, whilst ethyl diethylmeconate remains unchanged.

C. H. D.

Some New Data on the Preparation of Biguanide. Adriano Ostrogovich (*Chem. Zentr.*, 1910, ii, 1890; from *Bul. Soc. Ştiinţe, Bucureşti*, 1910, 19, 641—647).—The replacement of ammonium chloride by ammonium iodide in the preparation of biguanide from dicyanodiamide (compare Bamberger and Dieckmann, Abstr., 1892, 737) raises the yield from 21—23% to 45%. The yield is also increased by using ammonium chloride, but not to the same extent as when the iodide is employed. F. B.

Action of Hydrogen Sulphide on Fulminic Acid. Livio Cambi (*Gazzetta*, 1911, 41, i, 166—173).—Nef (Abstr., 1895, i, 9) found that the action of hydrogen sulphide, in the cold, on silver fulminate suspended in water results in the formation of an unstable compound, which decomposes, giving silver sulphide, which he supposed to be the silver salt of thioformhydroxamic acid, $SH\cdot CH:NOAg$. Ammonium thiocyanate forms the principal product of the action of hydrogen sulphide, in presence of water, on fulminates of the heavy metals, and the formation of this salt may be readily explained as due to the decomposition of the initial product, thioformhydroxamic acid, in the two following ways: (1) $SH\cdot CH:NOH = SH\cdot CN + H_2O$ and (2) $SH\cdot CH:NOH \longrightarrow SH\cdot CO\cdot NH_2 \longrightarrow COS + NH_3$.

The author has confirmed the formation of thioformhydroxamic acid in the action of hydrogen sulphide on mercury fulminate, as the solution, after removal of the mercuric sulphide, gives an intense, violet-blue coloration with ferric chloride (compare Abstr., 1909, i, 646). The acid may also be obtained by treating the product of the interaction of chloroform (1 mol.) and sodium sulphide (2 mols.) with hydroxylamine.

Benzyl thioformhydroxamate, $CH_2Ph\cdot S\cdot CH:NOH$, crystallises in nacreous scales or elongated prisms, m. p. 144—146°, has the normal molecular weight in boiling alcohol, and, when heated in aqueous alcoholic solution with hydrochloric acid, decomposes according to the equation:

$$C_7H_7\cdot S\cdot CH:NOH + 2H_2O = H\cdot CO_2H + NH_2\cdot OH + SH\cdot CH_2Ph.$$

The *sodium*, *cadmium*, *lead*, *mercuric*, *nickel*, *cobalt*, *cupric*, and *silver* salts of the acid have been prepared. In solution the acid decomposes more or less rapidly into thiocyanic acid and water, whilst the sodium salt gives ammonia and carbon oxysulphide. The benzyl ether melts without decomposition, but when fused at 80—85° with benzoic anhydride, it decomposes with formation of benzyl thiocyanate.

T. H. P.

The Existence of Other Gaseous Compounds of Carbon and Nitrogen Besides Cyanogen. Alexander P. Lidoff (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IVAI, 315).—When cyanogen is heated in contact with iron, the gas increases in volume, and a part becomes soluble in acid cuprous chloride. When nitrogen is passed over heated charcoal, an increase of volume also takes place, and a part of the gas becomes soluble in acid cuprous chloride. The soluble gas is oxidised by one-half its volume of oxygen, but the product is lighter than carbon dioxide. C. H. D.

An Isomeride of Potassium Ferricyanide. ITALO BELLUCCI and G. SABATINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 176—181).—By the application of Freund's reaction (Abstr., 1888, 571) by means of which both the ferrocyanide and the ferricyanide of potassium yield the ferroimino-ether, $H_4FeC_6{<}^{(NH)_6}_{(OEt)_6},2HCl$, the authors propose to elucidate the constitution of the green, isomeric potassium ferricyanide obtained by Locke and Edwards (Abstr., 1899, i, 557). R. V. S.

Case of Structural Isomerism in the Metallic Cyanides. ITALO BELLUCCI and G. SABATINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 239—243. Compare preceding abstract).—The amounts of iodine liberated by α- and β-potassium ferricyanides agree with what is required by the constitutions previously suggested. In very dilute solutions both salts are completely dissociated into four ions. The α-ferricyanide yields the ferroimino-ether, $C_{18}H_{41}O_6N_6FeCl_2$, so that all its cyanogen groups take part in Pinner's reaction. The β-ferricyanide does not enter into this reaction. The α-ferricyanide evolves hydrogen cyanide when boiled with potassium persulphate, whilst the β-form yields cyanic acid in those circumstances. These facts support the view previously advanced that the α-ferricyanide has the nitrilic, and the β-form the *iso*nitrilic, constitution. When an aqueous solution of the β-ferricyanide is treated with potassium hydroxide or with ammonia, its colour changes from green into the yellow characteristic of the α-form. R. V. S.

So-called Perferricyanides. LIVIO CAMBI (*Gazzetta*, 1911, **41**, i, 157—166).—When a ferrocyanide is converted into ferricyanide by the action of chlorine, prolonged action of the halogen results in attack of the ferricyanide with formation of an intensely violet solution. Uncertainty exists, however, as to the nature of the compound formed. According to Borg (this Journ., 1876, i, 907) a perferricyanide or "black prussiate" is obtained having the formula $K_2Fe(CN)_6$, which was regarded as probably correct by Skraup (Abstr., 1877, **32**, 597), and is quoted by Dammer (*Handbuch der anorg. Chemie*, **3**, 378) and by Moissan (*Traité de Chimie Min.*, **4**, 417). But Beilstein's *Handbuch* (3rd edition, 1, 1425; *Ergänzungsbände*, 1, 797) gives the formula $K_2Fe(CN)_5,H_2O$, which is agreement with Skraup's values for the relation Fe : C. The nature of the perferricyanide is rendered still more uncertain by the existence of sodium aquopentacyanoferrate (compare Hofmann, Abstr., 1900, i, 591).

The author has prepared potassium perferricyanide by Skraup's method, the salt being purified by repeated precipitation from aqueous solution by means of alcohol. This procedure yields a violet, amorphous powder, for which the relation Fe : K = 1 : 2; it liberates, from potassium iodide, one atom of iodine per atom of iron, whereas a compound having the formula given by Borg (*vide supra*) should liberate two atoms of iodine: $H_2Fe^{IV}(CN)_6 + 2HI = H_4Fe^{II}(CN)_6 + I_2$.

The reactions of potassium perferricyanide correspond with those of the pentacyanoferrates, and in solution the salt has a colour equal to that of $Na_2[Fe(CN)_5,H_2O]$, prepared by Hofmann's method. The formation of the perferricyanide is hence expressed by the equation: $K_3Fe'''(CN)_6 + Cl_2 = K_2Fe'''(CN)_5 + KCl + CN{\cdot}Cl$. The same reaction takes place if the chlorine is replaced by sodium chlorate and hydrochloric acid.

When reduced by means of alkaline hydroxylamine hydrochloride solution, alkali sulphide or formaldehyde and acetone in presence of alkali, potassium perferricyanide yields *potassium aquopentacyanoferrite*, $K_3[Fe(CN)_5,H_2O]$, the properties of which are similar to those of the corresponding sodium salt (compare Hofmann, *loc. cit.*). Reduction by means of excess of potassium sulphite in presence of potassium hydroxide yields *potassium ferrososulphitocyanide*, $K_5[Fe(CN)_5SO_3]$, which crystallises from aqueous alcohol in small, yellow prisms, and exhibits all the reactions of the pentacyanoferrites.

The formation of the "black prussiate" is regarded as occurring in the two stages: (1) $[Fe(CN)_6]''' + Cl_2 = [Fe(CN)_5Cl]''' + CN{\cdot}Cl$; (2) $[Fe^{III}(CN)_5Cl]''' + H_2O = [Fe^{II}(CN)_5,H_2O]'' + Cl'$. T. H. P.

Crystallographic-optical Investigations [Double Platinocyanides and Picrates]. HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1911, **49**, 113—132. Compare Abstr., 1907, ii, 689, 907; 1909, ii, 841).—Sodium platinocyanide, $Na_2Pt(CN)_4,3H_2O$, triclinic

$$[a:b:c = 0{\cdot}5879:1:0{\cdot}4757;\ \alpha = 87°42',\ \beta = 94°56\tfrac{3}{4}',\ \gamma = 90°59\tfrac{1}{2}'].$$

Rubidium platinocyanide, $Rb_2Pt(CN)_4,3H_2O(?)$, monoclinic

$$[a:b:c = 0{\cdot}9313:1:0{\cdot}5325;\ \beta = 99°48\tfrac{1}{4}'].$$

Optical determinations are given for these and also for the strontium and yttrium salts. The following, and other, details are collected respecting the double platinocyanides:

	Crystal system.	Colour.	Fluorescence.	Metallic sheen.
Sodium salt	Triclinic	Colourless	None	None
Strontium salt	Monoclinic	Colourless	Violet	None
Rubidium ,, ...	Monoclinic	Pale green	Sky-blue	None
Calcium ,, ...	Rhombic	Greenish-yellow	Green	Violet to blue
Barium ,, ...	Monoclinic	Yellow	Green	
Rubidium-lithium salt	Rhombic	Yellow	Green	Blue
Potassium-sodium salt	Monoclinic	Orange	Green	Purple-red to blue
Potassium-lithium ,,	Rhombic	Orange-red	Yellow	Blue
Yttrium ,,	Rhombic	Dark red	Cherry-red	Green

Potassium picrate, $C_6H_2(NO_2)_3{\cdot}OK$, rhombic

$$[a:b:c = 0{\cdot}6972:1:0{\cdot}3723];$$

ammonium picrate, $C_6H_2(NO_2)_3{\cdot}ONH_4$, rhombic

$$[a:b:c = 0{\cdot}6799:1:0{\cdot}3600].$$

L. J. S.

Constitution of Benzene from the Point of View of the Corpuscular-atomic Conception of Positive and Negative Valency. I. An Interpretation of the Crum Brown-Gibson Rule. II. Dynamical Formulæ and the Ultra-violet Absorption Spectrum of Benzene. III. Dynamical Formulæ and the Ultra-violet Absorption Spectrum of Naphthalene. HARRY S. FRY (*Zeitsch. physikal. Chem.*, 1911, **76**, 385—397, 398—412, 591—600).—I. The author uses the conception of the atomic nature of electricity, as developed by J. J. Thomson, Nernst, and Ramsay, and assumes that the atoms in a molecule are held together by the attraction of contrary electric charges. In the hydrogen molecule, for instance, one of the atoms has a positive, the other a negative, charge, and hence hydrogen can function as a univalent positive or negative element. On the same basis, the carbon atom having four valencies which may be all positive, all negative, or partly positive partly negative, gives five different types. The possible modes of representing benzene on this basis are then considered, and it is shown (1) that there is a structural basis for the similarity in behaviour of the ortho- and para-positions in contrast to the meta-position; (2) the electronic formula, like Collie's benzene formula, leads to the conclusion that there are two groups of hydrogen atoms; it is suggested that the 1 : 3 : 5 atoms are negative, the 2 : 4 : 6 atoms positive; (3) an explanation of the Crum Brown-Gibson rule can be given. The latter explanation depends upon the assumption of a difference between X in the compounds HX and HOX; in the former it is negative, in the latter positive. In a mono-substituted benzene derivative, C_6H_5X, therefore, X may be positive or negative, according as it is a derivative of HOX or HX. For details as to the application of these conceptions, the original paper should be consulted.

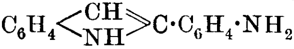
II. The views developed in the previous paper are applied to the interpretation of the absorption spectrum of benzene. Using Collie's space formula for benzene, it is shown that there are seven separate systems in dynamical equilibrium, and that there is a numerical relationship between these electronic isomerides and the vibration frequency of each of the seven bands in the ultra-violet region of the benzene spectrum. This results lends support to the suggestion of Baly and Desch (Trans., 1905, **87**, 766) that the bands are connected in some way with the vibrations of the benzene molecule.

III. The above conceptions are applied to the interpretation of the ultra-violet absorption spectrum of naphthalene, and in this case also it has been shown that there is a quantitative relationship between the vibration frequencies of the absorption bands and the number of transitions which can take place between the different electronic isomerides. G. S.

Preparation of Organic Iodo-compounds from the Corresponding Chloro- and Bromo-derivatives by the Action of Alkali Iodides. Knoll & Co. (D.R.-P. 230172).—The replacement of chlorine or bromine by iodine in organic compounds by treatment with an acetone solution of an alkali iodide has previously been described (compare Finkelstein, Abstr., 1910, i, 453); this reaction has now been extended to the preparation of iodoacetic, iodopropionic, and iodo*iso*valeric acids from the corresponding bromo-compounds. ωω′-Dibromo-*o*-xylene yielded *ωω′-di-iodo-*o*-xylene*, m. p. 110°; whilst *ωω′-di-iodo*-m- and *ωω′-di-iodo*-p-*xylene*, m. p. 106° and 174° respectively, *tetraiodo*-m-*xylene*, m. p. 140°, p-*nitrobenzyl iodide*, m. p. 124°, and *ω-iodo*-p-*toluic acid*, m. p. 335°, were also prepared. F. M. G. M.

Action of Ethyl Alcohol on Arylsulphonyl Chlorides. R. GOUBAU (*Bull. Acad. Roy. Belg.*, 1911, 233—252).—The action of alcohol on benzenesulphonyl, *o*-, *m*-, and *p*-toluenesulphonyl, and *p*-chloro-, *p*-bromo- and *p*-iodo-benzenesulphonyl chlorides has been studied with a view to the determination of the nature of the reaction in each case, and the experimental results are tabulated in the original. With cold dilute solutions of the sulphonyl chlorides, hydrochloric acid and the ethyl ester of the sulphonic acid are formed, but on warming, the ester is saponified by the excess of alcohol, ethyl ether and the sulphonic acid being produced. At 30° and for very dilute solutions in dry alcohol the second reaction is negligible. The first reaction is unimolecular, and Wilhelmy's formula is applicable; the value of k increases especially towards the end of the reaction. This is due to autocatalysis induced by the hydrochloric acid formed, since if this acid is added at the beginning of the experiment the reaction is greatly accelerated. The chief conclusions drawn from the results are that (1) for sufficiently dilute solutions the first reaction may be regarded as unimolecular, (2) the value of the ratio k_{t+10}/k_t is 2·63; (3) the group $-CH_3$, replacing a nuclear hydrogen atom, diminishes the velocity of reaction to the greatest extent in the meta-position, less in the para-position, and scarcely at all in the ortho-position with respect to the chlorine atom; (4) the replacement of a nuclear hydrogen atom by a halogen causes acceleration of the reaction, the effect increasing with the atomic weight of the substituent. T. A. H.

Supposed Action of Organo-magnesium Compounds on the Vinyl Group of the Cinchona Alkaloids and of Styrene. BERNARDO ODDO (*Gazzetta*, 1911, **41**, i, 320—329).—The author criticises Comanducci's work on the action of organo-magnesium compounds on styrene and cinchotoxine (Abstr., 1909, i, 409; *Gazzetta*, 1910, **40**, i, 582, 584). His experiments with styrene and with cinchonine show that in neither case does the vinyl group react with organo-magnesium compounds. T. H. P.

$o:o'$-Dinitrotolane. ALFRED KLIEGL and KARL HAAS (*Ber.*, 1911, **44**, 1209—1218).—The reaction between sodium ethoxide and alcoholic *o*-nitrobenzylidene chloride at 35—40° yields *o:o'-dinitrotolane*, $C_{14}H_8O_4N_2$, yellow needles, m. p. 189—189·5°, the identity of which is proved by the formation of the same substance by heating *o:o'-dinitrostilbene dichloride*, m. p. 152—152·5°, with alcoholic sodium ethoxide. By reduction with alcoholic hydrogen chloride and stannous chloride, it yields *o:o'-diaminotolane*, $C_{14}H_{12}N_2$, m. p. 154°, colourless leaflets with a blue fluorescence, which is best purified through the *picrate*. When heated with concentrated sulphuric acid on the water-bath, *o*:*o'*-diaminotolane changes into the isomeric 2-*o-aminophenylindole*,  $C_6H_4<\substack{CH\\NH}>C\cdot C_6H_4\cdot NH_2$, m. p. 154°, the *picrate* of which, m. p. about 187°, is also obtained by heating *o*:*o'*-diaminotolane picrate at 140—143°.

By oxidation with chromic and acetic acids, *o*:*o'*-dinitrotolane yields *o*:*o'*-dinitrobenzil, yellow prisms, m. p. 206°, which is shown to be identical with Golubeff's *iso*dinitrobenzil, obtained by the oxidation of the product formed by the action of nitric acid, D 1·52, on deoxybenzoin. Popovici's so-called *o* : *o*′-dinitrobenzil, m. p. 151° (Abstr., 1907, i, 628), cannot be such, since it is colourless.

Sodium methoxide and methyl alcoholic *o*-nitrobenzylidene chloride yield, not a tolane derivative, but *o*-nitrobenzylidenedimethyl acetal in the normal manner. *m*-Nitrobenzylidene chloride reacts with sodium ethoxide in ethyl alcohol in the normal way. C. S.

Preparation of 1 : 5-Dichloronaphthalene-3-sulphonic Acid and of 1 : 4-Dichloronaphthalene-6-sulphonic Acid. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 229912).—When the mixture of 1 : 4- and 1 : 5-dichloronaphthalenes obtained by the chlorination of naphthalene is sulphonated, it yields 1 : 4-dichloronaphthalene-6-sulphonic acid and 1 : 5-dichloronaphthalene-3-sulphonic acid, which can be separated by the different solubilities of their sodium salts; sodium 1 : 4-dichloronaphthalene-6-sulphonate is the more insoluble, as are also its magnesium and alkaline earth salts. F. M. G. M.

Triphenylmethyl and Triphenylcarbinol. WILHELM SCHLENK, LEOPOLD MAIR, and C. BORNHARDT (*Ber.*, 1911, **44**, 1169—1177).—When nitric oxide is passed into an ethereal solution of triphenylmethyl, the yellow coloration first produced rapidly changes into an intense bluish-green, and finally, in the course of one hour, into a pale yellow. The bluish-green coloration is doubtless due to the formation of *ω-nitrosotriphenylmethane*, $CPh_3{\cdot}NO$, which is then transformed into a colourless bisnitroso-compound. The substance is so unstable that its isolation was impossible. On evaporating the ethereal solution, it is decomposed into its constituents; small quantities of a colourless crystalline substance, m. p. 154—155°, seemingly formed by the combination of two molecules of triphenylmethyl and one of nitric oxide, are simultaneously produced. When treated with phenylhydrazine, the green solutions of triphenylnitrosomethane give off nitrogen.

A similar bluish-green coloration, evidently due to the formation of ω-nitrosotriphenylmethane and ω-chlorotriphenylmethane, is observed when nitrosyl chloride is passed into a solution of triphenylmethyl; by further introduction of nitrosyl chloride, the colour changes to deep yellowish-brown, owing to the formation of an additive compound of ω-chlorotriphenylmethane with nitrosyl chloride.

Triphenylmethyl interacts with nitrogen peroxide, yielding a mixture of *ω-nitrotriphenylmethane*, $CPh_3{\cdot}NO_2$, and *triphenylmethyl nitrite*, $CPh_3{\cdot}O{\cdot}NO$, the latter substance being produced in greater proportion. The nitro-compound is best prepared by passing a current of carbon dioxide through liquid nitrogen peroxide, then through a hot glass tube in order to increase the proportion of the unimolecular form of nitrogen dioxide in the mixture, and finally into a concentrated ethereal solution of triphenylmethyl. It separates in the form of a colourless powder, consisting of flexible leaflets, m. p. 147°. It is decomposed by hot glacial acetic acid with the evolution of oxides of nitrogen, and, when warmed with concentrated sulphuric acid, gives a yellow coloration; when heated with phenol, it develops a brown colour.

Triphenylmethyl nitrite is contained in the ethereal filtrate from the preparation of the preceding compound. It is more readily prepared by leading the nitrous gases, obtained by the addition of concentrated sulphuric acid to sodium nitrite and dried over phosphoric oxide, into a concentrated ethereal solution of triphenylcarbinol. It forms colourless crystals, m. p. 95—100°, which become red on exposure to moist air and give off oxides of nitrogen, with the formation of triphenylcarbinol; the same change is produced by warming the substance with glacial acetic acid. With phenol, it gives a brown coloration.

All attempts to prepare ω-nitrotriphenylmethane or triphenylmethyl nitrite by the interaction of ω-chlorotriphenylmethane and silver nitrite proved fruitless.

The authors find that triphenylmethyl is remarkably stable toward nascent hydrogen. When subjected to the prolonged action of aluminium amalgam in ethereal solution, it yields only a very small quantity of triphenylmethane, whilst, on treatment with sodium in the presence of water, it remains entirely unchanged. It is also different towards water; an ethereal solution of the substance, in the absence of air, undergoes no change even on prolonged contact with water.

The interaction of phenylhydrazine and triphenylmethyl leads to the formation of triphenylmethane and *s*-phenyltriphenylmethylhydrazine, $NHPh\cdot NH\cdot CPh_3$, which has m. p. 140°, and is oxidised with amyl nitrite to triphenylmethylazobenzene, m. p. 111° (compare Gomberg, Abstr., 1897, i, 40).

The behaviour of triphenylmethyl towards nascent carbon monoxide has also been investigated, by heating it with nickel carbonyl at 35—40°, but no combination occurred (compare Gomberg, Abstr., 1901, i, 77). Nickel carbonyl reacts with ω-chlorotriphenylmethane at the ordinary temperature, yielding nickel chloride and triphenylmethyl, with the evolution of carbon monoxide.

When triphenylcarbinol is heated at 185° with sodium, it yields a *sodium* derivative, which is obtained in the form of a white powder by removing unaltered carbinol with benzene or xylene. It decomposes at a high temperature, without melting, and, on treatment with water, is reconverted into the carbinol. Sodium has no action on triphenylcarbinol in xylene solution (compare Hemilian, this Journ., 1875, 152). F. B.

Mechanism of the Reaction in the Formation of Organomagnesium Compounds. GEORGE L. STADNIKOFF (*Ber.*, 1911, 44, 1157—1160).—According to Tschelinzeff (Abstr., 1905, i, 40), oxonium compounds of the type $R_3O\cdot X$ (where $X =$ halogen) are formed as intermediate products in the Grignard reaction. It should, therefore, be possible to find an ether, $R\cdot O\cdot R'$, the oxonium compound of which with an alkyl halide, $R\cdot X$, dissociates in two directions, according to the scheme: $R'X + R_2O \longleftarrow R_2R'O\cdot X \longrightarrow R'O\cdot R + RX$, and, in the presence of magnesium, gives rise to two magnesium compounds, $R\cdot MgX$ and $R'\cdot MgX$.

Evidence of the formation of two magnesium compounds has been found by the author in the reaction between propyl iodide, triphenylmethyl ethyl ether, and magnesium.

These substances react in xylene solution, yielding magnesium propyl iodide and magnesium triphenylmethyl iodide, which separates out; on passing carbon dioxide into the mixture, butyric acid and triphenylmethane together with unchanged triphenylmethyl ethyl ether were obtained. F. B.

Tri-α-naphthylmethane. ALEXEI E. TSCHITSCHIBABIN (*Ber.*, 1911, **44**, 1105—1107. Compare this vol., i, 277, 278).—The author's method of reduction with hydriodic and glacial acetic acids gives good, but not quantitative, results in the case of tri-α-naphthylcarbinol The chief product it *tri-α-naphthylmethane*, m. p. 191°. The hydrocarbon crystallises in glistening prisms with a faint bluish tinge, and melts in an atmosphere of carbon dioxide to a colourless liquid, with an intense blue fluorescence. The solutions of the substance also exhibit a blue fluorescence. By exposure to light, the hydrocarbon acquires a superficial brownish-yellow colour due to atmospheric oxidation. C. S.

Ortho-substituted Sulphinic Acids. MAX CLAASZ (*Annalen*, 1911, **380**, 303—316).—*o*-Acetylanilinesulphinic and *o*-nitrobenzenesulphinic acids have been prepared by reducing the corresponding sulphonic chlorides, in the former case with zinc dust and alcohol, and in the latter with the theoretical amount of stannous chloride and hydrochloric acid.

Unlike the majority of sulphinic acids these ortho-substituted acids are quite stable, and are not oxidised on exposure to the air; they are not so soluble in water as the corresponding sulphonic acids, but their sodium salts dissolve readily in both alcohol and water. With the exception of the *o*-nitrated acid they do not crystallise readily.

Sodium 4-bromoacetylaniline-2-sulphonate,

$$NHAc\cdot C_6H_3Br\cdot SO_3Na,H_2O,$$

obtained by acetylating Kreis's sodium 4-bromoaniline-2-sulphonate (Abstr., 1896, i, 48) with acetic anhydride at 170—180°, crystallises in colourless, felted needles. The *acid* is obtained by dissolving the sodium salt in ice-cold, concentrated hydrochloric acid, and washing with ether the crystals which are deposited after a time. It has m. p. 290—292° (decomp.). The *chloride*, $NHAc\cdot C_6H_3Br\cdot SO_2Cl$, has m. p. 121—122°, and the *sulphinic acid*, $NHAc\cdot C_6H_3Br\cdot SO_2H$, separates from boiling acetone as a crystalline powder, m. p. 138—140° (decomp.). *4-Bromo-1-aniline-2-sulphinic acid*, $NH_2\cdot C_6H_3Br\cdot SO_2H$, obtained by hydrolysing the acetyl derivative with 15% alcoholic potassium hydroxide solution, crystallises from pyridine in rosettes of needles, m. p. 160—163° (decomp.). The acid is insoluble in water, and the *sodium* salt, $C_6H_5O_2NSBrNa,2H_2O$, crystallises from alcohol. *Aniline-2-sulphinic acid*, $NH_2\cdot C_6H_4\cdot SO_2H$, cannot be obtained by reducing the bromo-acid, as the sulphinic group is reduced to the thiol group at the same time, but is formed when the somewhat unstable chloride of acetylaniline-2-sulphonic acid is reduced with zinc and then hydrolysed with alcoholic potassium hydroxide. It crystallises from 50% alcohol on the addition of ethyl acetate, and decomposes at 141°.

Bromophenylglycinesulphonyl chloride, $CO_2H \cdot CH_2 \cdot NH \cdot C_6H_3Br \cdot SO_2Cl$, prepared from the sodium hydrogen salt of the corresponding acid (Bradshaw, Abstr., 1906, i, 359), crystallises from benzene, decomposes at 158°, and on reduction yields 4-*bromo*-1-*glycylbenzene*-2-*sulphinic acid*, $CO_2H \cdot CH_2 \cdot NH \cdot C_6H_3Br \cdot SO_2H$; a better yield of the same acid is obtained by condensing 4-bromoaniline-2-sulphinic acid with formaldehyde and potassium cyanide. It is almost insoluble in water, and decomposes at 219—221°. 4-*Bromomethylaniline*-2-*sulphonic acid*, $NHMe \cdot C_6H_3Br \cdot SO_3H$, obtained by methylating the sodium salt of the amino-acid with methyl iodide at 100°, crystallises in long, slender needles, moderately soluble in water. The corresponding *chloride* forms a viscid, reddish-brown oil, and when reduced yields a small amount of the *sulphinic acid*, $NHMe \cdot C_6H_3Br \cdot SO_2H$, as a colourless, crystalline powder, m. p. 166°. Aniline-2-sulphonic acid is quantitatively methylated by methyl iodide at 100° (compare Smyth, *Ber.*, 1874, **7**, 1241).

o-Nitrobenzenesulphonyl chloride, prepared from the corresponding acid (Wohlfahrt, Abstr., 1903, i, 203), has m. p. 65°. It cannot be reduced by zinc dust or by sodium sulphide, but with the theoretical amount of stannous chloride and hydrochloric acid in alcoholic solution yields o-*nitrobenzenesulphinic acid*, $NO_2 \cdot C_6H_4 \cdot SO_2H$, which crystallises from concentrated solutions in glistening prisms, m. p. 134°. The *sodium* salt, $C_6H_4O_4NSNa$, crystallises from dilute alcohol in yellow plates, m. p. 123°. The *ethyl* ester, $C_8H_9O_4NS$, forms colourless, pointed plates, m. p. 58°. 1-*Chloro*-4-*nitrobenzenesulphinic acid*,

$$NO_2 \cdot C_6H_3Cl \cdot SO_2H,$$

obtained from the corresponding sulphonyl chloride, crystallises from ether in colourless, compact prisms, m. p. 140°. The chlorine atom cannot be replaced by the amino-group (P. Fischer, Abstr., 1892, 331); with alcoholic ammonia at 120° no reaction takes place, and at 150—155°, *p*-chloronitrobenzene is obtained.

By the action of phosphorus pentachloride on sodium 4-nitroacetylaniline-2-sulphonate, the acetylamino-group is replaced by chlorine.

J. J. S.

p-Nitrosomethylethylaniline: a New Intermediate Product for the Manufacture of Dyes. John C. Cain (*7th Inter. Congr. App. Chem.*, 1909, Sect. IV B, 95).—p-*Nitrosomethylethylaniline* is prepared by treating methylethylaniline hydrochloride with nitrous acid; it crystallises in green plates, m. p. 66—67°. The *hydrochloride* forms yellow needles. The new compound can be used in the production of a number of dyes, and as an instance the author has prepared the corresponding methylene-blue from it. This substance, to which the name *methylene-blue M.E.* is given, dyes tannin-mordanted cotton in shades much greener than those produced by ordinary methylene-blue.

R. V. S.

Preparation of p-Hydroxy-β-phenylethylamine and its Derivatives. Farbenfabriken vorm. Friedr Bayer & Co. (D.R.-P. 230043).—A description is given of the preparation of *p*-methoxy-β-phenylethylamine by methods already described (Rosenmund, Abstr., 1910, i, 106). The hydrochloride, which forms glistening leaflets, has m. p. 210° (Barger and Walpole, Trans., 1909, **95**, 1724, give 206°). *p*-Hydroxyphenylethylamine is obtained by the reduction of *p*-hydroxyphenylacetaldehyde-*p*-nitrophenylhydrazone (compare Langheld, Abstr., 1909, i, 557). F. M. G. M.

p-Aminostilbene. PAUL PFEIFFER and S. SERGIEWSKAJA (*Ber.*, 1911, **44**, 1107—1112).—By heating a mixture of *p*-nitrophenylacetic acid and benzaldehyde at 205°, Walther and Wetzlich obtained *p*-nitrostilbene-μ-carboxylic acid, but were unable to eliminate carbon dioxide from the acid. The author finds that this can be accomplished by heating the acid with piperidine at about 160°. The p-*nitrostilbene*, $CHPh\colon CH\cdot C_6H_4\cdot NO_2$, which is thus produced and which can also be prepared by heating a mixture of *p*-nitrophenylacetic acid, benzaldehyde, and piperidine at 150—160°, has m. p. 155°, crystallises in yellow needles, and forms a *dichloride*, m. p. 152°, and *dibromide*, m. p. 198°. It is reduced by stannous chloride and hydrogen chloride in glacial acetic acid, yielding p-*aminostilbene*, m. p. 151—152°, which is colourless, but becomes yellow in light. The base forms a *hydrochloride*, $C_{14}H_{13}N,HCl$, m. p. 245—250° (decomp.), an *acetyl* derivative, m. p. 225°, and a *benzoyl* derivative, m. p. 244—245°. C. S.

Preparation of Carbonic Acid Esters. CHEMISCHE FABRIK LADENBURG (D.R.-P. 230827).—An account of experiments which resulted in the isolation of carbonic acid esters of the general formulæ:

$$\underset{\text{(I.)}}{CR''(OR)_2} \qquad \underset{\text{(II.)}}{C(NHR)_2(OR)_2} \qquad \underset{\text{(III.)}}{NHR\cdot C(\colon NR)\cdot OR} \qquad \underset{\text{(IV.)}}{CSR'_2}$$

where R″ is a bivalent organic residue or sulphur, R′ a univalent organic radicle, and R an aryl or substituted aryl group.

Diphenyl thioncarbonate, $CS(OPh)_2$, m. p. 101°, was prepared by heating together lead oxide, phenol, and carbon disulphide.

*Triphenyl*iso*carbamide*, $NPh\colon C(OPh)\cdot NHPh$, colourless leaflets, m. p. 99°, was obtained by heating diphenylthiocarbamide with lead phenoxide.

Diphenyl allyliminocarbonate, $C_3H_5\cdot N\colon C(OPh)_2$, odourless and tasteless, greyish-white needles, m. p. 82°, was prepared in analogous manner with allylthiocarbimide, whilst phenylthiocarbimide yielded diphenyl phenyliminocarbonate, m. p. 134°.

p-*Dihydroxydiphenylthiocarbamide*, $CS(NH\cdot C_6H_4\cdot OH)_2$, colourless tablets which become purple on exposure, m. p. about 225° (decomp.), was prepared by boiling *p*-aminophenol with carbon disulphide in alcoholic solution; when heated at 120° with lead phenoxide it yielded the unstable, crystalline compound,

$$OH\cdot C_6H_4\cdot NH\cdot C(OPh)\colon N\cdot C_6H_4\cdot OH.$$

F. M. G. M.

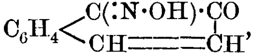
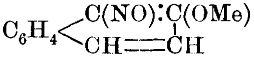
Preparation of *m*-Tolyl ortho-Oxalate. RÜTGERSWERKE-AKTIENGESELLSCHAFT and CURT GEUTSCH (D.R.-P. 229143).—When *m*-cresol (2 mols.) and anhydrous oxalic acid (1 mol.) are mixed together the mass solidifies, yielding m-*tolyl ortho-oxalate*,

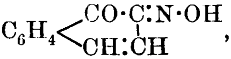
$$C_7H_7\cdot O\cdot C(OH)_2\cdot C(OH)_2\cdot O\cdot C_7H_7,$$

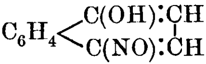
in which the powerful disinfectant properties of *m*-cresol are enhanced; at 51° it decomposes into its generators. F. M. G. M.

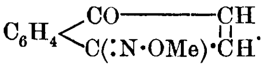
Chlorination of α-Naphthol. Hermann Kast (*Ber.*, 1911, **44**, 1337. Compare Reissert, this vol., i, 368).—By the action of sulphuryl chloride diluted with chloroform on α-naphthol dissolved in boiling chloroform, 4-chloro-α-naphthol, crystallising in long needles, m. p. 120—121°, is obtained in good yield. In the cold the yield is smaller, and a number of soluble by-products are formed. E. F. A.

Nitrosonaphthols or Naphthaquinoneoximes. Carl H. Sluiter (*Ber.*, 1911, **44**, 1327—1332. Compare Abstr., 1906, i, 255). —It is shown by conductivity measurements in mixtures of acetone and water, and by determinations of the molecular weight by the boiling point method in acetone and alcoholic solution that the three nitrosonaphthols have the following structure.

Brown nitrosonaphthol,  $C_6H_4{<}\begin{array}{l}C(\colon N\cdot OH)\cdot CO\\ CH{=\!=\!=\!=}CH\end{array}$, is an oxime, but the salts are nitroso-derivatives,  $C_6H_4{<}\begin{array}{l}C(NO)\colon C(OMe)\\ CH{=\!=}CH\end{array}$

Yellow nitrosonaphthol,  $C_6H_4{<}\begin{array}{l}CO\cdot C\colon N\cdot OH\\ CH\colon CH\end{array}$, is an oxime, and its salts are also derived from the same formula.

Colourless nitrosonaphthol,  $C_6H_4{<}\begin{array}{l}C(OH)\colon CH\\ C(NO)\colon CH\end{array}$, is a nitroso-compound, but the salts are derived from the oxime,

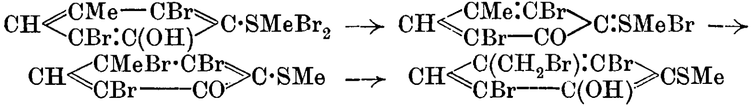


$$C_6H_4{<}\begin{array}{l}CO{-\!-\!-\!-}CH\\ C(\colon N\cdot OMe)\cdot CH\end{array}.$$

These conclusions are in agreement with the colour changes of the nitrosonaphthols and their salts. The solid, colourless nitrosonaphthol is dimolecular, but it is dissociated to green, single molecules in solution. E. F. A.

Action of Bromine and Chlorine on Phenols. Substitution Products. ψ-Bromides and ψ-Chlorides. XXV. A ψ-Bromide from *p*-Cresol containing Sulphur and its Transformations. Theodor Zincke, W. Frohneberg, and J. Kempf (*Annalen*, 1911, **381**, 28—51).—2 : 5-Dibromo-3-methylthiol-*p*-cresol ψ-bromide (this vol., i, 288) contains a reactive bromine atom which is readily replacable by hydroxy-, methoxy-, and ethoxy-groups. The view that the compound contains either of the groupings $\cdot SBr\colon CH_2$ or $S\cdot CH_2Br$ is shown to be untenable, since neither the perbromide derived from *o*-cresol nor the perbromide from the *p*-cresyl methyl ether (this vol., i, 198) yields a similar derivative. The constitution already suggested for the ψ-bromide is confirmed by its behaviour towards an acetic acid solution of nitric acid; the sulphur group is removed and replaced by a nitro-group, but all three bromine atoms are left intact. The resulting nitro-compound reacts as a ψ-bromide and yields a methoxy-derivative by the replacement of one bromine by methoxyl; this derivative is identical with the product prepared by the action of nitric acid on the methoxy-compound derived from the original ψ-bromide, namely, $NO_2 \cdot C_6HBr_2(NO_2) \cdot CH_2 \cdot OMe$.

It is suggested that the ψ-bromide is formed from the perbromide by the following series of reactions:



$$CH\begin{array}{l}\diagup CMe—CBr \diagdown \\ \diagdown CBr{:}C(OH) \diagup\end{array}C \cdot SMeBr_2 \longrightarrow CH\begin{array}{l}\diagup CMe{:}CBr \diagdown \\ \diagdown CBr—CO \diagup\end{array}C{:}SMeBr \longrightarrow$$

$$CH\begin{array}{l}\diagup CMeBr \cdot CBr \diagdown \\ \diagdown CBr——CO \diagup\end{array}C \cdot SMe \longrightarrow CH\begin{array}{l}\diagup C(CH_2Br){:}CBr \diagdown \\ \diagdown CBr——C(OH) \diagup\end{array}CSMe$$

and that this type of reaction is characteristic of *o*-alkylthiolphenols.

The simplest method of obtaining the ψ-bromide is by the action of potassium acetate on the perbromide in the presence of glacial acetic acid. When prepared by shaking the perbromide with water and ether, it is advisable to use a large volume of water, as otherwise much sulphoxide is formed. When treated with normal sodium hydroxide solution, the ψ-bromide yields a dark green sodium salt, which yields a sparingly soluble yellow product when acidified. With pyridine the ψ-bromide yields a *pyridinium* salt, which is decomposed by water, and when reduced the bromide yields 2 : 5-dibromo-3-methylthiol-*p*-cresol.

The *acetyl* derivative of the ψ-bromide, $OAc \cdot C_6HBr_2(SMe) \cdot CH_2Br$, crystallises from methyl alcohol in colourless cubes, m. p. 136°.

2 : 5-*Dibromo*-4-*hydroxy*-3-*methylthiolbenzyl alcohol*,

$$OH \cdot C_6HBr_2(SMe) \cdot CH_2 \cdot OH,$$

prepared by the action of water on an acetone solution of the ψ-bromide, crystallises in clear yellow, glistening plates, m. p. 125—126°, and is transformed into the ψ-bromide by a glacial acetic acid solution of hydrogen bromide. The corresponding *methyl ether*, $OH \cdot C_6HBr_2(SMe) \cdot CH_2 \cdot OMe$, forms small, colourless needles, m. p. 81—82°, and with nitric acid yields 2 : 5-*dibromo*-3-*nitro*-4-*hydroxybenzyl methyl ether*, $OH \cdot C_6HBr_2(NO_2) \cdot CH_2 \cdot OMe$, which crystallises from light petroleum in long, yellow needles, m. p. 120—121°. 2 : 5-*Dibromo*-4-*hydroxy*-3-*methylthiolbenzyl acetate*,

$$OH \cdot C_6HBr_2(SMe) \cdot CH_2 \cdot OAc,$$

crystallises in stout, colourless needles, m. p. 137°. It does not behave as a phenol, and probably has a quinonoid structure; with acetic anhydride it yields the *diacetyl* derivative,

$$OAc \cdot C_6HBr_2(SMe) \cdot CH_2 \cdot OAc,$$

in the form of small, colourless needles, m. p. 131°.

2 : 5-*Dibromo*-3-*nitro*-p-*cresol* ψ-*bromide*, $OH \cdot C_6HBr_2(NO_2) \cdot CH_2Br$, crystallises from light petroleum in brilliant yellow needles, m. p. 118—119°.

The black quinone (this vol., i, 288) obtained by the action of solid sodium acetate on an ethereal solution of 2 : 5-dibromo-3-methylthiol-*p*-cresol ψ-bromide is regarded as 2 : 5 : 2′ : 5′-*tetrabromo*-3 : 3′-*dimethylthiolstilbene* - p - *quinone*, $O{:}C_6HBr_2(SMe){:}CH \cdot CH{:}C_6HBr_2(SMe){:}O$ (compare Zincke and Fries, Abstr., 1903, i, 178). It forms a deep black powder, m. p. 240° (decomp.), and is practically insoluble in the usual solvents. With acetic acid, acetic anhydride, and a little sulphuric acid the quinone yields 2 : 5 : 2′ : 5′-*tetrabromo*-4 : 4′-*diacetoxy*-3 : 3′-*dimethylthiolhydrobenzoin diacetate*,

$$C_2H_2(OAc)_2\cdot[C_6HBr_2\cdot(SMe)OAc]_2,$$

which forms stout, colourless crystals, m. p. 236°. *Tetrabromodihydroxydimethylthiolhydrobenzoin dimethyl ether*,

$$C_2H_2(OMe)_2[C_6HBr_2(SMe)\cdot OH]_2,$$

obtained by warming the quinone with methyl alcohol and 2*N*-sodium hydroxide solution, forms glistening, colourless, rhombic crystals, m. p. 182°, and yields a *diacetyl* derivative, $C_{22}H_{22}O_6S_2Br_4$, m. p. 220—222° (decomp.). When reduced with stannous chloride and a glacial acetic acid solution of hydrogen chloride, the quinone yields 2 : 5 : 2′ : 5′-*tetrabromo*-4 : 4′-*dihydroxy*-3 : 3′-*dimethylthiolstilbene*, $C_2H_2[C_6HBr_2(SMe)\cdot OH]_2$ as colourless, glistening plates, m. p. 245°, which is readily oxidised to the quinone. The *diacetyl* derivative, $C_{20}H_{16}O_4S_2Br_4$, forms colourless needles, m. p. above 280°. When suspended in chloroform and treated with hydrogen bromide, the quinone yields the additive compound, *tetrabromodihydroxydimethylthiolstilbene dibromide*, $C_{16}H_{12}O_2S_2Br_6$, in the form of small, colourless needles, m. p. 205° (decomp.), which can be readily transformed back into the quinone.

In the preparation of the quinone from the ψ-bromide an appreciable amount of 2 : 5 : 2′ : 5′-*tetrabromo*-4 : 4′-*dihydroxy*-3 : 3′-*dimethylthioldibenzyl*, $C_2H_4[C_6HBr_2(SMe)\cdot OH]_2$, is obtained. It crystallises from glacial acetic acid in thin, glistening plates and needles, m. p. 202°, and yields a *diacetyl* derivative, $C_{20}H_{18}O_4S_2Br_4$, in the form of colourless plates, m. p. 219°. With nitric acid, the dibenzyl derivative yields a *nitro*-compound, $C_{14}H_8O_6N_2Br_4$, which crystallises from tetrachloroethane in small, yellow prisms, m. p. above 260° (decomp.). The dibenzyl derivative also yields a *perbromide*,

$$C_2H_4[C_6HBr_2(SMeBr_2)_2\cdot OH]_2,$$

which decomposes at about 150°. This perbromide reacts with 0·5*N*-sodium hydroxide solution in the presence of chloroform, yielding a black quinone very similar to the one described above.

In the preparation of the quinone and the dibenzyl derivative from the ψ-bromide, it is probable that an unstable methylenequinone is first formed, and that this is partly oxidised to the quinone and partly reduced to the dibenzyl-derivative. J. J. S.

Preparation of Nitrophenyl Mercaptans. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 228868. Compare Abstr., 1908, i, 631).—Satisfactory yields of nitrophenyl mercaptans are readily obtained when an alcoholic alkaline solution (8 to 10 parts NaOH) of the corresponding dinitrodiaryl disulphide (1 part) is heated with half an equivalent of sodium hydrosulphide on a water-bath.

With *pp′*-dinitrophenyl disulphide, glistening, golden-yellow leaflets of *sodium* p-*nitrothiophenoxide* separate from the reaction mixture.

F. M. G. M.

Phenol-*m*-sulphonic Acid and its Isolation. Its Non-formation from Phenol and Sulphuric Acid. JULIUS OBERMILLER (*Annalen*, 1911, 381, 114—122).—Phenol-*m*-sulphonic acid is best prepared by diazotising *m*-aminobenzenesulphonic acid and boiling with water containing 2% sulphuric acid (compare Berndsen, this Journ., 1875, 1028; Kreis, Abstr., 1896, i, 48). It is not readily isolated as its sodium salt, as this is readily soluble, but the *magnesium* salt, $(OH\cdot C_6H_4\cdot SO_3)_2Mg,6H_2O$, crystallises in long, brittle plates. Its saturated aqueous solution has D 1·190 at 15—20°.

The barium, strontium, calcium, lead, copper, aluminium, and potassium salts do not crystallise at all well. Their solutions are neutral to Congo-red, but slightly acid to litmus. The *sodium* salt crystallises in broad plates, and the *zinc* salt in thin, flat, pointed prisms.

The following salts of the type $MO\cdot C_6H_4\cdot SO_3M$ are stable:—sodium, potassium, calcium, strontium, and barium, but they do not crystallise. The corresponding magnesium, zinc, copper, and aluminium salt are hydrolysed by hot water, yielding precipitates of the hydroxides. A basic *lead* salt can be used for the isolation of the acid, and is best obtained by treating the crude sodium salt with lead acetate (0·5 mol.) and pure lead hydroxide (1·5 mol. obtained from lead acetate) in the form of a cream and much water. This basic salt yields the ordinary lead salt on the addition of sulphuric acid, and from this the other salts can be prepared.

A method has been worked out for isolating the meta-acid from a mixture of the ortho-, meta-, and para-acids. The para-acid can be removed in the form of its characteristic strontium salt, the ortho- and 2 : 4-acids can be removed by conversion into basic barium salts and addition of alcohol, and the meta-acid isolated from the final mother liquor as its characteristic magnesium salt. By means of this method it is shown that no trace of the meta-acid is formed by the action of sulphuric acid on phenol either at 15—20° or at 90—100° when 1·5 gram-mols. of sulphuric acid are used.

The sulphonic acid group of the meta-acid is not removed by the action of bromine (bromide and bromate mixture). J. J. S.

Action of Magnesium *p*-(or *o*-)Tolyl Bromide on *sym.*-Dibromomethyl Ether. Preparation and Properties of Xylyl Ether. N. PAWLOWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 214—218).—p-*Xylyl ether*, $(C_6H_4Me\cdot CH_2)_2O$, prepared by the interaction of *p*-bromotoluene, magnesium, and *s*-dibromomethyl ether, crystallises in white, shining scales, greasy to the touch, m. p. 61—62°, b. p. 310—311°, and has the normal molecular weight in freezing benzene or boiling ether.

o-*Xylyl ether*, $(C_6H_4Me\cdot CH_2)_2O$, prepared in a similar manner to its isomeride, is a colourless, oily liquid, b. p. 201—203°/26 mm., $n_D^{19\cdot 8}$ 1·55784, and has the normal molecular weight in freezing benzene or boiling ether.

When treated with hydrobromic acid, *p*- and *o*-xylyl ethers yield *p*- and *o*-xylyl bromides respectively.

p-*Xylyl iodide* C_8H_9I, prepared by the action of hydriodic acid on *p*-xylyl ether, forms long, transparent needles, m. p. 45·5—46·5°, and o-*xylyl iodide*, similarly prepared, long, transparent needles, m. p. 34°.

T. H. P.

Generalisation of the Formation of Mixed Organomagnesium Compounds with Oxygenated Compounds.

Bernardo Oddo (*Gazzetta*, 1911, 41, i, 273—294).—It was shown by Tschelinzeff (Abstr., 1904, i, 559) that tertiary cyclic amines, especially dimethylaniline, can replace ether in the preparation of Grignard's compounds, also (Abstr., 1905, i, 40) that the ethereal oxygen and the tertiary nitrogen act catalytically, it being possible to prepare mixed organo-magnesium compounds in presence of neutral solvents, such as benzene and toluene, containing a trace of ether or dimethylaniline.

The aim of the present work was to ascertain whether, by operating in presence of an indifferent solvent absolutely free from all trace of ether or tertiary base, it is possible to generalise the process of formation of organo-magnesium compounds. For this purpose a compound containing a carbonyl oxygen atom was employed, since the researches of von Baeyer and Villiger have shown that such oxygen appears capable of giving salts, that is, of displaying two supplementary valencies. It is found that the reaction proceeds according to the following equations: $\mathrm{R{\cdot}CO{\cdot}R' + CH_3I = CRR'{:}OIMe}$; $\mathrm{CRR'{:}OIMe + Mg = CRR'{:}OI{\cdot}MgMe}$; $\mathrm{CRR'{:}OI{\cdot}MgMe + R{\cdot}CO{\cdot}R' = CRR'Me{\cdot}O{\cdot}MgI + R{\cdot}CO{\cdot}R'}$; $\mathrm{CRR\,Me{\cdot}O{\cdot}MgI + H_2O = CRR'Me{\cdot}OH + MgI{\cdot}OH}$. The reaction takes place, not only with aldehydes and ketones, but also with esters, with compounds, such as β-naphthol, which exhibit a tendency to the formation of a carbonyl oxygen, and with compounds in which oxygen is doubly linked to an element other than carbon, such as nitro-derivatives; in all instances, the same compounds are obtained as are given by the action of Grignard's reagent. Under the conditions employed, magnesium exerts no action on an alkyl iodide alone. The benzene used as solvent was absolutely free from thiophen.

[With G. del Rosso.]—Benzaldehyde, magnesium, and ethyl iodide give (1) phenylethylcarbinol; (2) α-phenyl-Δ^α-propylene,

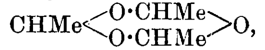
$$\mathrm{CHPh{:}CHMe},$$

formed by the loss of water from phenylethylcarbinol, and (3) the *ether*, $\mathrm{(CHPhEt)_2O}$, which is a dense liquid, b. p. 222°/30 mm., and crystallising in white needles, m. p. 82°.

Benzaldehyde, magnesium, and propyl iodide yield: (1) phenylpropylcarbinol (compare Klages, Abstr., 1904, i, 567); (2) *phenylpropylcarbinyl ether*, $\mathrm{(CHPhPr^\alpha)_2O}$, which forms acicular crystals, m. p. 131°, b. p. 208—210°/30 mm., has the normal molecular weight in freezing benzene, and can also be obtained by boiling phenylpropylcarbinol with a crystal of stannous chloride; (3) a small proportion of butenylbenzene.

p-Tolualdehyde, magnesium, and ethyl iodide give: (1) *p*-tolylethylcarbinol (compare Klages, Abstr., 1904, i, 27); (2) a *dimeride* of p-*tolualdehyde*, m. p. 130°, and (3) *p*-xylyl alcohol.

With paraldehyde, magnesium, and ethyl iodide, the reaction proceeds exceptionally readily, the products being: (1) β-hydroxybutane and (2) Δ^α- and Δ^β-butylenes. The facility with which the action takes place depends on the presence of the molecule:



$$\mathrm{CHMe}<\begin{matrix}\mathrm{O{\cdot}CHMe}\\ \mathrm{O{\cdot}CHMe}\end{matrix}>\mathrm{O},$$

the symmetrical ring organo-magnesium compound formed being decomposed by the heat developed during its formation into simple molecules of the type $\mathrm{CHMeR{\cdot}O{\cdot}MgX}$.

Acetone, magnesium, and ethyl iodide yield dimethylethylcarbinol. Treatment of the products of the reaction with acetyl chloride gave, not the acetyl derivative of the alcohol, but an unstable *liquid*, b. p. 54°/30 mm., probably of the structure $\mathrm{CMe_2Et{\cdot}OI}$.

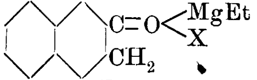
Acetone, magnesium, and methyl iodide give trimethylcarbinol.

Methyl benzoate, magnesium, and ethyl iodide yield: (1) phenyldiethylcarbinol, thus:

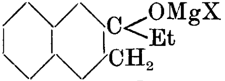
$$\mathrm{2R{\cdot}MgX + R'{\cdot}CO_2Me = OMe{\cdot}MgX + CR_2R'{\cdot}O{\cdot}MgX},$$

the last product giving the tertiary alcohol on treatment with water; (2) γ-phenyl-Δ^β-amylene (compare Klages, Abstr., 1904, i, 27).

In the reaction between β-naphthol, magnesium, and ethyl iodide, the naphthol seems to react in its ketonic form, giving the compound (I), which is then either transformed immediately into (II),



(I.)

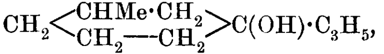


(II.)

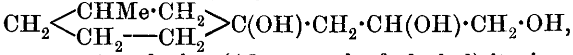
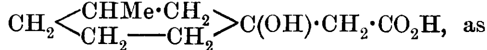
or, being in presence of naphthol with a hydroxylic function, yields ethane and the iodomagnesium derivative of β-naphthol. Nitrobenzene, magnesium, and ethyl iodide yield phenylethylamine and azobenzene. T. H. P.

Action of Zinc on a Mixture of 1-Methyl*cyclo*hexan-3-one and Allyl Iodide. MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 345—349).

—1-*Methyl*-3-*allyl*cyclo*hexen*-3-*ol*,



$$\mathrm{CH_2}<\begin{matrix}\mathrm{CHMe{\cdot}CH_2}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}>\mathrm{C(OH){\cdot}C_3H_5},$$

prepared by the action of zinc on a mixture of 1-methyl*cyclo*hexan-3-one and allyl iodide in ethereal solution, is a mobile liquid, b. p. 206—209°, D_0^0 0·92244, D_{20}^{20} 0·91343. When oxidised with permanganate (1 atom of oxygen per mol. of alcohol) it yields the white, crystalline, trihydric *alcohol*,  $\mathrm{CH_2}<\begin{matrix}\mathrm{CHMe{\cdot}CH_2}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}>\mathrm{C(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OH}$, whilst with 5% permanganate solution (40 per mol. of alcohol) it gives the *acid*,  $\mathrm{CH_2}<\begin{matrix}\mathrm{CHMe{\cdot}CH_2}\\ \mathrm{CH_2{-}{-}CH_2}\end{matrix}>\mathrm{C(OH){\cdot}CH_2{\cdot}CO_2H}$, as a viscous, dark yellow liquid; the *calcium* salt was prepared. T. H. P.

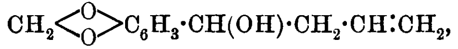
Action of Magnesium on a Mixture of Allyl Bromide and Benzaldehyde. Synthesis of Phenylallylcarbinol. D. KLIMENKO (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 212—213).

—The action of magnesium on allyl bromide and benzaldehyde (compare Javorsky, Abstr., 1908, i, 753) yields phenylallylcarbinol, b. p. 126—127°/

24 mm., $D_4^{25\cdot6}$ 1·0161, n_D 1·53251 (compare Fournier, Abstr., 1894, i, 19). When oxidised with permanganate (0·5—4%) it yields the quantitative proportion of benzoic acid and traces of a neutral syrupy product (? glycerol). T. H. P.

Action of Magnesium on a Mixture of Allyl Bromide and Piperonal.

N. D. KORJUKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 208—211).—*δ-Methylenedioxyphenyl-Δ^α-buten-δ-ol*,



$$CH_2\langle^{O}_{O}\rangle C_6H_3\cdot CH(OH)\cdot CH_2\cdot CH:CH_2,$$

obtained by the interaction of magnesium, allyl bromide, and piperonal, is a viscous liquid, b. p. 166—167°/23·5 mm., $D_4^{23\cdot6}$ 1·2016, $n_D^{23\cdot6}$ 1·55489, having the normal molecular weight in freezing benzene and in boiling ether.

On oxidation with permanganate it yields piperonylic acid (compare Jobst and Hesse, Abstr., 1880, 325). T. H. P.

Preparation of *o*-Chlorobenzotrichloride.

FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 229873).—When sodium *o*-chlorobenzylsulphonate is treated with phosphorus pentachloride, it yields *o-chlorobenzylsulphonyl chloride*, colourless crystals, m. p. 56—58°; this, on treatment with chlorine gas at a temperature of 150—180° until the evolution of hydrogen chloride ceases and subsequent distillation in a vacuum, yields *o-chlorobenzotrichloride*, b. p. 115—118°/5·6 mm. F. M. G. M.

The Influence of the Composition and Structure of Organic Acids on the Stability of their Carboxyl Group.

PAUL N. RAIKOFF and P. TISCHKOFF (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 91—96. Compare Cazeneuve, Abstr., 1892, 1332; Raikoff and Tischkoff, Abstr., 1906, i, 83).—A flask containing 40 c.c. of phosphoric acid, D 1·78, is heated to 200°, cooled to 50°, and 1/30 gram-equivalent of the acid to be studied is introduced. A reflux condenser is then attached, connected with a graduated tube provided with two taps and dipping into mercury. The flask is heated in an oil-bath, and the volume of gas is read off at temperatures rising by 10° from 100° to 190°, then at 195° and 200°. The total volume of gas is finally measured after expulsion by mercury. The proportions of carbon dioxide and monoxide are determined by analysis. A table in the paper contains the results from sixty-five organic acids.

The stability of the carboxyl group in benzoic acid is generally reduced by substitution in the ring. Substitution in one or both meta-positions is almost without influence on the stability, whilst ortho- and para-substituents exert an influence dependent on the nature of the radicle. The very active groups include OH, NH_2, OMe, COMe; the moderately active groups I, IO, Me, NO_2, and the inactive H, Cl, Br, CN, CO_2H, Ph, $C_6H_4\cdot CO_2H$, $C(C_6H_4\cdot OH)_2$, Bz, $CO\cdot C_{10}H_7$. The effect of two groups is shown by a comparison of seven substituted salicylic acids. C. H D.

Alkylation of Aromatic Amino-acids. V. 3-Amino-2:4-dimethylbenzoic Acid.

HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1911, **45**, 436—445).—It has been shown in an earlier paper (Abstr., 1910, i, 666) that 2-aminomesitylenic acid on alkylation yields the diethylamino-derivative (30 parts), the ethylamino-derivative (10 parts), and the ester (1 part), whereas 4-aminomesitylenic acid gives the ester only. In view of these results, a study has been made of the behaviour of 3-amino-2 : 4-dimethylbenzoic acid, which, like 4-aminomesitylenic acid, has the amino-group situated between two methyl groups, and it has been found that this acid also yields the ester as the chief product of alkylation.

3-*Nitro*-5-*amino*-2 : 4-*dimethylbenzoic acid*, m. p. 251°, obtained by reducing 3 : 5-dinitro-2 : 4-dimethylbenzoic acid (Frey and Horowitz, Abstr., 1891, 566) with ammonium sulphide, crystallises in straw-coloured prisms; its *hydrochloride* has m. p. 250° (decomp.), and its *acetyl* derivative, m. p. 247°, forms colourless needles. When this acid is diazotised and treated with alcohol, it is converted into 3-nitro-2 : 4-dimethylbenzoic acid, m. p. 179° (not 135° as stated by Clausius, Abstr., 1890, 980), which forms light brown prisms; its *amide*, m. p. 138°, crystallises in plates. 3-*Amino*-2 : 4-*dimethylbenzoic acid*, m. p. 146°, obtained by reducing the nitro-acid with ferrous hydroxide, forms needles or prisms, and, when distilled with calcium oxide, yields *vic.*-*m*-xylidine. The aqueous and alcoholic solutions of the acid have a green fluorescence. The *acetyl* derivative, m. p. 243° (decomp.), crystallises in needles. 3-*Iodo*-2 : 4-*dimethylbenzoic acid*, m. p. 167°, obtained by the action of potassium iodide on the diazotisation product of 3-amino-2 : 4-dimethylbenzoic acid, forms needle-like prisms. When 3-amino-2 : 4-dimethylbenzoic acid is heated with ethyl iodide, ethyl alcohol, and potassium hydroxide, the *ethyl* ester is obtained as an oil. On treating the acid with methyl iodide under similar conditions, the *methyl* ester is produced, together with a small quantity of 3-methylamino-2 : 4-dimethylbenzoic acid.

When 2 : 4 : 6-tribromo-3-aminobenzoic acid is heated with methyl iodide in presence of potassium hydroxide and methyl alcohol, the *methyl* ester, m. p. 93—94°, is obtained as the only product of the reaction and forms colourless needles.

It has been shown (this vol., i, 50) that the acid formerly described as 4-amino-*m*-toluic acid (Abstr., 1910, i, 666) is really 2-amino-*m*-toluic acid. This is now confirmed by the observation that when the acid is distilled with calcium oxide it yields *o*-toluidine. E. G.

Turmeric Oil. IV. Synthesis of α-*p*-Tolyl-α-methylbutyric Acid.

HANS RUPE and J. BÜRGIN (*Ber.*, 1911, **44**, 1218—1225. Compare this vol., i, 69, 293).—α-*p*-Tolyl-α-methylbutyric acid, the second of the three acids (*loc. cit.*), one of which the authors believe to be identical with curcumic acid, has now been synthesised, but, like γ-*p*-tolylvaleric acid, it is not identical with, although very similar to, curcumic acid.

In the earlier attempts to synthesise α-*p*-tolyl-α-methylbutyric acid, the authors used p-*tolylmethylethylcarbinol*, $C_{11}H_{16}O$, b. p. 108·5—109°/

10 mm., obtained in the usual way from magnesium *p*-tolyl bromide and methyl ethyl ketone, but abandoned the process owing to the difficulty of converting the alcohol into its chloride and making the latter react with magnesium.

Subsequently α-*p*-tolyl-α-methylbutyric acid, $C_{12}H_{16}O_2$, was obtained from ethyl α-bromo-α-methylbutyrate, toluene, and freshly distilled aluminium bromide by Wallach's process (Abstr., 1900, i, 229). It has the same b. p., 171°/13 mm., as curcumic acid, but could not be obtained in the solid state; moreover, the calcium salts of the two acids differ in solubility, and the synthetic acid, by oxidation with 4% potassium permanganate and sodium carbonate at 0°, yields products different from those obtained from the oxidation of curcumic acid.

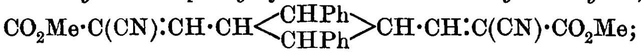
p-Tolylmethylethylcarbinol is converted by boiling acetic anhydride into *β-p-tolyl-Δ^{β}-butylene*, $C_6H_4Me\cdot CMe{:}CHMe$, b. p. 93·5—94°/10 mm., the constitution of which is proved by the production of *p*-tolyl methyl ketone by oxidation by alkaline 2% potassium permanganate. A bimolecular *polymeride*, $(C_{11}H_{14})_2$, b. p. 201—202°/9 mm., is obtained when the carbinol is dehydrated by 95% formic acid. C. S.

Action of Light on Esters of α-Cyanocinnamylideneacetic Acid.

MARIE REIMER (*Amer. Chem. J.*, 1911, **45**, 417—436).—During the course of some work on the behaviour of certain esters of cinnamylideneacetic and cinnamylidenemalonic acids towards Grignard's reagent, it was observed that the esters were decomposed by light. The nature of these changes is being investigated, and an account is now given of the action of light on esters of α-cyanocinnamylideneacetic acid.

Riiber (Abstr., 1902, i, 617) has shown that cinnamylidenemalonic acid is converted by the action of sunlight into diphenyltetramethylenebismethylenemalonic acid, and Macleod (Abstr., 1910, i, 846) has found that a similar change takes place in the case of α-methylcinnamylideneacetic acid.

Methyl α-cyanocinnamylideneacetate, m. p. 145°, can be readily prepared by the condensation of methyl cyanoacetate with cinnamaldehyde in presence of sodium methoxide, and forms yellow crystals. When exposed to sunlight it rapidly changes to a white substance, which separates from a mixture of acetone and light petroleum in the form of transparent crystals, and on oxidation with potassium permanganate yields truxillic, benzoic, and oxalic acids. The compound is therefore *methyl* 1 : 3-*diphenyl*cyclo*butane* 2 : 4-*di-α-cyanoacrylate*,

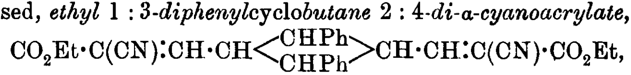


$$CO_2Me\cdot C(CN){:}CH\cdot CH<\begin{matrix}CHPh\\CHPh\end{matrix}>CH\cdot CH{:}C(CN)\cdot CO_2Me;$$

it has m. p. 172·5°, is but little affected by bromine, and when distilled under 20 mm. pressure is re-converted into methy α-cyanocinnamylideneacetate.

Ethyl α-cyanocinnamylideneacetate (Bechert, Abstr., 1894, i, 488) behaves quite differently from the methyl ester, and is converted by light into a *compound*, m. p. 166°, which probably has the structure $CO_2Et\cdot C(CN){:}CH\cdot CH_2\cdot CHPh\cdot C(CHPh)\cdot CH{:}C(CN)\cdot CO_2Et$; it forms white crystals and, when distilled under reduced pressure, yields a mixture of stable and unstable ethyl α-cyanocinnamylideneacetates.

On oxidation with potassium permanganate, benzaldehyde and benzoic acid are produced together with traces of an *acid*, $C_{11}H_{10}O_5$, m. p. about 179°. When oxidised with potassium dichromate, benzoic acid is formed together with an *acid*, $C_{18}H_{16}O_4$, m. p. 185°, which forms white, slender needles, and gives a *methyl* ester, m. p. 132°, crystallising in transparent rhombic crystals. When the compound (m. p. 166°) is treated at 0° with a solution of bromine in chloroform, a *dibromide*, m. p. 125—127°, is obtained, which forms white, lustrous crystals. In one experiment in which much less than the calculated quantity of bromine was used, *ethyl* 1 : 3-*diphenyl*cyclo*butane* 2 : 4-*di*-*a*-*cyanoacrylate*,



$$CO_2Et\cdot C(CN){:}CH\cdot CH\Big<\begin{matrix}CHPh\\CHPh\end{matrix}\Big>CH\cdot CH{:}C(CN)\cdot CO_2Et,$$

m. p. 128°, was produced, which forms colourless crystals and, on oxidation, behaves in the same way as the corresponding methyl ester.

The difference in the behaviour of methyl and ethyl α-cyanocinnamylideneacetates on exposure to light is probably due to a difference in their configuration, the former being an unstable, and the latter a stable form. An unstable modification of ethyl α-cyanocinnamylideneacetate has been obtained from the methyl ester by the action of potassium ethoxide on its solution in absolute alcohol (compare Pfannl, Abstr., 1910, i, 480); it has the same m. p. (113°) as the stable form, but is much less soluble in alcohol than the latter. It is affected by light in the same way as the methyl ester from which it is produced, being rapidly converted into ethyl diphenyl*cyclo*butanedicyanoacrylate. E. G.

Stilbene-*o*-carboxylic Acids. PAUL PFEIFFER and K. MATTON (*Ber.*, 1911, **44**, 1113—1124).—The authors have prepared derivatives of stilbene-*o*-carboxylic acids, partly to extend the knowledge of such substances, partly for stereochemical examination. A mixture of phthalonic acid, a little piperidine, and 2 : 4-dinitrotoluene, *o*-nitro-*p*-toluonitrile, or *p*-nitro-*o*-toluonitrile reacts at 150° to form 2′ : 4′-*dinitrostilbene*-2-*carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_3(NO_2)_2$, m. p. 176—177°, 2′-*nitro*-4′-*cyanostilbene*-2-*carboxylic acid*, m. p. 227°, and 4′-*nitro*-2′-*cyanostilbene*-2-*carboxylic acid*, m. p. 182°, respectively (compare Thiele and Escales, Abstr., 1901, i, 689; Ullmann and Gschwind, Abstr., 1908, i, 622). In the condensation, the elimination of carbon dioxide from the extra-nuclear carboxylic group of the phthalonic acid is proved by the fact that 2-nitro-4-cyanostilbene is obtained by heating *o*-nitro-*p*-toluonitrile and benzoylformic acid with a little piperidine at 120—140°.

The behaviour of the two preceding nitrocyanostilbenecarboxylic acids on esterification is interesting. When heated with methyl-alcoholic hydrogen chloride, 2′-nitro-4′-cyanostilbene-2-carboxylic acid yields *methyl* 2′-*nitrostilbene*-2 : 4′-*dicarboxylate*,

$$CO_2Me\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_3(NO_2)\cdot CO_2Me,$$

m. p. 138°, which is hydrolysed by a mixture of sulphuric and acetic acids and water to the corresponding *acid*, $C_{16}H_{11}O_6N$, m. p. 257°. 4′-Nitro-2′-cyanostilbene-2-carboxylic acid, however, is converted by methyl-alcoholic hydrogen chloride only into *ethyl* 4′-*nitro*-2′-*cyano*-

stilbene-2-carboxylate, m. p. 133°; when the acid is kept in concentrated sulphuric acid for a day and the product is boiled with aqueous sodium carbonate, *4′-nitrostilbene-2 : 2′-dicarboxylic acid*, m. p. 248°, is obtained. Similarly, 2-nitro-4-cyanostilbene (Ullmann and Gschwind, *loc. cit.*) is converted by methyl-alcoholic hydrogen chloride into *methyl 2-nitrostilbene-4-carboxylate*, m. p. 122° (the corresponding *ethyl* ester has m. p. 124—125°), whilst 4-nitro-2-cyanostilbene is unchanged under the same conditions. Also it is known that *o*-nitro-*p*-toluonitrile is hydrolysed by methyl-alcoholic hydrogen chloride, whilst *p*-nitro-*o*-toluonitrile is unchanged. From these examples it is tolerably certain that the hydrolysis of the cyano-group, when it does take place, is preceded by the formation of an imino-ether, since Pinner has shown that imino-ethers are not formed under normal conditions by nitriles which contain a methyl group in the ortho-position.

4-Nitrostilbene-2-carboxylic acid, $CHPh:CH\cdot C_6H_3(NO_2)\cdot CO_2H$, m. p. 206°, is produced by heating benzaldehyde and methyl *p*-nitro-*o*-toluate with a little piperidine at 200°. C. S.

The Reduction of Unsaturated Compounds.

ALADAR SKITA and CARL PAAL (D.R.-P. 230724. Compare Abstr., 1905, i, 397, 533; 1907, ii, 559; 1908, i, 599).—Much work has previously been recorded on the reduction of unsaturated compounds with hydrogen in the presence of palladium and a colloid; the employment of gum arabic and palladous chloride is now described, and the following compounds were obtained.

*Ethyl 1-methyl*cyclo*hexan-3-one-6-carboxylate*, an oil, b. p. 127—129°/15 mm., by the reduction of *ethyl 1-methyl*cyclo*hexen-3-one-6-carboxylate*, b. p. 142°/15 mm. 2 : 2 : *6-Trimethylhexahydrobenzaldehyde*, b. p. 58—60°/10 mm., from *cyclo*citral; and *dihydro*iso*phorol*, b. p. 172°, from phorone. F. M. G. M.

Basic Bismuth Salicylate.

MAX NYMAN and RICHARD BJÖRKSTÉN (*Pharm. Zentr.-h.*, 1911, **52**, 423—428).—Apart from the normal salt, $Bi(C_7H_5CO_3)_3,4H_2O$, prepared by Cousse (*Compt. rend.*, 1894, **119**, 1220; compare Abstr., 1906, i, 665), two basic salts are supposed to exist, namely, $OH\cdot C_6H_4\cdot CO\cdot O\cdot BiO$ (*loc. cit.*) and $(OH\cdot C_6H_4\cdot CO\cdot O)_4Bi_2O$. The former is that recognised in most pharmacopeias, but it cannot be prepared, since in contact with water it is dissociated. The authors have tried the various methods described for the preparation of basic bismuth salicylate, and find that the process of Fischer and Grützner (Abstr., 1894, i, 416) gives the best results for pharmaceutical purposes. The salt thus prepared furnishes 0·641—0·648 gram of bismuth sesquioxide per gram of salt, and is free from nitric acid, alkalis, and extraneous organic matter.

T. A. H.

Preparation of Zinc Hydrogen Borodisalicylate.

A. FOELSING (D.R.-P. 230725).—The preparation of borodisalicylic acid, with its lead and silver salts, has previously been recorded.

Zinc dihydrogen borodisalicylate was obtained by mixing the dry constituents according to the equation :

$$4HO\cdot C_6H_4\cdot CO_2H + 2H_3BO_3 + ZnCO_3 = Zn[O\cdot CO\cdot C_6H_4\cdot O\cdot B(OH)\cdot O\cdot C_6H_4\cdot CO_2H]_2 + 5H_2O + CO_2,$$

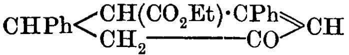
adding hot water and allowing the product to crystallise ; it is a colourless, crystalline powder (m. p. 100—110°), with powerful astringent and antiseptic properties. F. M. G. M.

Preparation of Nitrothioxanthones and their Derivatives.

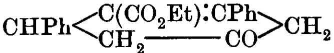
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 228756).—Mayer (Abstr., 1909, i, 823) stated that nitrodiphenyl-sulphide-carboxylic [nitrophenylthiolbenzoic] acids do not yield nitrothioxanthones when heated with sulphuric acid ; it is now found that if sulphuric acid containing sulphur trioxide is employed, a satisfactory yield of the corresponding nitrothioxanthone is obtained. The preparation of 4-nitrothioxanthone (m. p. 216—218°) from 2-*o*-nitrophenylthiolbenzoic acid is described, whilst 2-*o*-nitro-*p*-sulphothiolsulphonyl- and 2-*p*-nitro-6-sulphophenyl-thiolbenzoic acids and 2-*p*-nitrophenylthiolbenzoic acid are stated to be also applicable for this reaction. F. M. G. M.

Isomerism and Desmotropism with Ethyl 2 : 6-Diphenyl*cyclo*hexen-4-one-1-carboxylate.

WALTER DIECKMANN (*Ber.*, 1911, **44**, 975—981).—Ethyl 2 : 6-diphenyl*cyclo*hexen-4-one-1-carboxylate, as obtained by the elimination of water from the corresponding ethyl diphenyl*cyclo*hexanolonecarboxylate, gives no coloration with ferric chloride, is insoluble in aqueous alkali hydroxide and does not couple with diazobenzene; it is accordingly the ketonic form. Alkali ethoxide or hydroxide converts it into a yellow alkali salt, which when decomposed by mineral acids yields an ester which has the properties of an enol. This is relatively stable, but it is in time converted, particularly when warmed, into a second ketonic isomeride, which differs from the first in melting point and crystalline structure. Both ketonic forms are stable, but they pass over into one another when heated above 200° or when boiled in alcoholic solution with alkaline reagents, forming an equilibrated mixture in which the first-mentioned ketonic form predominates ; this is, therefore, regarded as the more stable isomeride. The formulæ

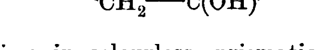

$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{CH(CO_2Et)\cdot CPh}\\ \mathrm{CH_2\text{———}CO}\end{matrix}{>}\mathrm{CH}$$

(I.)


$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{C(CO_2Et){:}CPh}\\ \mathrm{CH_2\text{———}CO}\end{matrix}{>}\mathrm{CH_2}$$

(II.)

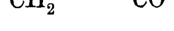
are ascribed to the two ketonic forms, (I) being the more stable and therefore assigned to the first-mentioned isomeride. Reasons are given for assigning the formula


$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{C(CO_2Et){:}CPh}\\ \mathrm{CH_2\text{——}C(OH)}\end{matrix}{>}\mathrm{CH}$$

to the enolic form.

The *ketonic* ester (I) crystallises in colourless, prismatic needles, m. p. 114—115°, and forms a semicarbazone separating in slender, yellow needles, m. p. 183—186°.

The 3-*phenylhydrazone* of *ethyl* 2 : 6-*diphenyl*-Δ^1-cyclo*hexene*-3 : 4-*dione*-1-*carboxylate*,


$$\mathrm{CHPh}{<}\begin{matrix}\mathrm{C(CO_2Et){:}CPh}\\ \mathrm{CH_2\text{———}CO}\end{matrix}{>}\mathrm{C{:}N\cdot NHPh}$$

produced on

coupling the enolic ester with diazobenzene, separates in red needles, m. p. 135°.

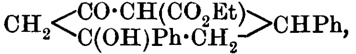
The *ketonic* ester (II) crystallises in small, colourless, rhombic plates, m. p. 105—106°, and yields a semicarbazone, m. p. 218°. E. F. A.

1 : 5-Diketones. Walter Dieckmann and Karl von Fischer (*Ber.*, 1911, **44**, 966—974).—When phenyl styryl ketone is condensed with ethyl acetoacetate in presence of sodium ethoxide, in addition to the compound, m. p. 120°, described by Knoevenagel and Speyer (Abstr., 1902, i, 226), there is formed a second isomeride, m. p. 168—169°. Two isomerides are similarly formed by the condensation of ethyl benzoylacetate and styryl *iso*propyl ketone. One form only is obtained on condensing ethyl benzoylacetate with phenyl styryl ketone or benzylidenepinacolin. According to Rabe and Elze (Abstr., 1902, i, 709), the primary additive products are 1 : 5-diketones, and the isomerides of higher melting point are *cyclo*hexanolones. Isomerism is always observed when the formation of *cyclo*hexanolone is possible; neither isomeride gives a coloration with ferric chloride.

Whereas ethyl 2 : 4-diphenyl*cyclo*hexan-4-ol-6-one-1-carboxylate from phenyl styryl ketone and ethyl acetoacetate is readily converted in presence of sodium ethoxide or piperidine in alcoholic solution into ethyl 2 : 4-diphenyl-Δ^4-*cyclo*hexene-6-one-1-carboxylate, the isomeric ethyl 2 : 6-diphenyl*cyclo*hexan-2-ol-6-one-1-carboxylate does not undergo a similar transformation, and is completely stable when boiled with piperidine.

By the action of concentrated sulphuric acid, the corresponding *cyclo*hexenone derivatives are obtained so long as the elimination of water between the hydroxyl and hydrogen attached to a carbon next the ketocarbonyl group is possible. An exception is afforded by ethyl 2 : 6-diphenyl-3 : 3-dimethyl*cyclo*hexan-2-ol-6-one-4-carboxylate, which forms *cyclo*hexenone with great difficulty.

Alkali breaks down into their components all those 1 : 5-diketo-derivatives which are unable to form *cyclo*hexanolones, for example, ethyl $\alpha\gamma$-dibenzoyl-β-phenylbutyrate, etc. The breakdown is also rapid in the case of ethyl α-benzoyl-γ-*iso*butyryl-β-phenylbutyrate, but it does not take place with ethyl γ-benzoyl-α-acetyl-β-phenylbutyrate.

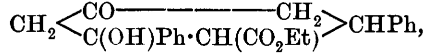
Ethyl γ-benzoyl-α-acetyl-β-phenylbutyrate, obtained by the condensation of the components in presence of traces of sodium ethoxide (compare Knoevenagel and Speyer, *loc. cit.*), has m. p. 120—121°; when more sodium ethoxide is used or the compound is set aside in alcoholic solution with piperidine, *ethyl* 2 : 4-*diphenyl*cyclo*hexan*-4-*ol*-6-*one*-1-*carboxylate*,  $CH_2<\begin{matrix}CO\cdot CH(CO_2Et)\\ C(OH)Ph\cdot CH_2\end{matrix}>CHPh$, is obtained, crystallising in colourless needles, m. p. 168—169°. The corresponding *pyrazolone*, $C_{19}H_{18}O_2N_2$, obtained by interaction of the ester with excess of hydrazine hydrate, forms colourless prisms, m. p. 274—275°.

Ethyl α-*benzoyl*-γ-*acetyl*-β-*phenylbutyrate*,

$$CH_3\cdot CO\cdot CH_2\cdot CHPh\cdot CHBz\cdot CO_2Et,$$

is the primary additive product from the components in presence of traces of sodium ethoxide or piperidine. It separates in colourless needles, m. p. 100—101°.

Ethyl 2 : 6-*diphenyl*cyclo*hexan*-2-*ol*-4-*one*-1-*carboxylate*,



$$CH_2<\begin{array}{l}CO\text{————————}CH_2\\C(OH)Ph\cdot CH(CO_2Et)\end{array}>CHPh,$$

prepared from the foregoing, forms colourless needles, m. p. 216—217°. When warmed with hydrazine in alcoholic acetic acid solution the corresponding *azine*, m. p. 248—250°, is obtained.

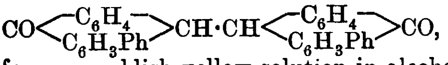
Ethyl α-*benzoyl*-γ-iso*butyryl*-β-*phenylbutyrate*,
$COPr^{\beta}\cdot CH_2\cdot CHPh\cdot CHBz\cdot CO_2Et$,
crystallises in slender, colourless needles, m. p. 98—99°. By the further action of sodium ethoxide or on boiling with piperidine, it is with difficulty in part converted into *ethyl* 2 : 6-*diphenyl*-3 : 3-*dimethyl*-cyclo*hexan*-2-*ol*-4-*one*-1-*carboxylate*, which separates in slender needles, m. p. 160°.

Ethyl αγ-*dibenzoyl*-β-*phenylbutyrate* crystallises in colourless, slender needles, m. p. 138—140°. With hydrazine it yields a badly characterised *pyrazolone*, m. p. about 110°.

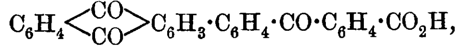
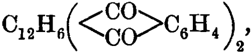
Ethyl α-*benzoyl*-γ-tert.-*butyryl*-β-*phenylbutyrate*,
$CMe_3\cdot CO\cdot CH_2\cdot CHPh\cdot CHBz\cdot CO_2Et$,
separates in colourless prisms, m. p. 141°.

ααγγ-*Tetrabenzoyl*-β-*phenylpropane*, $CHBz_2\cdot CHPh\cdot CHBz_2$, was obtained from a molecular mixture of phenyl styryl ketone and ethyl benzoylacetate in alcoholic solution at 38° in presence of traces of piperidine or sodium ethoxide. It forms colourless, slender needles, m. p. 154—155°, and is hydrolysed by sodium ethoxide to dibenzoylmethane. E. F. A.

Introduction of Several Phthaloyl Groups into Aromatic Hydrocarbons. I. Experiments with Diphenyl. ROLAND SCHOLL and WERNER NEOVIUS (*Ber.*, 1911, 44, 1075—1090).—The importance recently acquired by dianthraquinonyl derivatives in the production of vat dyes has induced the authors to investigate methods of introducing several phthaloyl groups into aromatic hydrocarbons. Commencing with diphenyl, the authors show that the reaction between this hydrocarbon, phthalic anhydride, and aluminium chloride in the presence of carbon disulphide leads only to the formation of diphenyl-4-phthaloylic acid. When heated, best with zinc chloride at 280—285° for thirty minutes, this acid is converted into 2-*phenyl*-*anthraquinone*, $C_6H_3Ph<\begin{array}{c}CO\\CO\end{array}>C_6H_4$, yellow needles, m. p. 160—161°, which is isolated by reducing it with alkaline sodium hyposulphite at 70°, filtering, and oxidising the filtrate by a current of air. 2-Phenylanthraquinone has also been obtained by reducing diphenyl-4-phthaloylic acid, best by 2*N*-sodium hydroxide, zinc dust, and ammoniacal copper sulphate, to 4-phenyldiphenylmethane-2′-carboxylic acid, converting this by zinc chloride at 180—185° into 2-*phenyl*-9-*anthrone*, $C_6H_3Ph<\begin{array}{c}CH_2\\CO\end{array}>C_6H_4$, m. p. 144—145°, and oxidising the latter, best by Goldmann's method with bromine and glacial acetic acid. A boiling solution of 2-phenyl-9-anthrone in glacial acetic acid is oxidised by aqueous ferric chloride, yielding 2 : 2′-*diphenyl*-10 : 10′-*dianthrone*-9 : 9′,

 $CO{<}\substack{C_6H_4\\C_6H_3Ph}{>}CH\cdot CH{<}\substack{C_6H_4\\C_6H_3Ph}{>}CO$, m. p. 222—222·5°, which forms a reddish-yellow solution in alcoholic potassium hydroxide.

Pawlewski's bis-diphenylyl-*o*-phthalide (in a purer state, m. p. 235—247°; the substance, however, is probably still a mixture) is obtained by heating diphenyl, phthalic anhydride, and aluminium chloride in nitrobenzene at 100° or, better, in fused phthalic anhydride at 130°.

The authors attained their object by heating an intimate mixture of diphenyl, phthalic anhydride, and aluminium chloride at 100° for nine and a-half hours. In addition to a little diphenyl-4-phthaloylic acid, the product contains 2-phenylanthraquinone, *diphenyl*-4:4′-*diphthaloylic acid*, $C_{12}H_8(CO\cdot C_6H_4\cdot CO_2H)_2$, and 4-(2″)-*anthraquinonylbenzophenone*-2′-*carboxylic acid*,  $C_6H_4{<}\substack{CO\\CO}{>}C_6H_3\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot CO_2H$, m. p. 217—230°. The separation of these three substances is difficult, but for the authors' purpose is unnecessary, since by heating the crude product with concentrated sulphuric acid at 100°, 2 : 2′-*dianthraquinonyl*,  $C_{12}H_6\left({<}\substack{CO\\CO}{>}C_6H_4\right)_2$, brownish-yellow needles, m. p. 387—388°, is easily isolated in the pure state.

[With Karl Holdermann.]—2 : 2′-Dianthraquinonyl is also obtained by heating 2-iodoanthraquinone with copper powder at 230—240°, and finally at 300° in a current of carbon dioxide. It is converted by boiling nitric acid, D 1·45, into *dinitro*-2 : 2′-*dianthraquinonyl*, $C_{28}H_{12}O_8N_2$, m. p. about 330°; this is reduced by boiling aqueous sodium sulphide to *diamino*-2 : 2′-*dianthraquinonyl*, a reddish-brown powder, m. p. above 400°, which is reduced by alkaline sodium hyposulphite to a reddish-brown vat, which, unlike that from diamino-1 : 1′-dianthraquinonyl, dyes unmordanted cotton. C. S.

Introduction of Several Phthaloyl Groups into Aromatic Compounds. II. Derivatives of Diphenyl. Roland Scholl and Christian Seer (*Ber.*, 1911, **44**, 1091—1103).—The behaviour of the methyl-, hydroxy-, and methoxy-derivatives of diphenyl has been examined under the same conditions as that of diphenyl itself (preceding abstract). When heated with aluminium chloride and phthalic anhydride in the presence of a solvent, di-*o*-tolyl (in carbon disulphide) yields 2 : 2′-*dimethyldiphenyl*-5 : 5′-*diphthaloylic acid*, $C_{12}H_6Me_2(CO\cdot C_6H_4\cdot CO_2H)_2$, m. p. 95—100°, di-*p*-tolyl (in carbon disulphide) yields 4 : 4′-*dimethyldiphenyl*-3-*phthaloylic acid*,

$$C_{12}H_7Me_2\cdot CO\cdot C_6H_4\cdot CO_2H,$$

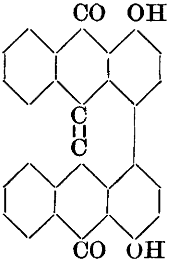
m. p. 177—179°, and *pp*′-dimethoxydiphenyl (in nitrobenzene at 70—85°) yields 4 : 4′-*dihydroxydiphenyl*-3-*phthaloylic acid*,

$$C_{12}H_7(OH)_2\cdot CO\cdot C_6H_4\cdot CO_2H,$$

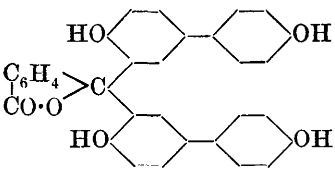
m. p. 75—80°, whilst *pp*′-dihydroxydiphenyl is unattacked. The position of the phthaloyl groups in the preceding compounds is determined by the fact that di-*o*-tolyl forms a diphthaloylic acid, whilst diphenyl gives only a phthaloylic acid; consequently it is assumed that the methyl groups exert a greater orientating influence that the aryl group, and therefore the phthaloyl groups occupy para-positions to the methyl groups in the dimethyldiphenyldiphthaloylic acid, whilst in the dimethyldiphenylphthaloylic acid the phthaloyl group is in the ortho-position to the methyl group.

After the discovery that two phthaloyl groups can be introduced into diphenyl by heating it with aluminium chloride and phthalic anhydride (*loc. cit.*), *pp*′-dihydroxydiphenyl was heated under similar conditions. At 130—135° is produced a mixture of 4 : 4′-dihydroxydiphenyl-3-phthaloylic acid and 4 : 4′-*dihydroxy*-2 : 3-*phthaloyldiphenyl*-3′-*phthaloylic acid*, $C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2(OH)\cdot C_6H_3(OH)\cdot CO\cdot C_6H_4\cdot CO_2H$, a reddish-brown, crystalline powder, m. p. 237—240°; the mixture is separated by taking advantage of the solubility of the *calcium* salt of the former acid in aqueous ammonia. 4 : 4′-*Dihydroxy*-1 : 1′-*dianthraquinonyl*, $C_{12}H_4(OH)_2\left({<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4\right)_2$, brown crystals, darkening at 325° and subliming at 360°, is produced when *pp*′-dihydroxydiphenyl or *pp*′-dimethoxydiphenyl is heated with aluminium chloride and phthalic anhydride at 150°. Under similar conditions at 160°, diresorcinol yields chiefly 2 : 4 : 2′ : 4′-*tetrahydroxy*-1 : 1′-*dianthraquinonyl*, $C_{12}H_2(OH)_4\left({<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4\right)_2$, green needles, which does not melt at 320°, forms a sparingly soluble, violet *sodium* salt, and is reduced by alkaline hyposulphite, yielding a green and, finally, a reddish-brown vat, in which cotton is dyed red, the colour changing to brown in air, violet in alkalis, and green in acids.

Attempts to convert the preceding phthaloylic acids into derivatives of anthraquinone by the action of concentrated sulphuric acid have been only partly successful, the products containing considerable quantities of sulphonated substances. When zinc chloride is used instead of sulphuric acid, phthalide derivatives are produced; thus 4 : 4′-dimethyldiphenyl-3-phthaloylic acid and zinc chloride at 140—150° yield *di*-p-*tolylenephthalide*, $\begin{matrix}C_6H_3Me\\ | \\ C_6H_3Me\end{matrix}{>}C{<}\begin{matrix}-C_6H_4\\ | \\ O\cdot CO\end{matrix}$, colourless needles, m. p. 225—226°. 4 : 4′-*Dihydroxy*-meso-*benzdianthrone* (annexed formula), reddish-brown, metallic crystals, is obtained by treating a solution of 4 : 4′-dihydroxy-1 : 1′-dianthraquinonyl in concentrated sulphuric acid at 55—60° with copper powder. It forms a *dibenzoate*, m. p. 185—195° (decomp.), gives a solution in concentrated, sulphuric acid which is violet by reflected and cherry-red by transmitted light, and is reduced by alkaline hyposulphite to a green vat dye which is deposited on the fibre more easily in the cold than at higher temperatures, giving a colour of a brilliant orange-red tone after exposure to the air and treatment with sodium hypochlorite.



When zinc chloride is added to a mixture of *pp*′-dihydroxydiphenyl



and phthalic anhydride at 185° and the temperature is then kept at 205° for seven hours, a *phthalide* which probably has the annexed constitution is formed. It sinters above 260°, has m. p. 300—310°, and gives only a faintly reddish-brown solution in hot dilute sodium hydroxide, since the hydroxy-groups are not in the para-positions to the triphenylmethane carbon atom. C. S.

Transformation of Allylphthalimide into Propenylphthalimide.

Treat B. Johnson and D. Breese Jones (*Amer. Chem. J.*, 1911, **45**, 343—356).—By the action of ethyl sodiomalonate on γ-bromopropylphthalimide, Gabriel (Abstr., 1890, 1129) obtained ethyl γ-phthalimidopropylmalonate. It was, therefore, expected that β-bromopropylphthalimide would react with ethyl sodiomalonate with formation of the isomeric ethyl β-methyl-γ-phthalimidoethylmalonate, $C_6H_4{:}(CO)_2{:}N{\cdot}CH_2{\cdot}CHMe{\cdot}CH(CO_2Et)_2$. It has been found, however, that when β-bromopropylphthalimide, prepared by the action of hydrogen bromide on allyl phthalimide (Seitz, Abstr., 1891, 1473), is heated with ethyl sodiomalonate, propenylphthalimide is obtained, together with ethyl malonate and a small quantity of a colourless, crystalline substance, m. p. 150—151°, isomeric with propenylphthalimide.

Propenylphthalimide, $C_6H_4{:}(CO)_2{:}N{\cdot}CH{:}CHMe$, m. p. 151°, forms stout, yellow crystals; it can also be obtained by the action of sodium phenoxide on β-bromopropylphthalimide. When heated with sodium ethoxide, it is converted into *propenylphthalamic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH{:}CHMe,$$

m. p. 152°, which is obtained as a viscous liquid and slowly changes to a crystalline solid. As allylphthalamic acid does not show this behaviour, it is suggested that propenylphthalamic acid exists in *cis*- and *trans*-modifications, one liquid at the ordinary temperature and the other solid. Propenylphthalamic acid can also be obtained by the action of sodium ethoxide on β-bromopropylphthalimide.

Allylphthalamic acid, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CH{:}CH_2$, m. p. 112°, obtained by the action of sodium ethoxide or alcoholic potassium hydroxide on allylphthalimide, crystallises readily, and, on prolonged heating with alkali hydroxide, is decomposed with formation of allylamine and *o*-phthalic acid.

Lists are given of organic radicles which favour the production of propenyl compounds and allyl compounds respectively. E. G.

Preparation of *o*-Nitroanthraquinonecarboxylic Acids.

Badische Anilin- & Soda-Fabrik (D.R.-P. 229394).—*o*-Nitroanthraquinonecarboxylic acids containing the nitro- and carboxylic groups in adjacent positions have not previously been prepared, as the nitro-group invariably entered the unsubstituted ring.

1-*Nitroanthraquinone*-2-*carboxylic acid*, faintly-coloured needles, m. p. 285—287°, is prepared by the oxidation of 1-nitro-2-methylanthraquinone with chromic acid, or in nitric acid (40° Bé) solution.

F. M. G. M.

[Preparation of Diaminocarboxydiphenyl Ethers.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 229966).—When diazotised aminophenols and aminocresols containing substituted nitro-groups or halogens (but not SO_3H or CO_2H) are coupled with substituted diphenyl ethers, valuable colouring matters are obtained.

The *diaminocarboxydiphenyl ethers* are prepared by the condensation of 4-chloro-1 : 3-dinitrobenzene with hydroxybenzoic acids in the presence of acid absorbing reagents and subsequent reduction; they possess both acidic and basic functions, are crystalline, sparingly soluble in water, and yield salts with either bases or acids (not acetic acid).

2 : 4-*Diamino-4'-carboxydiphenyl ether*, m. p. 190°, and 2 : 4-*diamino-3'-carboxydiphenyl ether*, m. p. 225°, when coupled with diazotised 6-chloro-4-nitro-2-aminophenol and picramic acid respectively, yielded azo-*dyes*, the properties of which are described in the patent.

F. M. G. M.

Preparation of *o*-Carboxylic Derivatives of Arylthiolacetic Acids. RUDOLF LESSER (D.R.-P. 229067).—The *o*-carboxylic derivatives of arylthiolacetic acids of the typical formula

$$CO_2H\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$$

can be technically prepared by treatment in aqueous solution (or fusion without solvent) of esters of the type $CO_2H\cdot C_6H_4\cdot S\cdot CS\cdot OEt$ with chloroacetic acid; a 93% yield of *o*-carboxyphenylthiolacetic acid is thus obtained from diazotised anthranilic acid by treating it with a hot aqueous solution of potassium xanthate, and acting on the product with chloroacetic acid.

5-*Acetylamino-2-carboxyphenylthiolacetic acid* is prepared from 4-acetylaminoanthranilic acid (m. p. 193—194°); it crystallises from hot water and sinters about 249°.

2-*Carboxy-5-methoxyphenylthiolacetic acid*, m. p. 224—225°, is obtained from 4-methoxyanthranilic acid.

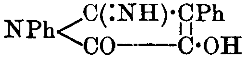
2-*Amino-4-ethylthiolbenzoic acid*, m. p. 168°, is prepared by treating diazotised *o*-nitro-*p*-aminobenzoic acid with potassium xanthate, followed by ethylation and subsequent reduction; the amino-compound when diazotised and treated with hot potassium xanthate and chloroacetic acid yields 2-*carboxy-5-ethylthiolphenylthiolacetic acid*, which forms yellowish-white crystals, m. p. 188°.

5-*Ethoxyanthranilic acid*, m. p. 174° (decomp.), obtained from *p*-aminophenol-*m*-carboxylic acid, furnishes subsequently 2-*carboxy-4-ethoxyphenylthiolacetic acid*, which forms yellow needles, m. p. 186—187°.

5-*Chloro-2-carboxyphenylthiolacetic acid*, m. p. 190—195°, is prepared by heating *ethyl -chloro-2-carboxyphenylxanthate* with chloroacetic acid at 150—170°.

F. M. G. M.

Acylation of Oxalylbenzylcyanide [Oxalylphenylacetonitrile] and Oxalylethylenecyanide [Oxalylsuccinonitrile]. WALTER DIECKMANN (*Ber.*, 1911, 44, 981—990).—Oxalylphenylacetonitrile reacts with phenyl carbimide to form the *anil* of O-*carboxy-β-cyano-α-hydroxy-β-phenylpropenoic acid*. This compound is broken down by sodium ethoxide in alcoholic solution into oxalylphenylacetonitrile and phenylurethane, whereas methyl-alcoholic potassium hydroxide produces an intense red compound, which is regarded as *iminohydroxymaleinanil*,

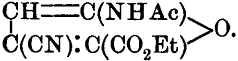


$NPh<\begin{array}{l}C(:NH)\cdot CPh \\ CO\text{———}C\cdot OH\end{array}$.

Similarly, oxalylsuccinonitrile and phenylcarbimide interact to form the *anil* of O-*carboxy-βδ-dicyano-α-hydroxy-Δ$^{\alpha}$-pentenoic acid.*

On the other hand, according to Wislicenus (Abstr., 1908, i, 965), oxalylsuccinonitrile and phenyl carbamide interact to form a normal *O*-carbanilide. It is now shown that this is not hydrolysed by alcoholic sodium ethoxide, forms salts, and is converted by alkali into the corresponding carboxylic acid.

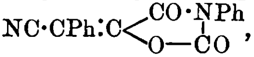
Whereas oxalylphenylacetonitrile and oxalylglutaronitrile form normal *O*-acyl derivatives, β-oxalylsuccinonitrile under similar conditions forms acyl derivatives, which are not hydrolysed by sodium ethoxide, form salts, and are converted by alkaline hydroxide into the corresponding carboxylic acids. They cannot accordingly be *O*-acyl derivatives, and are regarded as acyl derivatives of the isomeric *ethyl* 5-*amino*-3-*cyanofurfuran*-2-*carboxylate* of the constitution



$\begin{array}{l}CH{=\!=}C(NHAc) \\ C(CN):C(CO_2Et)\end{array}>O$.

The same formula may be applied to β-oxalylsuccinonitrile, and is supported by the fact that it fluoresces in alcoholic solution and lacks the characteristic ketone reactions.

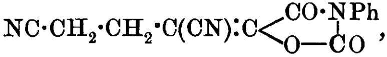
The *anil* of O-*carboxy-β-cyano-α-hydroxy-β-phenylpropenoic acid*,



$NC\cdot CPh:C<\begin{array}{l}CO\cdot NPh \\ O\text{—}CO\end{array}$,

forms colourless, slender needles, m. p. 210°.

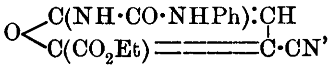
The *anil* of O-*carboxy - βδ - dicyano-α-hydroxy-Δ$^{\alpha}$-pentenoic acid*,



$NC\cdot CH_2\cdot CH_2\cdot C(CN):C<\begin{array}{l}CO\cdot NPh \\ O\text{—}CO\end{array}$,

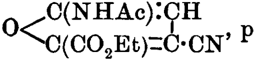
crystallises in colourless prisms, m. p. 133°. Neither of these compounds could be converted into an isomeride.

The *N*-carbanilide of ethyl 5-amino-3-cyanofuran-2-carboxylate,



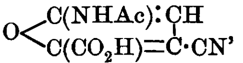
$O<\begin{array}{l}C(NH\cdot CO\cdot NHPh):CH \\ C(CO_2Et){=\!=\!=\!=}C\cdot CN\end{array}$,

prepared by the interaction of phenylcarbimide and β-oxalylsuccinonitrile, is identical with the compound described by Wislicenus (*loc. cit.*). The corresponding *acid* forms microscopic crystals, m. p. 210° (decomp.); the *acetyl* derivative,



$O<\begin{array}{l}C(NHAc):CH \\ C(CO_2Et){=}C\cdot CN\end{array}$,

prepared by heating β-oxalylsuccinonitrile with acetic anhydride, crystallises in colourless needles, m. p. 177°. Sodium methoxide converts it into the corresponding *methyl* ester, colourless, prismatic needles, m. p. 197°. The colourless alcoholic solution of the ester shows a faint yellow coloration, and an intense blue fluorescence on the addition of alcoholic potassium hydroxide. On hydrolysis, the acetyl ester is converted into 5-*acetylamino*-3-*cyanofuran*-2-*carboxylic acid*,



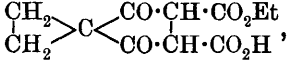
$O<\begin{array}{l}C(NHAc):CH \\ C(CO_2H){=}C\cdot CN\end{array}$,

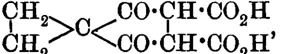
which crystallises in colourless prisms, m. p. 249° (decomp.).

Ethyl-5-benzoylamino-3-cyanofuran-2-carboxylate, prepared by the action of benzoyl chloride on β-oxalylsuccinonitrile in pyridine solution, crystallises in slender, colourless needles, m. p. 168—169°. The corresponding *acid* is obtained in colourless, microscopic prisms, m. p. 256° (decomp.). It forms a sparingly soluble *acid sodium* salt, crystallising in colourless needles. E. F. A.

α-Phenyltricarballylic Acid. Rudolf Wegscheider (*Ber.*, 1911, **44**, 908—909).—The α-phenyltricarballylic acid described by Hecht (Abstr., 1903, i, 700) melts at 110—115°, then solidifies, and finally melts again at 196—201°. It is probably identical with the α-phenyltricarballylic acid, having m. p. 199°, obtained by Stobbe and Fischer (Abstr., 1901, i, 276), the difference in the melting points being due to water of crystallisation. F. B.

Synthesis of Spyrocyclic Compounds. Dan Radulescu (*Ber.*, 1911, **44**, 1018—1022. Compare Abstr., 1909, i, 652).—By the condensation of ethyl succinate and ethyl *cyclo*propane-1 : 1-dicarboxylate in ether in presence of sodamide there is formed an *ester acid* and the corresponding *dibasic acid.*

The former, *ethyl hydrogen* cyclo*propane*cyclo*pentane*-(1 : 1)-*spiran*-2 : 5-*dione*-3 : 4 *dicarboxylate,*  $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!>C<\!\begin{matrix}CO\cdot CH\cdot CO_2Et\\ |\\ CO\cdot CH\cdot CO_2H\end{matrix}$, crystallises in slender, transparent, lustrous plates, m. p. 153—154° (decomp.), with liberation of carbon dioxide; it turns blue at 180—190° (decomp. again at 250°). When crystallised repeatedly from boiling water, it loses alcohol and forms the dibasic acid, which is converted into the ester by partial esterification. Both acids give the intense violet coloration characteristic of β-ketonic acids with ferric chloride. They are decomposed almost quantitatively by alkali hydroxides into succinic acid and *cyclo*propane-1 : 1-dicarboxylic acid.

cyclo*Propane*cyclo*pentane*-(1 : 1)-*spiran*-2 : 5-*dione*-3 : 4-*dicarboxylic acid,*  $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\!>C<\!\begin{matrix}CO\cdot CH\cdot CO_2H\\ |\\ CO\cdot CH\cdot CO_2H\end{matrix}$, crystallises with H_2O in leaf-like needles, m. p. 161° (decomp.). At higher temperatures a mixture of the blue compound and a granular anhydride are formed. E. F. A.

[Preparation of Triphenylmethane Derivatives.] Farbenfabriken vorm. Friedr. Bayer. & Co. (D.R.-P. 228838).—Numerous condensation products of the hydroxybenzaldehydes have been described previously; the work has now been extended to the compounds obtained by the condensation of *o*- and *p*-hydroxybenzaldehydes with aromatic carboxylic acids, and the subsequent oxidation of the leuco-compounds.

p-Hydroxybenzaldehyde (14 parts), *o*-cresotic acid (33 parts), 300 parts of sulphuric acid (60° Bé), and acetic acid (50 parts) are stirred together at a temperature of 70° during twenty hours, poured on to ice, and the dried product subsequently oxidised by air, or by treatment with hydrogen nitrosyl sulphate in sulphuric acid solution; the *product,* a reddish-brown powder, is sparingly soluble in water, and readily so with an intense red coloration in sodium hydroxide. The *p*-hydroxybenzaldehyde was also heated at 60—70° with sulphuric acid containing anhydride, and the sulphonated product subsequently condensed with *o*-cresotic acid, yielding an aqueous soluble *product* The following aldehydes are described: 3-*chloro*-2-*hydroxybenzaldehyde*, m. p. 54°; 4-*hydroxy*-3-*tolualdehyde*-5-*sulphonic acid* yields an orange crystalline *product* with *p*-toluidine in acetic acid solution, and with phenylhydrazine in the same solvent a colourless, crystalline precipitate; 4-*hydroxybenzaldehyde*-3-*sulphonic acid* yields a similar precipitate with phenylhydrazine; 4-*hydroxybenzaldehyde*-2-*sulphonic acid* yields a red precipitate with benzidine. A tabulated list of condensation products from these and other derivatives of hydroxybenzaldehyde with *o*-cresotic acid, and the colours of their solutions in various solvents is also appended. F. M. G. M.

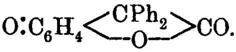
Trimethylene [*cyclo*Propane] Derivatives. LOUIS MICHIELS (*Bull. Soc. chim. Belg.*, 1911, **25**, 177—178).—The formula $C_3H_5{\cdot}CO{\cdot}CH_2Cl$ already assigned to *cyclo*propyl chloromethyl ketone (this vol., i, 63) is confirmed by the fact that the corresponding nitrile gives a violet coloration with ferric chloride.

*cyclo*Propylethylpropylcarbinyl bromide (*loc. cit.*) when left in contact with hydrobromic acid furnishes a *dibromide*, D^{20} 1·3848, indicating that the elements of hydrogen bromide are as easily added to the *cyclo*propane nucleus of tertiary alcohols as to that of the primary or secondary alcohols (*loc. cit.*). T. A. H.

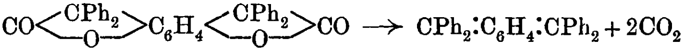
New Mordant Dyes derived from Gallic Acid. ED. EHRMANN (*7th Inter. Congr. Appl. Chem.*, 1909, Sect. IVB, 76—77).—A blue dye is obtained on heating in a sealed tube at 150° for five hours a mixture of gallic acid, diphenyl-*m*-phenylenediamine, and phosphoryl chloride. The substance gives a brown coloration with concentrated sulphuric acid, and is soluble in alkali hydroxides. To it is assigned the structure of 3 : 4 : 5-*trihydroxy*-2 : 4-*diphenyldiaminobenzophenone*, $C_6H_2(OH)_3{\cdot}CO{\cdot}C_6H_3(NHPh)_2$.

When a mixture of gallic acid, *m*-hydroxydiphenylamine, and phosphoryl chloride is heated in a sealed tube for four hours at 155°, a red dye is produced, which is probably a *tetrahydroxyanilinobenzophenone*, $C_6H_2(OH)_3{\cdot}CO{\cdot}C_6H_3(NHPh){\cdot}OH$. This substance is also soluble in alkalis.

Both dyes dye cotton previously treated with metallic mordants; the blue dye gives with iron a greyish-blue, with chromium a violet-blue, and with aluminium a clear blue. The red substance yields with iron a brownish-red, and with aluminium a yellowish-red. R. V. S.

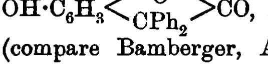
Ketens. III. Action of Diphenylketen on Quinones. HERMANN STAUDINGER and ST. BEREZA (*Annalen*, 1911, **380**, 243—277).—Diphenylketen reacts with quinones in much the same manner as with unsaturated ketones (compare Abstr., 1908, i, 410; 1910, i, 46). Almost any quinone in which the two ortho-positions with respect to one carbonyl group are unsubstituted reacts in the cold with a molecular proportion of diphenylketen, yielding β-lactones of the type  $O:C_6H_4\left<\begin{matrix}CPh_2\\O\end{matrix}\right>CO$. Benzoquinone, toluquinone, chlorobenzoquinone, and *m*-dichlorobenzoquinone react in this manner. When there are substituents in the positions ortho to both carbonyl groups, for example, xyloquinone, *p*-dichlorobenzoquinone, and trichloroquinone, the reaction proceeds very slowly, and when all four ortho-positions are substituted, as in chloranil, the reaction is completely inhibited. These results may be due to "steric hindrance," to a diminution in the basic character of the oxygen atom of the carbonyl group, or to a diminution of isorropesis; but the authors suggest the following explanation. Previous experiments have shown that the unsaturated character of the carbonyl group is increased by the presence of an olefine linking (Abstr., 1910, i, 46), and it is known that a chlorine substituent diminishes the unsaturated nature of an olefine compound. The ethylene linkings in chloranil are thus less reactive than those in benzoquinone, and therefore have a much smaller effect in increasing the unsaturated character of the carbonyl groups; in other words, the carbonyl groups in chloranil are somewhat more saturated than those in quinone. Kehrmann's observations on quinhydrone formation are in harmony with this view. Naphthaquinone yields a β-lactone less readily than benzoquinone does, and anthraquinone does not react in the cold with diphenylketen.

When an excess of diphenylketen is used in the cold, both carbonyl groups of a quinone can react, provided neither group is ortho-substituted. In such cases, and even in the case of toluquinone, unstable dilactones are formed, which are immediately transformed into the corresponding quinodimethanes by the elimination of 2 molecules of carbon dioxide:



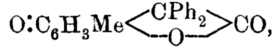
$$CO\left<\begin{matrix}CPh_2\\O\end{matrix}\right>C_6H_4\left<\begin{matrix}CPh_2\\O\end{matrix}\right>CO \longrightarrow CPh_2:C_6H_4:CPh_2 + 2CO_2$$

(compare Abstr., 1904, i, 491; 1908, i, 411).

The β-lactones are quinol derivatives, and are colourless; they give the usual carbonyl reactions, for example, yield phenylhydrazones, but these, unlike most of the phenylhydrazones of quinols (Bamberger, Abstr., 1902, i, 509), yield azo- and not benzene derivatives. When the solid β-lactone from quinone is exposed to sunlight, or when its benzene solution is boiled in bright sunlight, molecular rearrangement occurs, and the γ-lactone of 2:5-dihydroxytriphenylacetic acid,  $OH\cdot C_6H_3\left<\begin{matrix}O\\CPh_2\end{matrix}\right>CO$, is formed by the wandering of an alkyl group (compare Bamberger, Abstr., 1901, i, 141; 1907, i, 516). This rearrangement occurs in the absence of water, and is not therefore due to addition and subsequent removal of water. With a methyl-alcoholic solution of sulphuric acid (compare Bamberger) an additive compound of the β-lactone and methyl alcohol is obtained. When heated carefully below their melting points, the β-lactones yield carbon dioxide and the normal product, namely, a quinomethane; but when decomposed by heating until they melt, or by heating with a solvent of high boiling point, the products are carbon dioxide and a quinodimethane, provided the lactone is derived from a quinone with two reactive carbonyl groups. The formation of a quinodimethane under these conditions is probably due to the conversion of the β-lactone into diphenylketen and the quinone, the subsequent formation of a β-dilactone, and the decomposition of this into carbon dioxide and a quinodimethane.

The following numbers give the percentage of the quinone which has reacted when heated with two gram-molecules of diphenylketen at 130° for 1·5 hours: benzoquinone 70, toluquinone 71·5, xyloquinone 50, chlorobenzoquinone 27, *p*-dichlorobenzoquinone 17, *m*-dichlorobenzoquinone 14, trichlorobenzoquinone 6, tetrachlorobenzoquinone 3, naphthaquinone 72, and anthraquinone 2. The amount of decomposition of the β-lactones has been studied by measuring the volume of carbon dioxide formed when the lactones decompose, and also the addition of keten to the quinomethane (1 mol.) by measuring the carbon dioxide evolved. In the latter case the reaction proceeds violently, and gives a 95% yield of carbon dioxide in the case of the quinomethane derived from *m*-dichlorobenzoquinone, and only a 74% yield in the case of diphenylquinomethane.

The *β-lactone* of toluquinoldiphenylacetic acid,



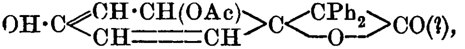
$$O{:}C_6H_3Me{<}\substack{CPh_2\\ O}{>}CO,$$

crystallises from ether, and has m. p. 123° (decomp.); the *β-lactone* from xyloquinone, $C_{22}H_{18}O_3$, crystallises from ether in large, colourless plates, m. p. 123—124° (decomp.); the *β-lactone* from chlorobenzoquinone, $C_{20}H_{13}O_3Cl$, crystallises from acetone, and has m. p. 129—130° (decomp.); the *β-lactone* from *m*-dichlorobenzoquinone, $C_{20}H_{12}O_3Cl_2$, has m. p. 143° (decomp.), and the isomeric *β-lactone* from *p*-dichlorobenzoquinone crystallises from acetone in colourless needles, m. p. 180—192° (decomp.). The *β-lactone* from *m*-dibromobenzoquinone, $C_{20}H_{12}O_3Br_2$, has m. p. 141° (decomp.); the *lactone* from trichlorobenzoquinone, $C_{20}H_{11}O_3Cl_3$, is sparingly soluble, crystallises from dichloroethylene, and has no definite m. p. The *β-lactone* from α-naphthaquinone, $C_{24}H_{16}O_3$, has m. p. 127°.

Well-defined compounds could not be obtained by the hydrolysis of the β-lactone from benzoquinone. The *phenylhydrazone* of the lactone crystallises from dichloroethylene at 0°, and, after recrystallisation from glacial acetic acid, forms red crystals, $C_{26}H_{20}O_2N_2$, m. p. 180° (decomp.). When heated, it evolves carbon dioxide, and forms a tarry mass. The *γ-lactone* of 2 : 5-dihydroxytriphenylacetic acid, $C_{20}H_{14}O_3$, obtained by the action of sunlight on the β-lactone from benzoquinone, or prepared by the condensation of benzilic acid with quinol in the presence of benzene and stannic chloride, separates from methyl alcohol or glacial acetic acid in large, colourless crystals, m. p. 196°, and gives a pale brown coloration with warm concentrated sulphuric acid.

The isomeric *γ-lactone* of 2 : 4-dihydroxytriphenylacetic acid, obtained by condensing benzilic acid with resorcinol in the presence of benzene and stannic chloride, crystallises from benzene and has m. p. 167°. The corresponding *acid* has m. p. 140°, but is gradually transformed into the lactone.

The *additive* compound of the β-lactone and acetic acid,



$$OH\cdot C<\begin{matrix}CH\cdot CH(OAc)\\CH=\!=\!=\!=CH\end{matrix}>C<\begin{matrix}CPh_2\\O\end{matrix}>CO(?),$$

forms colourless crystals from glacial acetic acid, and has m. p. 165°. With concentrated sulphuric acid, it gives the reddish-violet coloration of benzilic acid; it does not react with bromine, phenylhydrazine, or semicarbazide, and does not combine with methyl alcohol. When warmed with alkali in the absence of air, it yields benzilic acid and quinol. The *additive* compound of the β-lactone with methyl alcohol, $C_{21}H_{18}O_4$, forms large, colourless crystals, m. p. 122—123°, and with warm alkali yields methoxydiphenylacetic acid, $C_{15}H_{14}O_3$, m. p. 111—112°.

Diphenylquinomethane is best prepared by heating the β-lactone under reduced pressure for four days at 88°, then for two days at 110°, and crystallising from pure carbon disulphide. It may also be prepared by prolonged boiling of a benzene solution of the lactone in the dark, in an atmosphere of carbon dioxide to prevent oxidation. The compound obtained from the β-lactone from toluquinone is identical with the product, m. p. 176°, prepared by Bistrzycki and Zurbringen (Abstr., 1904, i, 44).

Diphenylchloroquinomethane, $O:C_6H_3Cl:CPh_2$, separates from carbon disulphide as red crystals, m. p. 157—160°, and the corresponding m-*dichloro*-derivative, $C_{19}H_{12}OCl_2$, forms red crystals, m. p. 215°. The *m*-dibromo-derivative is identical with Auwers' product (m. p. 231°) (compare Auwers and Schröter, Abstr., 1903, i, 820).

Tetraphenyltoluquinodimethane, $CPh_2:C_6H_3Me:CPh_2$, crystallises from acetone, and has m. p. 200—210°.

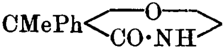
Tetraphenylchloroquinodimethane, $CPh_2:C_6H_3Cl:CPh_2$, also crystallises from acetone, and has m. p. 195—200°.

Tetraphenyl-m-*dichloroquinodimethane*, $CPh_2:C_6H_2Cl_2:CPh_2$, crystallises in glistening, deep red prisms, m. p. 225°.

The quinodimethanes may be prepared by a variety of methods, but in the majority of cases the best method is the fusion of diphenylketenquinoline with the necessary quinone in an atmosphere of carbon dioxide. J. J. S.

Ketens. IV. Phenylmethylketen. HERMANN STAUDINGER and LEOPOLD RUŽIČKA (*Annalen*, 1911, **380**, 278—303).—*Phenylmethylketen*, $CMePh:CO$, has been prepared in order to compare its properties with those of a purely aliphatic, and of a purely aromatic, keten. It is an orange-yellow liquid, paler in colour than diphenylketen, has b. p. 74°/12 mm. It combines with water to form α-phenylpropionic acid, and with aniline to form α-phenylpropionanilide. With benzylideneaniline it forms two distinct *products*, $C_{22}H_{19}ON$, by the union of 1 mol. of keten with one of the Schiff's base. They melt respectively at 125—126° and 146—147°. It also reacts with benzoquinone, and with quinoline forms a keten base, which is stable like that derived from dialkylketens. It polymerises only slowly, and is thus intermediate between dimethyl- and diphenyl-keten. The *polymeride*, $(C_9H_8O)_2$, has m. p. 161·5—162·5°, and is depolymerised when heated. A second polymeride, $(C_9H_8O)_n$, has m. p. 267° (decomp.). It has not been found possible to obtain the keten from phenylmethylmalonic acid, as the latter does not yield an anhydride, but it can be prepared from phenylmethylchloroacetyl chloride and zinc.

Phenylmethylmalonyl chloride, $CMePh(COCl)_2$, obtained by the action of phosphorus pentachloride and pure ether on the corresponding acid, is a yellow oil, b. p. 114—115°/12 mm. A 60—65% yield of acetophenonecyanohydrin (Jacoby, Abstr., 1886, 800) can be obtained by using a solution of acetophenone in ether (1 : 4) and an excess of concentrated potassium cyanide solution and stirring automatically whilst concentrated hydrochloric acid is run in slowly. After hydrolysing the crude nitrile for two days with concentrated hydrochloric acid at the ordinary temperature, and removing the hydrogen chloride by a current of air, the mass is extracted several times with a mixture of light petroleum (2 parts) and ether (1 part) to remove acetophenone. The tetrahydro-oxazolone is precipitated, and the solution contains atrolactinic acid and its amide. *a-Phenyl-lactamide*, $C_9H_{11}O_2N$, crystallises from dichloroethylene in plates, m. p. 101—102°, and, when heated for an hour at 100° with 5% hydrochloric or sulphuric acid, yields the corresponding acid, but when boiled for a longer time appreciable amounts of *iso*atropic acid are formed (*Annalen*, 1879, **195**, 184).

Atropamide, $CH_2{:}CPh{\cdot}CO{\cdot}NH_2$, is sparingly soluble in water, and has m. p. 121—122°. 2 : 5-*Diphenyl*-2 : 5-*dimethyltetrahydro-oxazol*-4-*one*,  $\mathrm{CMePh}<\begin{matrix}\mathrm{O}\\ \mathrm{CO{\cdot}NH}\end{matrix}>\mathrm{CMePh}$, crystallises from methyl alcohol in slender needles, m. p. 219—220°, and with phenylcarbimide it yields an additive *compound*, $C_{24}H_{22}O_3N_2$, m. p. 133—134°. It does not react with phenylhydrazine, and is hydrolysed when boiled for two hours with glacial acetic and concentrated hydrochloric acids to atropic acid and acetophenone. The oxazolone can be synthesised by keeping a mixture of α-phenyl-lactamide, acetophenone, and concentrated hydrochloric acid for three weeks.

α-Chloro-α-phenylpropionyl chloride is best obtained by carefully treating the hydrated atrolactic acid with phosphorus pentachloride (3 mols.), removing the oxy-chloride, and extracting with light petroleum. It is accompanied by $\alpha\beta$-dichloro-α-phenylpropionyl chloride, from which it can be freed by repeated distillation under very low pressures. It has b. p. 112—113°/12 mm., or 59—61°/0·02 mm. The *anilide*, $C_{15}H_{14}ONCl$, has m. p. 71—74°, and the p-*toluidide*, m. p. 91—92°. The *toluidide* of $\alpha\beta$-dichloro-α-phenylpropionic acid, $C_{16}H_{15}ONCl_2$, has m. p. 81—82·5°. The p-*toluidide* of α-*iso*atropic acid, $(C_{16}H_{15}ON)_2$, has m. p. 252°.

The crude chloride obtained from atrolactic acid when treated with p-toluidine yields the toluidides of α-chloro-α-phenylpropionic acid and of β-chloro-α-phenylpropionic acid. The latter *toluidide* is insoluble in light petroleum, crystallises from carbon disulphide, and has m. p. 182—182·5° (decomp.). β-Toluidine reacts with the product from atropic acid and phosphorus pentachloride, yielding the p-*toluidide* of atropic acid, $C_{16}H_{15}ON$, m. p. 229—231°, and the p-toluidide of $\alpha\beta$-dichloro-α-phenylpropionic acid.

a-Phenylpropionanilide, $C_{15}H_{15}ON$, crystallises from light petroleum, and has m. p. 133—134°. *Phenylmethylketenquinoline*, $C_{27}H_{23}O_2N$, crystallises from ethyl acetate in colourless needles, m. p. 175—175·5°, and when warmed with dilute hydrochloric acid yields an *acid*, $C_{27}H_{25}O_3N$, m. p. 94—96°. J. J. S.

Preparation of Acenaphthenone. Badische Anilin- & Soda-Fabrik (D.R.-P. 230237).—*a-Naphthylacetyl chloride*, a yellow oil with penetrating odour, b. p. 188°/23 mm., is dissolved in nitrobenzene and slowly treated with aluminium chloride in the same solvent; the product is poured on ice, and the acenaphthenone formed in this way is separated from nitrobenzene by means of steam and distilled under reduced pressure. F. M. G. M.

Benzylidenediacetyl [Styryl Methyl Diketone]. Otto Diels and Erich Andersonn (*Ber.*, 1911, **44**, 883—888).—Although styryl methyl diketone cannot be prepared by the direct condensation of diacetyl and benzaldehyde, several of its derivatives have been obtained by condensing benzaldehyde with the substituted hydrazones of diacetyl. Of these derivatives only the acetyl compound could be transformed into styryl methyl diketone.

Benzylidenediacetylphenylmethylhydrazone,

$$CHPh:CH\cdot CO\cdot CMe:N\cdot NMePh,$$

prepared by condensing benzaldehyde with diacetylphenylmethylhydrazone by means of sodium hydroxide in methyl-alcoholic solution, crystallises in citron-yellow needles, m. p. 138—139°.

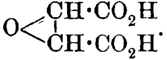
The corresponding *phenylhydrazone*, $CHPh:CH\cdot CO\cdot CMe:N\cdot NHPh$, obtained in a similar manner, forms yellow needles, m. p. 189—190° (corr.).

Styryl methyl diketone monoacetylhydrazone,

$$CHPh:CH\cdot CO\cdot CMe:N\cdot NHAc,$$

prepared by the condensation of diacetylmonoacetylhydrazone and benzaldehyde with aqueous barium hydroxide, crystallises in needles having a green lustre, m. p. 185—186°.

Styryl methyl diketone, $CHPh:CH\cdot CO\cdot COMe$, is obtained in a yield of 8% by distilling the monoacetylhydrazone with dilute sulphuric acid. It crystallises from light petroleum in yellow leaflets, m. p. 52—53°, and on treatment with phenylhydrazine yields the above-mentioned phenylhydrazone. When kept it is transformed into an almost colourless substance, which crystallises from alcohol in greenish needles, m. p. 168—169°. The constitution of the latter compound has not yet been determined. F. B.

Electrolytic Oxidation of *p*-Benzoquinone. Richard Kempf (*J. pr. Chem.*, 1911, [ii], **83**, 329—394).—In order to examine systematically the course of the electrolytic oxidation of benzene it is necessary first to study the oxidation of *p*-benzoquinone, the chief product of the reaction. The apparatus is figured and described in detail. It consists essentially of the electrolytic vessel divided by a porous partition into cathodic and anodic compartments. The latter is as small as possible (200 c.c.) compared with the area of the anode, which consists of a lead disk, 2 mm. thick, 17 cms. in diameter, making 100—120 revolutions per minute. The electrolytes in the cathodic and anodic compartments are 30% and 10% sulphuric acids respectively. At the top of the anodic compartment is connected an apparatus for collecting the gases evolved. The electrolytic vessel is completely immersed in a bath of flowing water. Nine experiments are described in which the amount of *p*-benzoquinone varies between 15 and 25 grams, the amount of 10% sulphuric acid between 200 and 250 c.c., the current between 4 and 5 amperes (at 3·4 volts), and the time between six and ten hours. The results are similar to those obtained by the oxidation of *p*-benzoquinone by silver peroxide (Abstr., 1907, i, 63). Maleic, formic, and racemic acids are obtained together with carbon monoxide and dioxide, occasionally also an *acid*, $C_4H_4O_5$, m. p. 141·5—145·5° (corr.) (*barium* salt, $C_4H_2O_5Ba,2H_2O$), which is probably maleglycidic acid,  $O<\begin{matrix}CH\cdot CO_2H\\ |\\ CH\cdot CO_2H\end{matrix}$. Possible methods by which these substances are produced are discussed. The author inclines to the view that in all processes of electrolytic oxidation the actual oxidising agent is a metallic peroxide formed by the action of the nascent oxygen on the anode. C. S.

Structure of Naphthaquinone Derivatives. II. OSWALD MILLER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 440—454. Compare this vol., i, 308).—The m. p. (decomp.) of 1 : 2 : 4-hydroxynaphthaquinone varies, according to the source of the compound, from 183° to 191°. This variation is apparently not due to inaccuracy of reading the m. p owing to decomposition, and is also far greater than would be caused by differences in the size of the crystals.

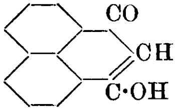
Conversion of the hydroxynaphthaquinone, m. p. 191°, into the ethyl ether results in the formation of two ethers : (1) O : O : OEt = 1 : 2 : 4, m. p. 127°, and (2) O : O : OEt = 1 : 4 : 2, m. p. 98°. Hydroxynaphthaquinone must hence be regarded as an equilibrated mixture of the dynamic isomerides corresponding with these two ethers.

When this mixture is treated with aniline so as to form the anilide, virtually only the first of the two forms reacts, the velocity in the case of the latter being nearly zero. But, as the yield of anilide approximates to the theoretical, the formation of the anilide from form (1) is accompanied by transformation of the inactive compound into the active one. T. H. P.

***peri*-Naphthindandione.** GIORGIO ERRERA (*Gazzetta*, 1911, **41**, i, 190—197).—The aim of the work here described was to prepare from naphthalic acid a compound corresponding with indandione (diketohydrindene) and to ascertain whether ethyl acetoacetate and ethyl malonate act on naphthalic anhydride in the same manner as on phthalic anhydride (compare Gabriel, Abstr., 1884, ii, 176).

Ethyl naphthalate, $C_{10}H_6(CO_2Et)_2$, obtained together with ethyl sodioacetoacetate by heating a mixture of methyl naphthalate and excess of ethyl acetate with sodium, forms transparent crystals, m. p. 54·5°.

Naphthalic anhydride does not react with ethyl malonate in presence of sodium acetate (Gabriel, *loc. cit.*), but when zinc chloride is used as condensing agent, the reaction yields *peri-naphthindandione* (annexed formula), which forms golden-yellow plates or needles, or reddish-brown crystals, m. p. 265° (decomp.), decomposition beginning at 250°. With methyl sulphate in potassium hydroxide solution, it gives the *methyl ether*, $C_{13}H_7O\cdot OMe$, in hard, yellowish-brown plates, m. p. 144°. The *ethyl ether*, $C_{13}H_7O\cdot OEt$, forms yellowish-brown crystals, m. p. 147·5° (compare Freund and Fleischer, Abstr., 1910, i, 490).



By treating *peri*-naphthindandione with phenylhydrazine, the following compounds were obtained: (1) a complex derivative of the naphthindandione, containing about 5% of nitrogen and forming golden-yellow scales, m. p. 260—265°; (2) pale brown, flattened needles, m. p. 128—129°, possibly acetylphenylhydrazine; (3) brown needles, m. p. 219°, probably consisting of the naphthindandionephenylhydrazone.

T. H. P.

Preparation of Halogenated Anthraquinones. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 228876).—Halogenated anthraquinones can be readily prepared in aqueous solution by the action of sodium chlorate on the corresponding anthracenesulphonic acids. Sodium 1 : 8-anthracenedisulphonate (30 parts) is dissolved in water, hydrochloric acid added, and slowly treated with a solution of sodium chlorate (60 parts); the mixture is then heated at 100°, when 1 : 8-*dichloroanthraquinone*, m. p. 202—203°, separates in needles.

2-Chloroanthraquinone and 2 : 6- and 2 - 7-dichloroanthraquinones are similarly prepared.

F. M. G.M.

Preparation of Chloro-substitution Products of Anthraquinones and of Halogenated Anthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 228901).—1 : 4 : 5 : 8-*Tetrachloroanthraquinone*, yellow needles, is obtained by heating anthraquinone (50 parts) dissolved in fuming sulphuric acid (500 parts) in the presence of iodine (1 part) to 130° and leading in chlorine until the required weight is absorbed. Two *hexachloroanthraquinones* are prepared in analogous manner from 2 : 6- and 2 : 7-dichloroanthraquinones, whilst β-chloroanthraquinone yielded a *pentachloroanthraquinone*.

F. M. G. M.

Anthraquinone Series. FRITZ ULLMANN (*Annalen*, 1911, **380**, 317—341).—I. [With OTTO FODOR.]—*a-Aminoanthraquinone* (compare Abstr., 1910, i, 270, 751).—1-*p*-Toluenesulphonylaminoanthraquinone (*loc. cit.*, 751) has m. p. 228·5° (corr.). With concentrated sulphuric acid (10 parts) it yields an orange-coloured solution, which quickly turns yellow; after warming for a short time, the hydrolysis is complete, and on pouring on to ice-water pure 1-aminoanthraquinone (Abstr., 1897, i, 427) is obtained.

1-p-*Toluenesulphonylmethylaminoanthraquinone*,

$$C_6H_4{:}C_2O_2{:}C_6H_3\cdot NMe\cdot SO_2\cdot C_6H_4Me,$$

obtained from 1-chloroanthraquinone and *p*-toluenesulphonylmethylamide, crystallises from alcohol in pale yellow plates, or large, glistening needles, m. p. 198° (corr.), and on hydrolysis with concentrated sulphuric acid yields 1-*methylaminoanthraquinone*,

$$C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}NHMe,$$

which crystallises in red needles, m. p. 170° (corr.), and is soluble in warm dilute hydrochloric acid.

1-p-*Toluenesulphonylanilinoanthraquinone*,

$$C_{14}H_7O_2{\cdot}NPh{\cdot}SO_2{\cdot}C_6H_4Me,$$

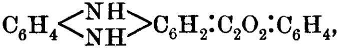
crystallises from alcohol in pale yellow, felted needles, m. p. 198°, and on hydrolysis yields 1-*anilinoanthraquinone*, $C_{14}H_7O_2{\cdot}NHPh$, which can be prepared more readily by boiling 1-chloroanthraquinone with an excess of aniline, potassium acetate, and a little copper acetate and finely divided copper. It crystallises from alcohol in glistening, red plates, m. p. 147·5° (corr.). 1-p-*Nitroanilinoanthraquinone*, $C_{14}H_7O_2{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$, crystallises from nitrobenzene in red needles, m. p. 311° (corr.), and when reduced with an alcoholic solution of sodium sulphide yields 1-p-*aminoanilinoanthraquinone*, $C_{20}H_{14}O_2N_2$, which crystallises in brilliant, dark violet needles with a metallic lustre, and has m. p. 203° (corr.). Its solutions in most organic solvents are violet, its acetic acid solution is red, and its concentrated sulphuric acid solution green. The *acetyl* derivative, $C_{22}H_{16}O_3N_2$, crystallises in red needles, m. p. 176°.

1 : 1-*Dianthraquinonyl*-p-*phenylenediamine*,

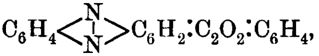
$$C_6H_4[NH{\cdot}C_6H_3{:}C_2O_2{:}C_6H_4]_2,$$

crystallises from pyridine in dark violet-coloured needles with a metallic lustre, and has m. p. 328°. Its solution in concentrated sulphuric acid has a violet-blue colour.

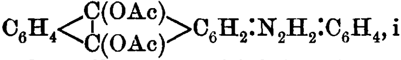
II. [With OTTO FODOR.]—*Anthraquinoneazines.*—1-o-*Nitroanilinoanthraquinone*, $C_{20}H_{12}O_4N_2$, obtained by condensing 1-chloroanthraquinone with *o*-nitroaniline or 1-aminoanthraquinone with *o*-chloronitrobenzene, crystallises from pyridine in glistening, reddish-brown prisms, m. p. 293° (corr.), and when reduced with an alcoholic solution of sodium sulphide yields *anthraquinone*-1 : 2-*dihydrophenazine*,



$C_6H_4{<}{\genfrac{}{}{0pt}{}{NH}{NH}}{>}C_6H_2{:}C_2O_2{:}C_6H_4$, which crystallises from pyridine or nitrobenzene in glistening, blue needles, resembling indigotin; it has m. p. 310° (decomp.), after sintering at 300°. When oxidised with a mixture of glacial acetic and nitric acids, it yields *anthraquinone*-1 : 2-*phenazine*,



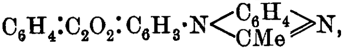
$C_6H_4{<}{\genfrac{}{}{0pt}{}{N}{N}}{>}C_6H_2{:}C_2O_2{:}C_6H_4$, as yellow crystals, m. p. 253° (corr.). This dissolves in concentrated hydrochloric acid, yielding a yellowish-brown solution, and in sulphuric acid to an orange-coloured solution. When reduced with hyposulphite, it yields the dihydrophenazine, and this when boiled with acetic anhydride and potassium acetate yields 9 : 10-*diacetylanthraquinol*-1 : 2-*dihydrophenazine*,



$C_6H_4{<}{\genfrac{}{}{0pt}{}{C(OAc)}{C(OAc)}}{>}C_6H_2{:}N_2H_2{:}C_6H_4$, in the form of glistening, yellowish-red needles, m. p. 256° (corr.). The solutions have a yellow colour with a green fluorescence. 1-o-*Aminoanilinoanthraquinone*,

$$C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2,$$

obtained by reducing the corresponding nitro-compound with an alkaline solution of sodium hyposulphite, crystallises from alcohol in violet, felted needles, m. p. 204° (corr.), and forms a *hydrochloride* in the form of pale red needles. The *acetylamino*-compound, $C_{22}H_{16}O_3N_2$, forms small, red crystals, m. p. 257° (corr.), and is obtained by acetylating the amino-compound with acetic anhydride; if potassium acetate is also used, the product is *methyl*-1-*anthraquinonylbenzoiminazole*,



$C_6H_4{:}C_2O_2{:}C_6H_3\cdot N{<}\substack{C_6H_4\\ CMe}{>}N$, which crystallises from alcohol in glistening, lemon-yellow prisms, m. p. 237°.

1-o-*Nitro*-p-*toluidinoanthraquinone*,

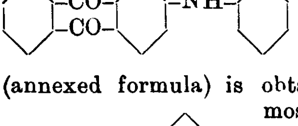
$$C_6H_4{:}C_2O_2{:}C_6H_3\cdot NH\cdot C_6H_3Me\cdot NO_2,$$

prepared from 1-chloroanthraquinone and *o*-nitro-*p*-toluidine in the presence of potassium carbonate, copper acetate, and nitrobenzene, crystallises from pyridine in red needles, m. p. 254° (corr.), and on reduction with sodium sulphide yields *anthraquinone* 1 : 2-*dihydro*-4′-*methylphenazine*, $C_{21}H_{14}O_2N_2$, which crystallises from pyridine or nitrobenzene in greenish-blue needles. 4′-*Chloro*-2′-*nitroanilino*-1-*anthraquinone*, $C_6H_4{:}C_2O_2{:}C_6H_3\cdot NH\cdot C_6H_3Cl\cdot NO_2$, crystallises in coppery-red, glistening needles, m. p. 341° (corr.), and on reduction yields *anthraquinone*-4′-*chloro*-1 : 2-*dihydrophenazine*, $C_{20}H_{11}O_2N_2Cl$. This crystallises from nitrobenzene in glistening, violet needles with a green iridescence, m. p. 310—320°.

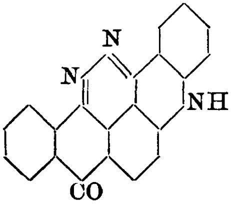
III. [With Masuo Sone.]—*Anthraquinone*-1 : 2-*acridone* (compare Abstr., 1910, i, 696).—p-*Bromobenzoylbenzoic acid*,

$$C_6H_4Br\cdot CO\cdot C_6H_4\cdot CO_2H,$$

obtained by condensing phthalic anhydride with bromobenzene in the presence of aluminium chloride at 50—85°, crystallises from dilute alcohol in colourless, glistening plates, m. p. 173°, and when heated for one hour at 160° with concentrated sulphuric acid yields 2-bromoanthraquinone (compare Kaufler, Abstr., 1904, i, 256), which condenses with anthranilic acid at 140—160° in the presence of amyl alcohol, potassium acetate, and small amounts of copper acetate and finely-divided copper (compare Goldberg, Abstr., 1906, i, 426; Ullmann, *ibid.*, 1903, i, 692; 1906, i, 459, 953), yielding *anthraquinone*-2-*anilino*-o-*carboxylic acid*, $C_6H_4{:}C_2O_2{:}C_6H_3\cdot NH\cdot C_6H_4\cdot CO_2H$, in the form of orange-red, felted needles, m. p. 296° (corr.). The same acid can also be obtained by condensing 2-amino-anthraquinone with *o*-bromobenzoic acid, but the yield is only 40%. When the acid is heated with benzene and phosphorus pentachloride and then aluminium chloride added, *anthraquinone*-1 : 2-*acridone* (annexed formula) is obtained as orange-red needles, insoluble in most organic solvents.



Its solution in alcoholic sodium hydroxide has a violet colour, and that in concentrated sulphuric acid a wine-red colour. A pyridine solution of the acridone condenses with hydrazine hydrate, yielding *anthraquinone*-1 : 2-*acridonazine* (annexed formula) as orange-red needles, which dissolve in alcoholic sodium hydroxide, yielding an orange-coloured solution with a yellowish-green fluorescence.



J. J. S.

Preparation of 1 : 2-Diaminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 231091).—When a 1-halogen-2-aminoanthraquinone-3-sulphonic acid is boiled with aqueous ammonium hydroxide in the presence of a catalyst (such as copper), the halogen is replaced by an amino-group, and the so-obtained 1 : 2-*diaminoanthraquinone*-3-*sulphonic acid*, when heated with 80% sulphuric acid, is converted into 1 : 2-diaminoanthraquinone. F. M. G. M.

Preparation of Methoxyanthraquinones and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 229316. Compare Abstr., 1906, i, 192, 677 ; 1910, i, 751).—The preparation of methoxyanthraquinones by heating the corresponding nitro- or amino-anthraquinones with sodium methoxide, or a methyl-alcoholic solution of sodium hydroxide, has previously been described ; it is found that halogen anthraquinones readily undergo this change, and the preparation of 1- and 2-methoxyanthraquinones from 1- and 2-chloroanthraquinones is now recorded. 1 : 8-Dichloroanthraquinone yields dark crystals of the leuco-compound of *chrysazine dimethyl ether*, which on oxidation by air (or sodium hypochlorite) and subsequent crystallisation from acetic acid is converted into golden-yellow crystals.

4-*Bromo*-1-*benzoylaminoanthraquinone*, yellowish-brown needles, soluble in concentrated sulphuric acid with a scarlet coloration, yields 1-benzoylamino-4-methoxyanthraquinone, whilst 1-*methylamino*-4-*methoxyanthraquinone*, violet prisms, was similarly obtained from 4-*bromo*-1-*methylaminoanthraquinone*.

4-*Chloro*-1-*methoxyanthraquinone*, yellow needles, obtained by chlorinating 1-methoxyanthraquinone in acetic acid solution, yields 1 : 4-*dimethoxyanthraquinone* in the form of yellow needles.

F. M. G. M.

Preparation of Arylanthraquinonylcarbamides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 229111).—The hitherto unknown arylanthraquinonylcarbamides can be readily prepared by the action of arylcarbamides or the corresponding arylthiocarbimides on aminoanthraquinones in an indifferent solvent.

Phenyl-1- and -2-*anthraquinonylcarbamide*, yellow crystals, are obtained by boiling 1- or 2-aminoanthraquinone respectively with carbanil (3 parts) and subsequent extraction with benzene.

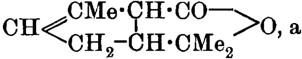
The action of phenylthiocarbimide (10 parts) on 2-aminoanthraquinone yields *phenyl*-2-*anthraquinonylthiocarbamide*, a yellow, crystalline powder, soluble in alkali with a blue coloration. F. M. G. M.

Terpenes and Ethereal Oils. CV. Reduction of Alicyclic Compounds. OTTO WALLACH (*Annalen*, 1911, 381, 51—95).—Paal's method of reducing at the ordinary temperature with hydrogen in the presence of colloidal palladium (Abstr., 1905, ii, 397 ; 1907, ii, 559 ; 1908, i, 599 ; 1909, i, 358, 381, 545, 926) has been extended to the reduction of alicyclic terpene derivatives. It has the great advantage that the reduction can be accomplished under conditions such that molecular rearrangements are practically excluded, and further brings about reductions which cannot be effected by other methods. It is shown that all unsaturated cyclic ketones, not merely those with the ethylene linking in the $\alpha\beta$-position, can be reduced by Paal's method. Thus carvone yields tetrahydrocarvone, whereas when the usual methods of reduction are used a dihydrocarvone is obtained. In the great majority of reactions the ketone is not reduced to a secondary alcohol, the process stopping at the addition of hydrogen to olefine linkings. Pinacone formation does not occur and resinous matters are not formed, so that the yields of reduced ketones are good. It is essential that the compounds to be reduced should be pure; unsaturated terpene derivatives which have been kept for some time contain substances which destroy the activity of the catalyst.

I. *Reduction of Unsaturated Cyclic Alcohols.*—*p*-Menthan-8-ol, $CH_3\cdot C_6H_4\cdot CMe_2\cdot OH$, obtained by reducing inactive α-terpineol, has b. p. 209—210°, D_{20} 0·905, and n_D^{20} 1·4629. The *phenylurethane*, $C_{17}H_{25}O_2N$, crystallises from a mixture of benzene and light petroleum, or from dilute methyl alcohol, and has m. p. 117—118°. According to Behal (Abstr., 1910, i, 572) the m. p. is 94—95°, and the compound appears to exist in two stereoisomeric forms, one melting at 117° and the other at a lower temperature. The product, m. p. 94—95°, is a mixture of the two. β-Terpineol when reduced yields 1-menthanol (Baeyer, Abstr., 1903, i, 722), which has b. p. 208—209°, D^{20} 0·9000, and n_D^{20} 1·4619. The *phenylurethane* has m. p. 100—101°, and the saturated alcohol, when warmed with zinc chloride, yields a hydrocarbon, $C_{10}H_{18}$, which consists mainly of Δ^1-tetrahydro-*p*-cymene (carvomenthene). It has b. p. 174—175°, D^{21} 0·821, and n_D^{21} 1·14551, and with nitrosyl chloride yields two additive compounds. The one, $(C_{10}H_{18}ONCl)_2$, crystallises from acetone or methyl alcohol, has m. p. 95—96°, and with piperidine yields a nitrolpiperidide, m. p. 159°, from which by the elimination of hydrogen chloride a solid oxime is obtained. After this has been purified by conversion into the semicarbazone, m. p. 177—178°, an oxime identical with carvotanacetoxime, m. p. 93—94° (Abstr., 1895, i, 672), is obtained, and as carvotanacetone is readily reduced to tetrahydrocarvone, these reactions afford a method of passing from β-terpineol to tetrahydrocarvone.

Sylveterpineol (Abstr., 1907, i, 1061) on reduction yields a *m*-menthanol, $C_{10}H_{19}\cdot OH$, with b. p. 206—208°, D^{18} 0·9090, and n_D^{18} 1·4645. The *phenylurethane* has m. p. 71—74°. The position of the hydroxyl group in the reduction product has not been determined. *i*-Pinol hydrate when reduced yields a *menthandiol*, $C_{10}H_{20}O_2$, with m. p. 139—140°. According to the formula usually ascribed to pinol hydrate the reduction product should be menthan-2 : 8-diol (Rupe and Schloschoff, Abstr., 1905, i, 450), but the *d*- and *l*-modifications of this have m. p. 112—113°, and the *dl*-compound, m. p. 108—109°.

II. *Carvone Series.*—On reduction in the presence of colloidal palladium, *d*-carvone yields *l*-tetrahydrocarvone; this has b. p. 221°, D^{20} 0·9025, n_D^{20} 1·4544, and $[\alpha]_D - 20°20'$. The corresponding *oxime* has m. p. 99—100° and $[\alpha]_D - 35·7°$, and the *semicarbazone*, m. p. 193°. When small amounts of *r*-carvone are present in the original compound, the reduction product is not homogeneous, and yields a mixture of two oximes. Tetrahydroeucarvone (Abstr., 1905, i, 451), obtained by reducing eucarvone, yields two semicarbazones, and the ketone regenerated from the less fusible product (m. p. 201°, not 191—192°) also yields a similar mixture. α-Dicarvelone (Abstr., 1899, i, 530), when reduced in aqueous acetone solution, yields *tetrahydrodicarvelone*, $C_{20}H_{34}O_2$, which crystallises from alcohol in long, flat plates, m. p. 129—130°.

Carvenolide (Abstr., 1895, i, 622; 1899, i, 532) yields *dihydrocarvenolide*, $C_{10}H_{16}O_2$, and hence contains only one olefine linking. The addition of hydrogen takes place very readily in methyl-alcoholic solution, and the product is more volatile than carvenolide in steam. It has b. p. 260—261° (uncorr.) and m. p. 36—38°. It is suggested that carvenolide is probably the lactone,  $CH<\begin{matrix}CMe\cdot CH\cdot CO—\\ CH_2—CH\cdot CMe_2\end{matrix}>O$, and the dihydro-derivative would then be the lactone of hydroxydihydropulegenic acid.

III. [With Erwin Meyer.]—*Reduction of Pulegenolide and of Pulegenamide.*—Pulegenolide (Abstr., 1898, i, 484) is not a saturated lactone as it yields a *dihydro*-derivative, $C_{10}H_{16}O_2$, which crystallises from dilute methyl alcohol in long, pointed needles, m. p. 49—50°, has an odour resembling that of menthone, and is accompanied by another readily fusible reduction product, which so far has not been obtained in a pure state. The amide of pulegenic acid on reduction yields a *product*, m. p. 149—150°.

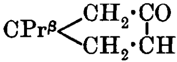
IV. *Fenchone Series* (compare this vol., i, 310).—α-Fenchonitrile when reduced yields *dihydro-α-fenchonitrile*, $C_{10}H_{17}N$, with b. p. 214—215°, D^{20} 0·8730, n_D^{20} 1·4434, and α_D $-5°$ in 1-dcm. tube. α-Fencholenamide yields a *dihydro*-derivative, $C_{10}H_{19}ON$, with m. p. 134° and $[\alpha]_D$ $+4·95°$, and when dehydrated by means of phosphoric anhydride yields the corresponding dihydronitrile. The amide of β-fenchonelic acid is not reduced so readily as the isomeride, and yields as the reduction product the amide of fencholic acid; the corresponding nitrile, $C_{10}H_{17}N$, has b. p. 217—218°, D^{20} 0·8680, and n_D^{20} 1·4426.

[With Friedrich Pohle.]—*α-Dihydrofencholenic acid*, $C_{10}H_{18}O_2$, obtained by hydrolysing the corresponding amide with concentrated hydrochloric acid at 150°, has b. p. 259—260°, D^{20} 0·9740, n_D^{20} 1·4583, and α_D $+2°45'$ in a 1-dcm. tube.

V. [With Frederik Challenger.]—*Thujone Series.*—Thuja ketone is readily reduced to *dihydrothuja ketone*, $CHMe_2\cdot CHMe\cdot CH_2\cdot CH_2Ac$, the *semicarbazone* of which, $C_{10}H_{21}ON_3$, crystallises from methyl alcohol and has m. p. 152—153°. The pure ketone obtained by hydrolysing the semicarbazone with 30% sulphuric acid has b. p. 185·5—186°, D^{20} 0·8340, and n_D 1·4254. When reduced with sodium and alcohol, the saturated ketone yields *dihydrothujaketol*, $C_9H_{20}O$, with b. p. 191·5—192·5°, D^{18} 0·835, and n_D 1·4352. The *tertiary alcohol*, $CHMe_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CMe_2\cdot OH$, prepared by the action of magnesium methyl iodide on dihydrothuja ketone, is a liquid with an odour of roses, and has b. p. 192—194°, D^{18} 0·833, and n_D^{18} 1·4363.

With zinc chloride at 155°, the tertiary alcohol yields the *hydrocarbon*, $C_{10}H_{20}$, with b. p. 159·5—161°, D^{19} 0·7575, and n_D^{19} 1·4315. δ-*Acetyl*-β-iso*propylvaleric acid*, $CH_2Ac\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H$, obtained by reducing β-thujaketonic acid, is an oil and yields a *semicarbazone*, $C_{11}H_{21}O_3N_2$, with m. p. 140°. When oxidised with hypobromite, the acid yields β-iso*propyladipic acid*,

$$CO_2H\cdot CH_2\cdot CH_2\cdot CHPr^{\beta}\cdot CH_2\cdot CO_2H.$$

This is readily soluble in water, does not crystallise well, has m. p. 80—84°, and when its calcium salt is distilled yields 1-iso*propyl*cyclo*pentan*-3-*one*,  $CPr^{\beta}<\begin{matrix}CH_2\cdot CO\\ CH_2\cdot CH_2\end{matrix}$, the *semicarbazone* of which has m. p. 190—191°. The same ketone is formed when Semmler's tanacetophorone is reduced. Tanacetophorone semicarbazone has m. p. 187—188°, and the ketone regenerated from the semicarbazone has b. p. 212—214°, D^{20} 0·938, and n_D^{20} 1·4788. *iso*Thujone combines with hydrogen slowly and incompletely to thujamenthone.

VI. *Methylheptenone.*—β-*Methylheptane*-ε-*one* (iso*amylacetone*),

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COMe,$$

obtained by reducing methylheptenone, has b. p. 164—165°, D_{19} 0·8165, and n_D^{19} 1·4144. It shows no tendency to intramolecular condensation. The *semicarbazone* has m. p. 157—158° (compare Auden, Perkin, and Rose, Trans., 1899, **75**, 909).

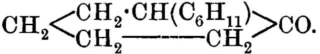
VII. [With FRIEDRICH RITTER].—*Preparation of* 4-*Acetyl*-1-*methyl*cyclo*hexane and its Transformation into* p-*Menthan*-8-*ol.* 4-*Acetyl*-1-*methyl*cyclo*hexane*, $C_6H_{10}MeAc$, can be prepared by the following methods: (1) Reduction of the nitrosochloride from 1-methyl-4-ethylidene*cyclo*hexane (Perkin and Wallach, Trans., 1910, **97**, 1429) with zinc dust and glacial acetic acid. (2) Reduction of an aqueous suspension of 4-acetyl-1-methyl-Δ^3-*cyclo*hexene (*loc. cit.*, 1431) with hydrogen and palladium hydrosol. (3) Reduction of the isomeric 4-acetyl-1-methyl-Δ^1-*cyclo*hexene with hydrogen and palladium. The last method is the most economical, and the product has b. p. 195—197°, D_{18} 0·9055, n_D^{18} 1·4509. The *semicarbazone*, $C_9H_{16}:N\cdot NH\cdot CO\cdot NH_2$, does not crystallise at all readily, and has m. p. 159°. A specimen which had been kept for several months crystallised from methyl alcohol in well-developed needles, and had m. p. 175°. The *oxime*, $C_9H_{17}ON$, has m. p. 57—59° and b. p. 125—130°/15 mm. The *secondary alcohol*, $C_6H_{10}Me\cdot CHMe\cdot OH$, obtained by reducing the ketone with sodium and alcohol, is a liquid with a pleasant odour and b. p. 96°/15 mm. The *phenylurethane* crystallises from methyl alcohol and has m. p. 62—63°. 1-Methyl*cyclo*hexane-4-carboxylic acid (hexahydro-*p*-toluic acid: Perkin and Pickles, Trans., 1905, **87**, 1639) is formed when the ketone is oxidised with hypobromite. *p*-Menthan-8-ol can be synthesised by the action of the Grignard reagent on the saturated ketone.

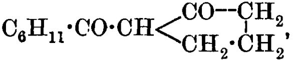
VIII. *Reduction of Unsaturated Alicyclic Acids.*—The two isomeric *cyclo*hexeneacetic acids (Abstr., 1907, i, 616) and the isomeric 1-methyl*cyclo*hexene-4-acetic acids (*ibid.*, 1906, i, 566; 1907, i, 618) are readily reduced by hydrogen and palladium to the corresponding saturated acids.

J. J. S.

Terpenes and Ethereal Oils. CVI. Dicyclic Compounds from *cyclo*Hexanone. Otto Wallach (*Annalen*, 1911, **381**, 95—113).—I. [With Alexander Wacker and Friedrich Pauly.]—cyclo*Hexenhexanone* and cyclo*Hexenhexanol*.—The constitutional formula previously ascribed to *cyclo*hexene-2-*cyclo*hexanone (Abstr., 1907, i, 220) is confirmed.

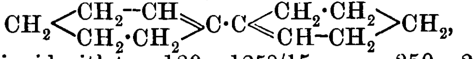
The ketone has b. p. 273—275°, D_{18} 1·005, and n_D^{18} 1·5082. Its *semicarbazone* has m. p. 179—181°. The corresponding unsaturated alcohol has m. p. 34—35°, b. p. 272—273°, D_{37} 0·974, and n_D^{37} 1·5007. Its *phenylurethane*, $C_{19}H_{25}O_2N$, has m. p. 118—119°. The same alcohol is formed when sodium is added to a boiling solution of *cyclo*hexanone in toluene. When carefully oxidised with chromic acid, it yields the *cyclo*hexene-*cyclo*hexanone, but when a benzene solution of the alcohol is oxidised at 0° with 2% permanganate the products are a *trihydric alcohol*, $C_{12}H_{19}(OH)_3$, b. p. 202—205°/10 mm., but mainly the *ketonic acid*, $C_6H_9\cdot CO\cdot[CH_2]_4\cdot CO_2H$. The acid crystallises from benzene in yellow needles, m. p. 74—75°, yields a *semicarbazone*, $C_{13}H_{21}O_3N_3$, m. p. 190—200°, and with hydrogen chloride forms an additive *compound*, $C_{12}H_{19}O_3Cl$, which crystallises from light petroleum in plates, m. p. 48—51°. The ketonic acid is not formed when the original ketone is oxidised, but can be obtained from the *oxime* of the ketone. This has m. p. 146—151°, and on reduction yields bicyclo*hexenhexylamine*, $C_{12}H_{19}NH_2$, m. p. 33—35°, which is oxidised by permanganate to the ketonic acid.

II. [With Walter Ost.]—cyclo*Hexyl*cyclo*hexanone*.—*cyclo*Hexene-*cyclo*hexanone is reduced in methyl-alcoholic solution by hydrogen and palladium to the corresponding saturated ketone, cyclo*hexyl*-2-cyclo*hexanone*,  $CH_2<\begin{matrix}CH_2\cdot CH(C_6H_{11})\\ CH_2 \text{———} CH_2\end{matrix}>CO$. This has b. p. 137°/12 mm., D_{18} 0·978, and n_D^{18} 1·4887. The *semicarbazone* has m. p. 203°; the *oxime*, $C_{12}H_{21}ON$, m. p. 100°, and the *benzylidene* derivative, $C_{19}H_{24}O$, crystallises from alcohol in glistening plates, m. p. 100°. When reduced with sodium and alcohol the saturated ketone yields 2-cyclo*hexyl*cyclo*hexanol*, $C_6H_{11}\cdot C_6H_{10}\cdot OH$, with b. p. 264° (uncorr.) and m. p. 42°. The *phenylurethane* has m. p. 117°. 2-cyclo*Hexyl*-Δ^1-cyclo*hexene*, $C_6H_{11}\cdot C_6H_9$, formed when the saturated alcohol is heated with zinc chloride, has b. p. 237°, D_{20} 0·9010, n_D^{20} 1·4910. Its *nitrosochloride* has m. p. 140°, and resembles *cyclo*hexene nitrosochloride. When oxidised with an acetic acid solution of chromium trioxide, the saturated ketone yields δ-*hexahydrobenzoyl*-n-*valeric acid*, $C_6H_{11}\cdot CO\cdot[CH_2]_4\cdot CO_2H$, which crystallises from a mixture of ether and light petroleum. It has m. p. 58°, and yields a *semicarbazone*, which crystallises from methyl alcohol in needles, m. p. 172—173°. The *oxime*, $C_{12}H_{21}ON$, has m. p. 105°, and the *methyl* ester of the acid, b. p. 173°/13 mm., D_{18} 1·0175, and n_D^{18} 1·4658.

The same acid can be obtained by reducing the unsaturated ketonic acid (m. p. 74—75°) with hydrogen in the presence of colloidal palladium. The acid itself is not affected by chromic acid, by hydrogen chloride at 100°, or by dilute sulphuric acid at 160°, but the methyl ester reacts with metallic sodium in the presence of toluene at 120°, and finally at 130°, yielding 1-*hexahydrobenzoyl*-2-*pentanone*,  $C_6H_{11}\cdot CO\cdot CH<\begin{matrix}CO-CH_2\\ CH_2\cdot CH_2\end{matrix}$, which, after purification by conversion into its *copper* salt, forms a colourless liquid, b. p. 150°/11 mm. The ketone does not yield a semicarbazone or oxime, and cannot be hydrolysed to *cyclo*hexanecarboxylic acid and *cyclo*pentanone. When boiled with sodium hydroxide solution it yields the original ketonic acid, m. p. 58°, and when methylated yields a *methyl* derivative, $C_{13}H_{20}O_2$, which gives a *semicarbazone*, $C_{14}H_{23}O_2N_3$, m. p. 203°.

The *hydroxy-acid*, $C_{12}H_{22}O_3$, obtained by reducing the ketonic acid with sodium and alcohol, forms a thick syrup, and when distilled under reduced pressure yields the *lactone*, $C_{12}H_{20}O_2$, m. p. 45°, which reacts with sulphuric acid (1 : 1·5), yielding an unsaturated *acid*, $C_{12}H_{20}O_2$, with b. p. 182—186°/20 mm. When fused with potassium hydroxide and a little water at 230°, the saturated ketonic acid yields a sparingly volatile, unsaturated acid, m. p. 172°.

III. [With FRIEDRICH PAULY.]—$\Delta^{1:1'}$-*Dicyclohexene*.—Di*cyclo*hexyl-1 : 1′-diol (*cyclo*hexane-pinacone : Zelinsky, Abstr., 1901, i, 683) when boiled with dilute sulphuric acid yields $\Delta^{1:1'}$-*dicyclohexene*,



$$CH_2<\begin{matrix}CH_2-CH\\ CH_2\cdot CH_2\end{matrix}>C\cdot C<\begin{matrix}CH_2\cdot CH_2\\ CH-CH_2\end{matrix}>CH_2,$$

as a colourless liquid with b.p. 120—125°/15 mm. or 250—253°/760 mm., D_{20} 0·9485, and n_D^{20} 1·5287. The *dihydrobromide*, $C_{12}H_{20}Br_2$, crystallises from methyl alcohol in colourless needles, m. p. 68—69°.

Dimethyldicyclohexene, obtained from 1-methyl-3-*cyclo*hexanone, has b. p. 265—267°. J. J. S.

Action of Ethyl Iodide and Magnesium on Menthone and Carvone.

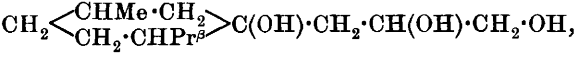
IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 353).—The action of ethyl iodide and magnesium (or zinc) on menthone yields a *hydrocarbon*, $C_{12}H_{22}$, b. p. 195—197°. The action of ethyl iodide and magnesium (or zinc) on carvone yields an *alcohol*, $C_{12}H_{20}O$, b. p. 248—253°, which, on oxidation, gives a trihydric alcohol.

T. H. P.

Action of Zinc on a Mixture of Menthone and Allyl Iodide.

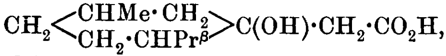
MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 329—344).—By the action of zinc on a mixture of menthone and allyl iodide, the author has obtained 1-methyl-4-*iso*-propyl-3-allyl*cyclo*hexan-3-ol, or 3-allylmenthan-3-ol (compare Javorsky, Abstr., 1909, i, 168; Ryschenko, Abstr., 1910, i, 181), D_4^{20} 0·90794, n_a^{20} 1·47234, n_D^{20} 1·475, n_β^{20} 1·48145, $[\alpha]_D^{20}$ −56°13′48″, b. p. 246—252°.

Oxidation of the alcohol proceeds in two different directions according to the conditions employed. With 1% permanganate solution in the proportion corresponding with 1 atom of oxygen per mol. of the alcohol, the latter yields the *trihydric alcohol*,



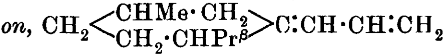
$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2\cdot CHPr^\beta\end{matrix}>C(OH)\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot OH,$$

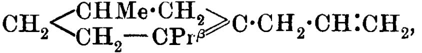
whilst a more concentrated solution of permanganate (40 per mol. of alcohol) yields oxalic acid and the *acid*,



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{matrix}>C(OH)\cdot CH_2\cdot CO_2H,$$

of which the *calcium*, *silver*, *barium*, and *zinc* salts were prepared. The action of bromine on 1-methyl-4-*iso*propyl-3-allyl*cyclo*hexan-3-ol gives the *dibromide*, $C_{13}H_{24}OBr_2$, as a viscous, brown, unstable liquid.

The action of hydrogen chloride or bromide on 1-methyl-4-*iso*propyl-3-allyl*cyclo*hexan-3-ol in the cold gives the corresponding *chloro*-, $C_{13}H_{23}Cl$, or *bromo*-derivative, $C_{13}H_{23}Br$. When either of these compounds is treated with alcoholic potassium hydroxide, it yields the *hydrocarbon*,  $CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{matrix}>C:CH\cdot CH:CH_2$ or



$$CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2-CPr^{\beta}\end{matrix}>C\cdot CH_2\cdot CH:CH_2,$$

b. p. 212—218°, which takes up bromine, giving the *compound*, $C_{13}H_{22}Br_4$, as a viscous, brown liquid. T. H. P.

Some Derivatives of Dicamphor. GIUSEPPE ODDO (*Gazzetta*, 1911, **41**, i, 126—131).—A criticism of the work of Castellana and Ferrero (this vol., i, 217), principally as regards nomenclature.

T. H. P.

Constituents of Ethereal Oils. Enolisation of Citral; Preparation of *iso*Geraniol, $C_{10}H_{18}O$. FRIEDRICH W. SEMMLER and E. SCHOSSBERGER (*Ber.*, 1911, **44**, 991—995).—Aldehydes containing labile hydrogen atoms are converted on boiling with acetic anhydride and sodium acetate into enolic acetates. In the case of citral such process would lead to the formation of a carbon atom with two double bonds, but one of these wanders to the conjugated position, and the physical data of the compound obtained point to this being to the CH_2- rather than to the CH_3-group. enol-*Citral acetate*, $C_9H_4:CH\cdot OAc$, has b. p. 118—126°, D^{20} 0·942, n_D 1·501, and a high molecular refraction. It is reduced by sodium amalgam and methyl alcohol to iso*geraniol*, isomeric with geraniol and nerol, having b. p. 102—103°/9 mm., D^{20} 0·879, n_D 1·473, and an odour of roses. The *diphenylurethane* has m. p. 73°; the *phenylurethane* and *tetrabromide* are oily. E. F. A.

Essential Oils. SCHIMMEL & Co. (*Bericht*, April 1911, pp. 1—208). —*Andropogon* (*Cymbopogon*) *Schoenanthus* var. *nervatus* from the Sudan furnished 1·9% of a brown oil, D^{15} 0·9405, α_D + 26°22′, n_D^{20} 1·49469, acid number 4·6, ester number 9·3, acetyl ester number 99·1, which resembled gingergrass oil in odour, and was soluble in 0·5 or more volumes of 80% alcohol, but deposited a paraffin when further diluted.

Cananga oil from Java had D_4^{25} 0·9068—0·9108, α_D − 20·3° to − 21·8°, n_D^{40} 1·4906 to 1·4919, saponification number 24·2—28·4, and was soluble with slight opalescence in 96% alcohol.

The wood of *Cinnamomum Parthenoxylon* gave a yellow oil having D^{15} 1·0799, α_D + 1°22′, n_D^{20} 1·53229, which was soluble in 2·6 vols. or more of 90% alcohol and had a strong odour of safrole.

Investigations carried out at the Imperial Institute have shown that the citronella grasses of Ceylon are of four kinds, namely: (1) *Cymbopogon Nardus*, Rendle var. *Linnaei*, Stapf (*typicus*); (2) *C. Nardus*, Rendle var. *confertiflorus*, Stapf; (3) *C. Nardus*, Rendle, *lenabatu*, and (4) *C. Winterianus*, Jowitt, the first two being wild and the last two cultivated varieties. Sixteen samples of oil prepared from different specimens of the first variety have been examined, and, omitting two which exhibited certain irregularities, these show the following range of constants: D^{15} 0·894—0·926, α_D + 4°54′ to − 6°32′, and "total alcohols" 43·5—64·7%. Nine samples of oil prepared from different specimens of the second variety had D^{15} 0·900—0·929, α_D + 12°12′ to − 2°11′, and "total alcohols" 39·1—64·2%. The yield of oil from these wild grasses was 0·06—0·45%. The oils from the two cultural varieties resembled common citronella oil from Ceylon and Java respectively (compare *Bull. Imp. Inst.*, 1910, **8**, 144, and *Agric. Journ. Bot. Gard. Ceylon*, 1910, **5**, 115).

The fruit rinds of *Citrus Hystrix* from Java furnished 4% of yellow oil, D^{26} 0·942, α_D + 9°, containing 40% of citral.

Turmeric roots furnished 3·23% of a golden-yellow oil, D^{15} 0·9430, α_D − 23°, n_D^{20} 1·51236, acid number 1·6, ester number 7·8, acetyl ester number 30·0, which gave a marked reaction for phellandrene (compare Bacon, Abstr., 1911, i, 73).

Cymbopogon coloratus oil from Fiji had D^{15} 0·920, contained 42% of aldehydes and 15% of geraniol, and had an odour recalling those of lemongrass and citronella oils (compare *Bull. Imp. Inst.*, 1910, **8**, 145).

C. Jwarancusa (?) from the Sudan furnished an oil, which resembles pennyroyal oil in odour, and consists principally of an aromatic ketone (*loc. cit.*).

C. polyneuros oil from Ceylon gave 0·20—0·34% of yellow to reddish-brown oil, D^{15} 0·936—0·951, α_D + 30°53′ to + 55°15′, which was soluble in 1 vol. of 80% alcohol, and contained 38·7—51·8% of "total alcohols" (*loc. cit.*).

Warburgia Stuhlmanni bark furnished 0·6% of a viscous, yellowish-red oil, D^{20} 0·9864, α_D^{20} − 41·2°, n_D^{20} 1·51269, saponification number 11·2, acetyl ester number 111·5, which is miscible with anhydrous alcohol, has an odour recalling that of sandalwood oil, and contains an aldehydic constituent and some sulphur compounds.

Andropogon (*Cymbopogon*) *citratus* roots from Java gave an oil, α_D − 1°40′, containing 82% of citral, whilst the rhizomes yielded an oil, D^{20} 0·94, α_D − 3°40′, containing 11% of citral.

The leaves and twigs of *Melaleuca trichostachya* furnish, according to Baker and Smith, 2·5% of oil containing 85—95% of cineol, whilst, according to the same authors, *M. bracteata* leaves and twigs furnish 1% of oil containing methyleugenol, cinnamaldehyde, and free and combined cinnamic acid.

Monarda citriodora, according to Lefebvre and Wakeman, furnishes an oil, D^{15} 0·9603, containing phenols 72%, and aldehydic substances 4%. The non-phenolic portion contains 16·98% of alcohols.

The bark of *Myristica fragrans* from Java gave 0·14% of oil, D^{26} 0·871, having a rotation − 12°14′ in a 10 cm. tube.

Origanum oil from Greece had $D^{15\cdot5}$ 0·9351, α_D ±0°, n_D^{22} 1·502, contained 63% of phenols, and was soluble in four or more volumes of 70% alcohol.

Mentha canadensis var. *piperascens*, grown in Germany, furnishes, according to Thoms, a peppermint oil very similar to Japanese peppermint oil. Irk's examination of Hungarian peppermint oil shows that this closely resembles American peppermint oil.

Prunus sphaerocarpa bark, according to Peckolt, furnishes 0·046% of oil, D^{18} 1·0409, which has an odour of bitter almond oil. Amygdalin was isolated from the seeds of the same plant, whilst the leaves furnished from 0·0016% (in winter) to 0·085% (in summer) of hydrogen cyanide.

The fraction of savin oil boiling at 170—180° contains *α*-terpinene.

Majorana Onites from Smyrna gave 2% of dark brown oil, D^{15} 0·9572, α_D $-1°30'$, which contained 74% of phenols, principally carvacrol. The non-phenolic portion contained *α*-pinene, *p*-cymene, *l*-linalool, and *d*-camphor, with one or more sesquiterpenes.

Indian turpentine oil contains *α*-pinene, *β*-pinene, sylvestrene, and a *sesquiterpene*, D^{15} 0·9371, α_D $+37°4'$, n_D^{20} 1·50252, which furnishes a *hydrochloride*, m. p. 59·5—60·5°, crystallising in long needles (see also *Bull. Imp. Inst.*, 1911, **9**, 9).

Thymus mastichina, according to Dorronsoro, furnishes an oil D_{15}^{20} 0·907—0·945, α_D $-0°50'$ to $+4°40'$, n_D^{23} 1·4630 to 1·4654, saponification number 12·7—18·5, and acetyl ester number 29·2 to 49·3, which contains *d*-*α*-pinene 7—8%, cineol 64—72%, phenols and ketones less than 0·1%, linalyl acetate 4·4—6·4%, and free alcohols 8·2—14·1%, with small quantities of free and combined acetic and *iso*valeric acids.

Balan oil from Java, D^{15} 0·9042, n_D^{20} 1·47715, acid number 13·0, ester number 20·5, which is used in native medicine as a vermifuge, furnished on extraction with sodium hydrogen sulphite solution a product from which a *semicarbazone*, m. p. 152°, was obtained.

Eugenia occlusa leaves gave 0·05% of dark brown oil, D^{15} 0·9567, α_D $-1°40'$, n_D^{20} 1·48614, which deposits paraffin (?) at 12° and contains citral and other aldehydes.

The cones of *Pinus excelsa* from India yielded a yellow oil, D^{15} 0·8757, α_D $-32°45'$, n_D^{20} 1·47352, acid number 0·5, ester number 5·6 (corresponding with 2·0% of bornyl acetate), which was soluble in five or more volumes of 90% alcohol.

A résumé is also given of recent work on the botany, pharmacology, analysis, chemistry, and physical constants of essential oils.

T. A. H.

The Pines of Australia. Richard T. Baker and Henry George Smith (*Technical Education Series, Technological Museum, New South Wales*, 1910, No. 16, p. 1—458).—The morphology, anatomy, physiology, and chemistry of the principal genera of the Coniferæ, occurring in Australia and Tasmania, have been studied with a view to (1) their more exact botanical classification, (2) the determination of their economic importance as sources of resins, volatile oils, timbers, and other products. The genera dealt with are *Callitris*, *Actinostrobus*, *Diselma*, *Microcachrys*, *Athrotaxis*, *Araucaria*, *Agathis*, *Dacrydium*, *Pherosphaera*, *Phyllocladus*, and *Podocarpus*. The following are the chief general results of chemical interest obtained: (1) A sequence of *Callitris* species is outlined, based in part on the composition of the leaf oils obtained from them; (2) a relationship is shown to exist between the anatomical characters of *Callitris* leaves and the composition of the oils they furnish, and (3) a number of new facts relating to the composition and characters of the volatile oils, resins, etc., furnished by the species studied are recorded.

The oils yielded by the leaves of *Callitris* species are mostly dextrorotatory and generally colourless, but become acid on keeping. They contain *d*- and *l*-pinene, *d*- and *l*-limonene, sesquiterpenes, *d*-borneol, and geraniol and terpineol, as their acetic esters, and terpineol and an ester of this, probably the butyrate. In a few cases traces of phenols are present. The sesquiterpenes are present in small amount as a rule. The other constituents all reach a maximum in the leaves of one species. In *C. Drummondii* leaf oil *d*-pinene is at a maximum, in *C. Muelleri* *l*-pinene, in *C. arenosa* *d*-limonene, in *C. intratropica* *l*-limonene, in *C. Tasmanica* geranyl acetate, and in *C. gracilis* terpineol. Though the leaf oils practically all contain the same constituents, yet the amounts of these present vary with each species, so that the composition of the oil is often enough to determine its botanical source. The principal constants and constituents of the oil from each species are given in detail in the original: those for *C. Macleayana* leaf oil are D^{20} 0·8484, $[\alpha]_D$ +42·5°, n_D 1·4791, esters 3·5%. This oil differs considerably from *Callitris* leaf oils in general; it contains *d*-pinene, *d*-limonene, dipentene, a sesquiterpene (cadinene?), a small quantity of esters, and a large proportion of a hydrocarbon, $C_{10}H_{18}$, which may be *d*-menthene.

The constituents of the oils from the fruits of *Callitris* species, as a rule, are the same as those of the leaf oils of the same species, but the terpenes present are often of opposite optical activity.

The wood of *Callitris glauca* yields 0·82% of volatile oil, which is semi-solid owing to the separation of guaiol. The liquid portion, which still contains guaiol, has D^{16} 0·9854, acid number 68·8, and saponification number 106·6, and distils as follows: 60% from 248—255°, 21% from 255—265°, and 10% from 266—296°. The first fraction is largely sesquiterpene, D^{15} 0·9266, n_D^{15} 1·4926, and b. p. 250—252°. The second and third fractions are dark blue in colour. On saponification and separation of guaiol the liquid portion furnishes a *phenol*, which also occurs free in the oil. This is a viscous oily substance giving with acetic acid and bromine a characteristic purple coloration, which changes to blue. It is proposed to call this phenol *callitrol*. Both guaiol and callitrol occur in other *Callitris* timbers.

The barks of *Callitris* species all appear to contain tannins of the catechol group; the richest are the barks of *C. calcarata* and *C. arenosa*, which may contain up to 36 and 34% respectively. The specific rotations and relative solubilities of the resins of *Callitris* spp. are recorded.

Actinostrobus pyramidalis leaves furnish 0·256% of oil, D^{15} 0·8726,

$[\alpha]_D + 40·9°$, n^{19}_D 1·4736, which differs from *Callitris* oils in containing no limonene, but *d*-pinene and geranyl acetate are present.

Athrotaxis selaginoides leaves yield 0·076% of volatile oil, D^{16}_{15} 0·8765, $[\alpha]_D + 74·8°$, n^{16}_D 1·4905, containing *d*-limonene, pinene (?), sesquiterpene (? cadinene), carvacrol (?), and a small quantity of esters.

Araucaria Cunninghamii leaves give 0·005% of oil, D^{21} 0·8974, n^{21}_D 1·4977, consisting mainly of high boiling terpenes with a small quantity of esters. The bark contains a catechol tannin. The exudation from wounded stems of this species is an oleo-gum resin. The oil, D^{22}_{15} 0·80577, n^{22}_D 1·457, $[\alpha]_D$ + 3·2° has an odour recalling that of menthene, and consists largely of a *hydrocarbon*, $C_{10}H_{20}$, b. p. 151—153°, with some unsaturated hydrocarbons, probably of the menthane group. The aqueous portion of the distillate is acid and contains acetic and butyric acids. The gum resembles "gum arabic"; it furnishes mucic acid on oxidation with nitric acid, and arabinose on hydrolysis with acids. The resin has acid number 107, and can be separated by treatment with ether into (1) *dundathic acid*, $C_{21}H_{32}O_3$, m. p. 234—235°, $[\alpha]_D$ + 55°, and (2) an *isomeride* of abietic acid, $C_{20}H_{30}O_2$, m. p. 90—91°, $[\alpha]_D$ − 11·25°, and (3) a *bitter* substance. The exudation also contains protein, water, and impurities. The exudation of *A. Bidwilli* also contains gum, resin, and volatile oil, but the two latter are present in very small proportions. The oleo-resin of *Agathis robusta* contains resin 62·0%, volatile oil 11·64%, and small quantities of gum, reducing sugar, nitrogenous matters, and acetic and butyric acids. The volatile oil, D^{16}_{15} 0·8629, $[\alpha]_D$ + 20·2°, n^{16}_D 1·476, consists principally of *d*-pinene.

The resin consists of (1) dundathic acid (see above); (2) *dundatholic acid*, $C_{19}H_{28}O_3$, m. p. 101—102°, $[\alpha]_D$ + 21·5° in alcohol, which is amorphous, and (3) a bitter resin.

Dacrydium Franklini leaves yield 0·5% of oil, D^{17}_{15} 0·8667, $[\alpha]_D$ + 20·5°, n^{25}_D 1·4815, containing the methyl ether of eugenol, *d*-limonene, *l*-pinene, and *dacrydene*, $C_{10}H_{16}$, D^{22}_{0} 0·8524, $[\alpha]_D$ + 14·48°, n^{22}_D 1·4749, b. p. 165—166° (corr.), having a turpentine-like odour and giving a *nitrosochloride*, m. p. 120—121°, and a liquid *tribromide*. The wood yields 0·56% of oil, D^{18}_{15} 1·035, $[\alpha]_D$ + 1·4°, n^{23}_D 1·5373, consisting chiefly of methyleugenol with some sesquiterpene (cadinene ?).

Pherosphaera Fitzgeraldi leaves contain 0·108% of oil, D^{22}_{15} 0·8705, $[\alpha]_D$ + 15·1°, n^{23}_D 1·4841, containing *d*-pinene, limonene (?), cadinene, an aldehydic substance, and a small quantity of esters.

Phyllocladus rhomboidalis leaves (phylloclades) furnish 0·215% of oil, D^{16} 0·8892, $[\alpha]_D$ − 12·3°, n^{16}_D 1·4903, which contains *l*-pinene, a *sesquiterpene*, D^{24} 0·9209, $[\alpha]_D$ + 3·4°, and n^{23}_D 1·5065, a small quantity of an alcohol, and a diterpene, *phyllocladene*, m. p. 95°, $[\alpha]_D$ + 16·06° in chloroform, which crystallises from alcohol in nacreous, colourless tablets and appears to be a saturated substance. It is suggested that phyllocladene is formed from 2 mols. of pinene.

In various parts of all the Australian Coniferæ studied, a brown, bronze-coloured substance containing manganese was observed microscopically and the ashes from these contained manganese. Manganese was also found in association with the gum in the exudations of *Araucaria Cunninghamii* and *Agathis robusta*. T. A. H.

Saponin from Trevesia Sundaica Leaves. J. FLIERINGA (*Arch. Pharm.*, 1911, **249**, 161—173; *Pharm. Weekblad*, 1911, **48**, 433—439).—A description is given of the method of isolation of crude saponin from this material and of its resolution into five different fractions, the principal properties and reactions of which are detailed.

An alcoholic extract of the leaves was concentrated, dissolved in very dilute alcohol, freed from fat by extraction with ether, heated under reduced pressure to remove alcohol and ether, and the saponin salted out with ammonium sulphate. This crude saponin possessed hæmolytic properties, and was precipitated from aqueous solution by basic lead acetate, whilst lead acetate only removed brown impurities. By treatment with magnesium hydroxide, it was separated into (1) green saponin, and (2) yellow saponin, the former strongly hæmolytic, the latter scarely so. The yellow saponin by solution in alcohol and fractional precipitation with ether gave four fractions, the first three amorphous, the fourth crystalline. All four fractions differed in physical properties, in the facility with which they were salted out by magnesium sulphate, and in composition. All were glucosides, and furnished sapogenin and sugars on hydrolysis by acids. Under these conditions fractions 1, 2, and 3 furnished a hexose (? dextrose), a pentose (? arabinose), and a methylpentose, whilst fraction 4 gave only the hexose and pentose. On hydrolysis with potassium hydroxide solution, fraction 1 furnished an amorphous acid glucoside, which was strongly hæmolytic, gave a crystalline potassium salt, and on further hydrolysis by acids yielded sapogenin and methylpentose, with small quantities of a pentose and hexose.

T. A. H.

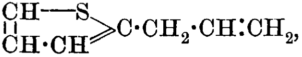
Preparation of Aloin Derivatives. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 229191).—*Aloin carbonate*, a brownish-yellow, tasteless powder, is prepared by treating a cooled pyridine solution of anhydrous aloin with carbonyl chloride; after remaining some time at the ordinary temperature, water is added, the pyridine removed with dilute sulphuric acid, and the product washed with alcohol.

Aloin ethyl carbonate, a green, tasteless powder, is prepared in a similar manner with ethyl chloroformate; and *aloin allophanate*, a brownish-yellow powder, by means of carbamide hydrochloride in benzene solution. F. M. G. M.

Colour and Constitution. BRONISLAW PAWLEWSKI (*Ber.*, 1911, **44**, 1103—1104).—An example is given of the influence of the relative positions of chromophoric and auxochromic groups on the colour of compounds. The nine azomethine compounds obtained by condensing each of the three aminobenzoic acids with each of the three nitrobenzaldehydes contain the chromophore, $\cdot N:CH\cdot$, in a fixed position, whilst the positions of the auxochromic CO_2H group and the chromophoric NO_2 group vary in the different substances. In the three derivatives of anthranilic acid the colour is more intense the nearer the CO_2H and the NO_2 groups are to one another; in the derivatives of the other two aminobenzoic acids the converse is the case. C. S.

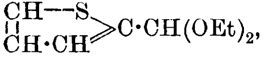
Action of Amines on Triphenylcarbinol and Tritolylcarbinol. ARTHUR G. GREEN and ARTHUR E. WOODHEAD (*7th Intern. Congr. App. Chem.*, 1909, Sect. IV B, 89).—On heating triphenylcarbinol with aniline and aniline hydrochloride for ten or twelve hours at 180°, a deep blue mass is obtained, from which only a small quantity of dye can be isolated, the main product being aminotetraphenylmethane. The properties of the dye correspond with those of a substance of the induline class, so that no introduction of a phenylimino-group seems to occur, and the triphenylcarbinol merely acts as an oxidiser on the aniline. This is confirmed by the fact that when *p*-toluidine is substituted for aniline no colour is produced. *o*-Toluidine gives a red similar to magenta, and dimethylaniline a violet like methyl-violet. Tri-*p*-tolylcarbinol reacts similarly with the amines mentioned. In all cases the yield of dye is small. R. V. S.

Action of Magnesium Thienyl Iodide on Allyl Bromide. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 201—203. Compare Thomas, Abstr., 1908, i, 360).—2-*Allylthiophen*,



$\begin{array}{l}CH\text{—}S\\ \|\\ CH\cdot CH\end{array}\!\!>C\cdot CH_2\cdot CH{:}CH_2$, obtained by the interaction of allyl bromide, magnesium, and 2-iodothiophen, is a colourless, mobile liquid, b. p. 158·5—159°/732 mm., $D_4^{20\cdot5}$ 1·0175, $n_D^{20\cdot5}$ 1·52813. It decolorises bromine, and combines almost quantitatively with liquid nitrogen dioxide, giving a brownish-black, indistinctly crystalline product. With an acetic acid solution of 2-allylthiophen, phenanthraquinone dissolved in sulphuric acid gives a reddish-brown coloration, whilst, under similar conditions, isatin gives a cinnamon-red coloration. When oxidised with permanganate, 2-allylthiophen yields thiophen-2-carboxylic acid, m. p. 125—126°. T. H. P.

New Method of Preparation of, and Certain Derivatives of, Thiophen-2-aldehyde. E. GRISHKEWITSCH-TROCHIMOWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 204—207).—The interaction of ethyl orthoformate and magnesium thienyl iodide yields the acetal,



$$\begin{array}{l}CH\text{—}S\\ \|\\ CH\cdot CH\end{array}\!\!>C\cdot CH(OEt)_2,$$

which, on hydrolysis, is converted into thiophen-2-aldehyde (compare Biedermann, Abstr., 1886, 536, 870; Hantzsch, Abstr., 1890, 129).

The *acetal*, $C_9H_{14}O_2S$, is a colourless, mobile liquid, b. p. 222·5—223·5°/748 mm. (corr.), D_4^{17} 1·0571, n_D^{17} 1·49020.

The action of alcoholic ammonia on thiophen-2-aldehyde yields the *hydramide*, $C_4SH_3\cdot CH(N{:}CH\cdot C_4SH_3)_2$, in colourless, shining, crystalline rosettes, m. p. 111·5°. T. H. P.

[Preparation of a "Chlorothioindigo."] GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 230308).—A continuation of previous work on the production of dyes in the "thioindigo" series.

"Chlorothioindigo," m. p. 245—260°, a dark violet-coloured powder, crystallising from nitrobenzene in needles, is prepared by passing chlorine into a nitrobenzene suspension of thioindigo in the presence of a halogen carrier, such as antimony pentachloride. F. M. G. M.

Angostura Alkaloids. JULIUS TRÖGER and H. RUNNE (*Arch. Pharm.*, 1911, **249**, 174—208).—In a previous paper (Tröger and Müller, Abstr., 1910, i, 414) it was shown that Angostura bark contains, in addition to amorphous alkaloids, cusparine, galipine, cusparidine, galipidine, cuspareine, and a new alkaloid, now named galipoidine; the second and fourth of these were characterised and their oxidation studied. In the present paper cusparine, cuspareine and galipoidine are dealt with, and it is shown especially that cuspareine should be represented by the formula $C_{18}H_{19}O_2N$ instead of $C_{34}H_{36}O_5N_2$ (Beckurts and Frerichs, Abstr., 1904, i, 84) or $C_{35}H_{44}O_3N_2$ (Müller, *Apoth. Zeit.*, 1909, No. 73). Galipine and galipidine are probably dihydro-derivatives of cusparine and cusparidine respectively.

The various melting points ascribed by different authors to cusparine, $C_{20}H_{19}O_3N$ (Körner and Böhringer, Abstr., 1884, 341; Beckurts and collaborators, Abstr., 1892, 642; 1896, i, 66; 1904, i, 84, and Müller, *loc. cit.*), are due to the fact that the base exists in two forms: (*a*) colourless needles, m. p. 90—91°, and (*b*) amber-coloured crystals, m. p. 110—122°. Both forms yield the same platinichloride, $B_2,H_2PtCl_6,3H_2O$, which crystallises in glancing, yellow needles, sinters at 197°, and melts at 210°.

The nitro-base prepared by Beckurts and Frerichs (Abstr., 1904, i, 84) from cusparine has the formula $C_{17}H_{14}O_4N_2,H_2O$, m. p. 142·5—143°, contains one methoxyl group like the parent base and furnishes a crystalline *nitrate*, B,HNO_3,H_2O, m. p. 168°, yellow needles; *hydrochloride*, B,HCl,H_2O, m. p. 149° (decomp.); *sulphate*, $B_2,H_2SO_4,4H_2O$, yellowish-white needles, m. p. 120°; *platinichloride*, B_2,H_2PtCl_6, m. p. 204°; *aurichloride*, $(B,HCl)_2,AuCl_3$, m. p. 200°; and *methiodide*, small, yellow needles, decomposing at 105°. On reduction, the nitro-base gives the corresponding *amino*-compound, $C_{17}H_{16}O_2N_2$, m. p. 205—206°, which crystallises in colourless needles and yields a crystalline *hydrochloride*, $B,2HCl$, m. p. 224° (decomp.), *platinichloride*, B,H_2PtCl_6, m. p. 248° (decomp.), and *mercurichloride*, $B,2HCl,HgCl_2$, m. p. 231° (decomp.). The sulphate on diazotisation furnishes a crystalline *substance*, which gives a *platinichloride*, m. p. 220° (decomp.), crystallising in broad prisms. On adding β-naphthol to an aqueous solution of the diazo-substance, a red *azo-dye*,

$$C_{17}H_{14}O_2N{:}N\cdot C_{10}H_6\cdot OH,C_2H_5\cdot OH,$$

m. p. 206°, is produced, which crystallises from alcohol in iridescent needles.

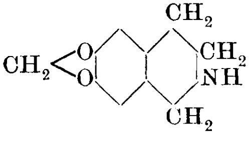
When heated in a closed vessel with dilute nitric acid, cusparine furnishes a *product*, $C_5H_5O_5N_3$, crystallising in brownish-yellow needles.

Cuspareine, $C_{16}H_{13}N(OMe)_2$, m. p. 55·5—56°, crystallises in long, colourless needles, forms salts with difficulty, but yields a crystalline methiodide, B,CH_3I,H_2O, m. p. 156° (decomp.), and this on treatment with silver chloride, followed by the addition of platinic chloride to the filtrate, yields the *methochloride platinichloride*, $(B,CH_3Cl)_2,PtCl_4,H_2O$, which is crystalline, sinters at 85°, and melts at 150° (decomp.). The free cuspareinemethylammonium base could not be isolated. On distillation with zinc dust, cuspareine furnishes quinoline. No definite products could be obtained by the oxidation or reduction of the base.

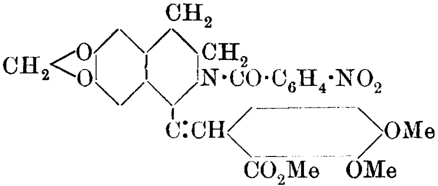
Galipoidine, $C_{19}H_{15}O_4N$, m. p. 233°, is the name suggested for the new alkaloid described already (*loc. cit.*); it yields a *platinichloride*, $B_2,H_2PtCl_6,2\frac{1}{2}H_2O$, which crystallises in stout, yellow prisms and decomposes at 158°, and an *aurichloride*, $(B,HCl)_2,AuCl_3,1\frac{1}{2}H_2O$, m. p. 170° (decomp.), which crystallises in bright yellow needles.

T. A. H.

Synthesis of Oxyberberine. AMÉ PICTET and ALPHONSE GAMS (*Compt. rend.*, 1911, **152**, 1102—1105. Compare Perkin, Trans., 1889, **55**, 63; 1890, **57**, 992).—Piperonal condenses with opianic acid to form homopiperonylamine (Medinger, Abstr.. 1906, i, 421). With formaldehyde in presence of hydrochloric acid, this furnishes *methylenedioxytetrahydro*iso*quinoline*, b. p. 197—199°/15 mm. (formula I).



(I.)



(II.)

The *o-nitrobenzoyl* derivative of this substance (needles, m. p. 103—105°) is dissolved in sulphuric acid and treated with methyl opianate, when the *compound* (formula II) is obtained having m. p. 156—158°. On treatment with alcoholic potassium hydroxide, the latter undergoes hydrolysis with subsequent elimination of water between the imino- and carboxyl groups, and a substance is produced identical with Perkin's oxyberberine. The synthetic product is colourless, whereas the natural compound is coloured by impurities.

Oxyberberine yields a *chloro*-derivative when treated with phosphorus pentachloride, which on reduction forms a base resembling tetrahydroberberine, but not identical with it.

W. O. W.

Corydalis Alkaloids. VII. (Protopine, Glaucine.) JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 224—233).—Previous investigations (Haars, Abstr., 1905, i, 462; Schmidt, 1909, ii, 85) have left it uncertain whether *Corydalis cava* contains protopine, although the widespread occurrence of this alkaloid in the order Papaveraceæ and its discovery by Makoshi in the tubers of *C. ambigua* (Abstr., 1908, i, 825) and *C. Vernyi* (*ibid.*, p. 908) made it probable that protopine was also present in *C. cava.* The author has therefore re-investigated the amorphous alkaloids obtained by Haars from the sub-aerial portion of *C. cava,* and finds that these consist of a mixture of phenolic and non-phenolic bases. The latter include protopine, glaucine, Haars' alkaloid, $C_{21}H_{23}O_7N$ (*loc. cit.*), a fourth *alkaloid*, giving a crystalline perchlorate, and a small quantity of alkaloid from which no crystalline derivatives could be obtained. The phenolic bases include bulbocapnine and at least two new *alkaloids*, which have as yet only been obtained crystalline as the *l*-acid tartrates, of which one (base S) has $[\alpha]_D$ +20°, and the other (base R) has $[\alpha]_D$ +42°. These two bases are closely related to glaucine, and, like it, appear to belong to the bulbocapnine group. Full details are given of the method adopted in the separation of these alkaloids, and a list of the colour reactions of protopine and glaucine with various reagents.

The supposed new alkaloid obtained by Gaebel (Abstr., 1910, i, 501) from *Corydalis cava* is now shown to consist of *i*-corycavine with corycavidine in equal parts, but it is not quite certain whether a definite molecular compound of these two substances, having the properties noted by Gaebel, exists or whether his material is merely a mixture of the two. T. A. H.

Double Salts of Antimony Pentachloride with Various Alkaloid Hydrochlorides. TH. SV. THOMSEN (*K. Danske Selsk. Overs,* 1911, 41—55).

—Ten grams of the alkaloid are dissolved in 200—300 c.c. of 90% alcohol, if necessary, with warming; to the solution are added 30—40 c.c. of 40% hydrochloric acid, and then the calculated quantity of antimony pentachloride, also dissolved in 40% hydrochloric acid (1 gram of antimony pentachloride in 4 c.c. of acid). The double salts separate after some time.

The antimony pentachloride does not have a chlorinating action on the alkaloid. The yield of double salt is 80—90%, except in the case of morphine, where it amounts to 50% only; in this latter case the mother liquors deposit an amorphous mass, which is probably a transformation product.

Quinine hydrochloride antimony pentachloride,

$$C_{20}H_{24}O_2N_2,2HCl,SbCl_5,$$

forms a sulphur-yellow, crystalline powder. *Quinidine hydrochloride antimony pentachloride,* $C_{20}H_{24}O_2N_2,2HCl,SbCl_5$, is obtained as yellow, three-sided prisms. *Cinchonine hydrochloride antimony pentachloride,* $C_{19}H_{22}ON_2,2HCl,SbCl_5,2H_2O$, forms pale yellow, prismatic columns.

Cinchonidine hydrochloride antimony pentachloride,

$$C_{19}H_{22}ON_2,2HCl,SbCl_5,H_2O,$$

forms pale yellow, rectangular plates. *Morphine hydrochloride antimony pentachloride,* $2C_{17}H_{19}O_3N,2HCl,SbCl_5,4H_2O$, is obtained as light brown, thin, irregular plates with serrated edges. *Codeine hydrochloride antimony pentachloride,* $2C_{18}H_{21}O_3N,2HCl,SbCl_5$, forms reddish-brown, irregular plates. *Strychnine hydrochloride antimony pentachloride,* $C_{21}H_{22}O_2N_2,HCl,SbCl_5$, is obtained as red, rhombic plates or short, rhombic prisms. *Cocaine hydrochloride antimony pentachloride,* $C_{17}H_{21}O_4N,HCl,SbCl_5$, forms colourless, thin, irregular plates with a satin glance. *Caffeine hydrochloride antimony pentachloride,* $C_8H_{10}O_2N_4,HCl,SbCl_5,H_2O$, forms yellow crystals of no definite shape. *Nicotine hydrochloride antimony pentachloride,*

$$2(C_{10}H_{14}N_2,2HCl),3SbCl_5,3H_2O,$$

is obtained as pale rose-red, columnar crystals. T. S. P.

Conversion of Glutamic Acid and of Pyrrolidonecarboxylic Acid into Proline. EMIL FISCHER and REGINALD BOEHNER (*Ber.,* 1911, 44, 1332—1337).

—Ethyl pyrrolidonecarboxylate, the anhydride of *d*-glutamic acid, when reduced by sodium and ethyl alcohol is converted into racemic proline.

Ethyl 5-*pyrrolidone*-2-*carboxylate*, prepared by esterification of *d*-glutamic acid with alcohol and anhydrous hydrogen chloride, and heating at 160—170° after removal of the alcohol, crystallises in needles or slender, colourless prisms, which soften at 49°, m. p. 54°. It has $[\alpha]_D^{16}$ $-2{\cdot}47°$, and contains no racemic compound, since on hydrolysis pure *d*-glutamic acid is formed. The corresponding *methyl* ester is a colourless oil, b. p. 180°/12 mm.

5-*Pyrrolidone*-2-*carboxylamide*, obtained by interaction of the ethyl ester with ammonia, has m. p. 165°, and is strongly lævorotatory.

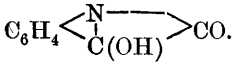
E. F. A.

Pseudo-bases of the Pyridine Series. Wilhelm König (*J. pr. Chem.*, 1911, [ii], **83**, 406—418).—Kaufmann and Strübin have recorded their opinion that the pseudo-ammonium bases of the quinoline, *iso*quinoline, and acridine series function as either carbinols or as unsaturated aldehydeamines (this vol., i, 321). This view, which which has been advanced and discussed by the author in 1907, is supported by the behaviour of the pseudo-bases of the pyridine series. The following example is an instance of the method by which such pseudo-bases are conveniently prepared. *m*-Chloroaniline and cyanogen bromide yield by Zincke's method (Abstr., 1904, i, 449, 921; compare also König, Abstr., 1904, i, 449, 816) the *pyridine dye*,

$$C_6H_4Cl{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH(OEt){\cdot}NH{\cdot}C_6H_4Cl,HBr,$$

m. p. 165°, red needles with blue shimmer, which is converted by phenylhydrazine (2 mols.) into α-m-*chloroanilino*-ε-*phenylhydrazinopiperylene*, $C_{17}H_{16}N_3Cl$, m. p. 141°, yellow needles, and by warming with nitrobenzene yields m-*chlorophenylpyridinium bromide*, $C_{11}H_9NClBr$, m. p. 87—89°, colourless crystals, corresponding with which a *ferrichloride*, $C_{11}H_9NCl_2,FeCl_3$, m. p. 127—128°, sulphur-yellow leaflets, *ferribromide*, m. p. 120°, reddish-brown needles, *picrate*, m. p. 137—138°, citron-yellow needles, *dichromate*, decomp. 198°, orange leaflets, *platinichloride*, m. p. 191° (decomp.), and *aurichloride*, m. p. 182°, are described. By decomposing it with bromine, best in methyl alcohol (in glacial acetic acid, 3-*chloro*-2 : 4 : 6-*tribromoacetanilide*, m. p. 225°, is obtained as a by-product), the pyridine dye yields 3-*chloro*-2 : 4 : 6-*tribromophenylpyridinium perbromide*, $C_5H_5NBr_3{\cdot}C_6HClBr_3$, m. p. 171°, a solution of which in acetone is decomposed by ether with the formation of the corresponding *bromide*, $C_{11}H_6NClBr_4,2H_2O$ (from water), m. p. above 275° (*picrate*, m. p. 170°, *aurichloride*, m. p. 237°, *ferrichloride*, m. p. 154°, *platinichloride*, m. p. 233°). Finally, the *pseudo-base*, m. p. about 78° (decomp.), is obtained as a yellow precipitate, darkening in light, by treating a cold aqueous solution of the chlorotribromophenylpyridinium bromide with ammonium carbonate; it regenerates pyridinium salts by boiling with acids. When boiled with ethyl alcohol the pseudo-base yields a nearly colourless *ethyl alcoholate*, $C_{13}H_{13}O_2NClBr_3$, m. p. 122°; also with methyl alcohol a *methyl alcoholate*, $C_{12}H_{11}O_2NClBr_3$, m. p. 129°, is produced, which can also be obtained by crystallising the ethyl alcoholate from methyl alcohol. The formation of these compounds is explained by ascribing the aldehydeamine formula, $C_6HClBr_3{\cdot}NH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CHO$, to the pseudo-base; the alcoholates are then produced by the addition of the alcohols at the carbonyl group, C. S.

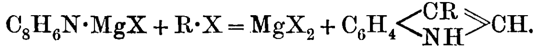
The Tautomerism of Isatin. F. Carlo Palazzo and G. Scelsi (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 243—244).—Isatin reacts with diazomethane or diazoethane at the ordinary temperature, forming *O*-ethers differing from those previously known, and assumed to be derived from a third modification of isatin,



$$C_6H_4<\begin{matrix}N\text{———}\\ |\\ C(OH)\end{matrix}>CO.$$

C. H. D.

Syntheses in the Indole Group. I. Alkylindoles. Bernardo Oddo (*Gazzetta*, 1911, **41**, i, 221—234).—The preparation of homologues of indole has not previously been effected by the direct action of alkyl iodides, but the author finds that by using magnesium indolyl iodide these homologues can be readily obtained. The inorganic portion of the molecule is eliminated and the two organic radicles unite, giving the indole substituted in the 3-position:



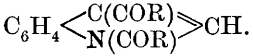
$$C_8H_6N{\cdot}MgX + R{\cdot}X = MgX_2 + C_6H_4<\begin{matrix}CR\\NH\end{matrix}>CH.$$

In some cases, owing to differences in the experimental conditions difficult to define, the alkyl enters in the 1-position, and in these cases traces of the 1:3-dialkyl derivative are also formed. The elimination of the inorganic portion of the magnesium indolyl iodide is facilitated by the presence of a small proportion of calcined potassium chloride. Since it is observed that when the halogen is the same in the two molecules the double decomposition occurs with difficulty, but that chloro-derivatives react readily with magnesium alkyl iodides, the action of the potassium chloride may be regarded as catalytic in nature: $RI + KCl = KI + RCl$. In this way the author has prepared the following indole derivatives:

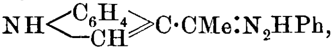
(1) Scatole (3-methylindole), which is accompanied by a small proportion of a non-basic compound forming microscopic, pale yellow, bipyramidal crystals, m. p. 197—200°. (2) 1-Methylindole, which is formed along with traces of a product forming yellow crystals, m. p. 197—200°; and (3) 3-ethylindole.

Magnesium indolyl iodide forms an additive compound with pyridine, $C_{11}H_{11}N_3MgI$, as a flocculent, white precipitate; with water this compound yields indole, pyridine and magnesium iodide and hydroxide.

Addition of saturated mercurous nitrate solution to an alcoholic solution of scatole (or indole) results in the formation of a yellow (or greyish-green) precipitate insoluble in water. With mercuric nitrate, under the same conditions, scatole gives a pale yellow and indole a grey precipitate. With mercuric chloride, scatole or indole or 2-methylindole gives a white precipitate. T. H. P.

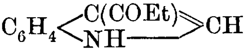
Syntheses in the Indole Group. II. Alkylindolyl Ketones and Indole Acids. Bernardo Oddo and Luigi Sessa (*Gazzetta*, 1911, **41**, i, 234—248. Compare preceding abstract).—The action of acyl chlorides on magnesium indolyl iodide in presence of ether at the ordinary temperature gives rise to 3-acylindoles (indolyl alkyl ketones), $C_6H_4{<}\substack{C\cdot COR\\NH}{>}CH$, which are accompanied by small proportions of 1 : 3-diketones,  $C_6H_4{<}\substack{C(COR)\\N(COR)}{>}CH$.

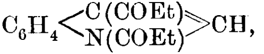
Thus, acetyl chloride and magnesium indolyl iodide yield 3-acetylindole (3-indolyl methyl ketone) (compare von Baeyer, Abstr., 1879, **36**, 937), the *phenylhydrazone* of which,



$$NH{<}\substack{C_6H_4\\CH}{>}C\cdot CMe{:}N_2HPh,$$

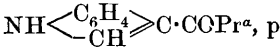
forms pale yellow, acicular crystals, m. p. 118°. 1 : 3-Diacetylindole (compare von Baeyer, *loc. cit.*) is formed in small amount with the 3-acetyl compound.

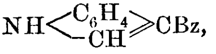
3-*Indolyl ethyl ketone* (3-*propionylindole*),  $C_6H_4{<}\substack{C(COEt)\\NH}{>}CH$, prepared from propionyl chloride and magnesium indolyl iodide, forms crystals, m. p. 157—158°, and, on fusion with potassium hydroxide, yields indole-3-carboxylic acid. Its *oxime*, $C_{11}H_{12}ON_2$, forms white crystals, m. p. 120—122°, and its *phenylhydrazone*, $C_{17}H_{17}N_3$, red crystals, m. p. 109—110°. It is accompanied by 1 : 3-*dipropionylindole*,



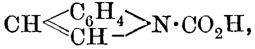
$$C_6H_4{<}\substack{C(COEt)\\N(COEt)}{>}CH,$$

m. p. 128—130°, which is converted into 3-propionylindole on boiling with 50% potassium hydroxide solution.

3-*Indolyl propyl ketone* (3-*butyrylindole*),  $NH{<}\substack{C_6H_4\\CH}{>}C\cdot COPr^a$, prepared from butyryl chloride and magnesium indolyl iodide, forms white crystals, m. p. 169°, and yields a crystalline phenylhydrazone, m. p. 107°.

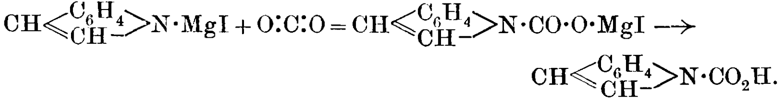
3-*Indolyl phenyl ketone* (3-*benzoylindole*),  $NH{<}\substack{C_6H_4\\CH}{>}CBz$, prepared from benzoyl chloride and magnesium indolyl iodide, forms red crystals, m. p. 170°, and is probably mixed with a little 1 : 3-dibenzoylindole, since, on boiling with 50% potassium hydroxide solution and a small quantity of alcohol, the m. p. rises to 227°. The *phenylhydrazone*, $C_{21}H_{17}N_3$, forms yellow crystals, m. p. 192—194°, and the *silver* derivative is a precipitate soluble in excess of ammonia.

The action of carbon dioxide on magnesium indolyl iodide in anhydrous ethereal solution, yields *indole*-1-*carboxylic acid*,



$$CH{<}\substack{C_6H_4\\CH}{>}N\cdot CO_2H,$$

m. p. 108°, which is decomposed by boiling water into indole and carbon dioxide and gives a white precipitate with barium chloride or lead acetate solution. The formation of the acid proceeds thus:

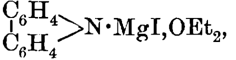


$$CH{<}\substack{C_6H_4\\CH}{>}N\cdot MgI + O{:}C{:}O = CH{<}\substack{C_6H_4\\CH}{>}N\cdot CO\cdot O\cdot MgI \longrightarrow CH{<}\substack{C_6H_4\\CH}{>}N\cdot CO_2H.$$

Ethyl indole-2-carboxylate, $C_6H_4{<}\begin{smallmatrix}CH\\NH\end{smallmatrix}{>}C\cdot CO_2Et$, prepared by the interaction of ethyl chlorocarbonate and magnesium indolyl iodide, forms white crystals, m. p. 107°. T. H. P.

Transpositions with the Organo-magnesium Compounds. I. BERNARDO ODDO (*Gazzetta*, 1911, **41**, i, 255—272; and, in part, *7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI., 226—231).—In order to ascertain whether it is possible to obtain organo-magnesium compounds in which the MgX-radicle shall be attached first and with certainty to a nitrogen atom, the author has made use of carbazole, which is analogous in constitution to pyrrole and indole (compare preceding abstracts and this vol., i, 496), and of diphenylamine; in both of these compounds the iminic nitrogen is united to two quaternary carbon atoms, and in carbazole, in addition, two of the carbon atoms adjacent to these quaternary carbon atoms are devoid of hydrogen.

It is found that carbazole readily gives the compound



$$\begin{array}{l}C_6H_4\\ \,|\\ C_6H_4\end{array}\!\!>N\cdot MgI,OEt_2,$$

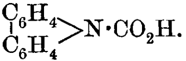
and a similar result is obtained with diphenylamine.

The iodomagnesium derivative of carbazole is readily acted on by acyl chlorides, but not by alkyl iodides, and the latter act the less readily with organo-magnesium indole compounds. The action of an acid chloride seems to be favoured by the presence of the double linking between oxygen and carbon, an additive product being formed first:

$$R\colon N\cdot MgI + O\colon CR'Cl = R\colon N\cdot CR'Cl\cdot O\cdot MgI = MgICl + R\colon N\cdot CO\cdot R'.$$

It was shown by Oddo and Mameli (Abstr., 1902, i, 33) that Kolbe's reaction between sodium phenoxides and carbon dioxide for the formation of the aromatic hydroxy-acids takes place, in some cases, in presence of neutral solvents. The author has now investigated the action of carbon dioxide on the iodomagnesium derivatives of various phenols, which undergo conversion into the corresponding hydroxy-acids. With the phenol and the resorcinol derivatives, this change occurs only in absence of solvent, and at a high temperature, the acid in latter case having the constitution: $CO_2H:(OH)_2 = 1:2:4$. With derivatives of the following phenols, the reaction proceeds in presence of solvent (benzene or toluene): β-naphthol, which gives β-naphthol-α-carboxylic acid; phloroglucinol, giving phloroglucinolcarboxylic acid; thymol, giving *o*-thymotic acid $[CH_3:CO_2H:OH:C_3H_7 = 1:2:3:4]$; *o*-cresol, giving *o*-cresotic acid; and carvacrol, giving carvacrotic acid $[CH_3:OH:C_3H_7:CO_2H = 1:2:4:6]$.

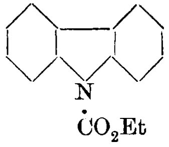
The *compound*, $C_{12}H_8N\cdot MgI,OEt_2$, is obtained as a white, amorphous powder, and, on treatment with carbon dioxide in presence of ether, toluene or cymene, it is converted into the unstable *acid*,



$$\begin{array}{l}C_6H_4\\ \,|\\ C_6H_4\end{array}\!\!>N\cdot CO_2H.$$

If, however, the carbon dioxide acts at a high temperature (265—270°) and in absence of solvent, Ciamician and Silber's carbazole-carboxylic acid, $CO_2H\cdot C_6H_3{<}\begin{smallmatrix}NH\\ |\\ C_6H_4\end{smallmatrix}$ (Abstr., 1882, **42**, 1103), is obtained.

Diphenyleneurethane [*Ethyl carbazole-9-carboxylate*] (annexed formula), prepared by the action of ethyl chlorocarbonate on the iodomagnesium derivative of carbazole, crystallises in needles, m. p. 77·5°, and has the normal molecular weight in freezing benzene. On heating with alcoholic potassium hydroxide or with ammonia in a sealed tube, it is decomposed into carbazole, alcohol, and carbon dioxide. Acetylcarbazole, $\begin{matrix}C_6H_4\\ | \\ C_6H_4\end{matrix}\!>\!NAc$, and the corresponding benzoylcarbazole may be readily prepared by the action of acetyl and benzoyl chlorides on the iodomagnesium compound.



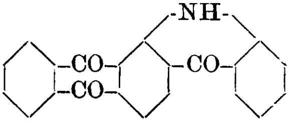
The *iodomagnesium* derivative of *diphenylamine*, $NPh_2{\cdot}MgI$, forms a greyish-brown oil, and is converted by carbon dioxide into the *acid*, $C_6H_5{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H$, which forms silvery-white scales, m. p. 152°; the *silver* and *barium* salts of this acid were prepared. With ethyl chlorocarbonate the iodomagnesium derivative gives diphenylurethane, $CO_2Et{\cdot}NPh_2$. T. H. P.

Anthraquinone Series. IV. Anthraquinone-1 : 2-acridone and Anthraquinonediacridone. FRITZ ULLMANN and PAUL OCHSNER (*Annalen*, 1911, **381**, 1—11. Compare Abstr., 1910, i, 270, 696; this vol., i, 136; following abstract).—A 95% yield of 1-chloroanthraquinone can be obtained by dropping a solution of sodium chlorate into a well-stirred boiling solution of potassium anthraquinone-1-sulphonate and concentrated hydrochloric acid. It crystallises from alcohol in yellow needles, m. p. 162°. The method appears to be a general one for replacing sulphonic acid groups in the anthraquinone series by chlorine (compare D.R.-P. 77179 and 205195). It affords a convenient method for identifying the various sulphonic acids, as the corresponding chlorine derivatives have definite melting points.

Anthraquinone-1-*anilino*-o-*carboxylic acid*,

$$C_6H_4{:}(CO)_2{:}C_6H_3{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,$$

may be obtained by the catalytic action of copper on *o*-chlorobenzoic acid and 1-aminoanthraquinone, or, better, on anthranilic acid and 1-chloroanthraquinone. In the latter case, amyl alcohol is used as solvent, together with potassium acetate and finely-divided copper at a temperature of 150—160°. It crystallises from glacial acetic acid in Bordeaux-red plates, m. p. 282°. Its solution in pyridine has a red colour, but turns violet on the addition of a little water. The *alkali* salts are sparingly soluble in water, and have a bluish-violet colour. The anhydride, *anthraquinone*-1 : 2-*acridone* (annexed formula), is formed by the action of concentrated sulphuric acid on the acid at 100—110°, or in a purer form by transforming the acid into its chloride and boiling this for some minutes with nitrobenzene. It forms violet crystals with a coppery lustre, is readily reduced by alkali and hyposulphite, and dyes cotton a reddish-blue. The *bromo*-derivative, $C_{21}H_{10}O_3NBr$, obtained by the

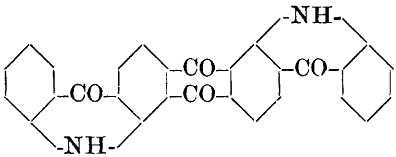


action of bromine on a nitrobenzene solution of the acridone, crystallises in red needles, m. p. 339° (corr.).

1 : 5-Dichloroanthraquinone and anthranilic acid with nitrobenzene, potassium acetate, copper acetate, and a little copper powder at 200° yield *anthraquinone*-1 : 5-*dianilinodi*-o-*carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot NH\cdot C_6H_4\colon(CO)_2\colon C_6H_4\cdot NH\cdot C_6H_4\cdot CO_2H\ ;$$

it crystallises from glacial acetic acid, in which it is sparingly soluble, in reddish-violet needles, m. p. 349° (corr.). *Anthraquinone*-2 : 1 : 6 : 5-*diacridone* :



crystallises from nitrobenzene in bluish-violet needles, m. p. 360°, and it dyes cotton the same colour. Its solubility in boiling nitrobenzene is only 1 in 1000. J. J .S.

Anthraquinone Series. V. Dichloroanthraquinones. FRITZ ULLMANN and GERHARD BILLIG (*Annalen*, 1911, **381**, 11—28).—1 : 2-, 2 : 3-, and 1 : 4-Dichloroanthraquinones have been synthesised from the corresponding dichlorophthalic acids. The product described by Kircher (Abstr., 1887, 831) as 1 : 2-dichloroanthraquinone is shown to be the 2 : 3-compound. The product described by Hammerschlag (Abstr., 1886, 717) has the same m. p. as the 1 : 2-dichloroanthraquinone, namely, 208°, but a mixture of the two melts at 175—180°.

The 1 : 4-derivative is reactive, and the two chlorine atoms can be replaced by phenoxy-, anilino-, and similar groups ; with anthranilic acid, however, only one chlorine atom is replaced.

3 : 6-*Dichloro-2-benzoylbenzoic acid*, $CO_2H\cdot C_6H_2Cl_2\cdot COPh$, crystallises from benzene in glistening, colourless prisms, m. p. 168·5° (corr.). 1 : 4-Dichloroanthraquinone, $C_{14}H_6O_2Cl_2$, is obtained when the finely divided acid (1 part) is added gradually to concentrated sulphuric acid (20 parts) heated at 160°, cooled to 70—80°, and ice added. It crystallises from glacial acetic acid in orange-yellow needles, m. p. 187·5° (corr.), and reacts with sodium phenoxide in the presence of finely divided copper, yielding 1 : 4-diphenoxyanthraquinone, $C_{26}H_{16}O_4$, which crystallises from alcohol in yellow needles, m. p. 165°. The solution in concentrated sulphuric acid has a bluish-violet colour (compare Walsh and Weizmann, Trans., 1910, **97**, 685).

1 : 4-*Di*-p-*tolylsulphonamidoanthraquinone*,

$$C_6H_4(CO)_2\cdot C_6H_2(NH\cdot SO_2\cdot C_7H_7)_2,$$

prepared by boiling for two hours a solution of the chlorinated quinone in nitrobenzene with *p*-toluenesulphonamide, potassium carbonate, and a little copper acetate, crystallises from boiling acetic acid in large, glistening, reddish-brown needles, m. p. 225°. Its solubility in boiling glacial acetic acid is 1 in 200. 1 : 4-Diaminoanthraquinone (Noelting and Wortmann, Abstr., 1906, i, 291) gives a violet-blue solution in glacial acetic acid, and reddish-violet solutions in benzene or pyridine. 1 : 4-*Dianilinoanthraquinone*, $C_{26}H_{18}O_2N_2$, crystallises from glacial acetic acid in glistening, blue plates with a brown lustre; it has m. p. 217°, and is coloured greenish-blue by concentrated sulphuric acid.

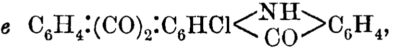
1 : 4-*Di-a-aminoanthraquinoylanthraquinone*,

$$C_6H_4{:}(CO)_2{:}C_6H_2(NH{\cdot}C_{14}H_7O_2)_2,$$

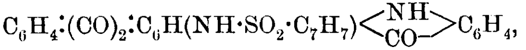
obtained by condensing the chlorinated quinone with 1-aminoanthraquinone, is insoluble in practically all organic solvents, and, after purifying by extracting successively with toluene, aniline, alcohol, and dilute hydrochloric acid, forms glistening, violet needles, which are not fused at 410°.

4-*Chloro*-1-o-*carboxyanilinoanthraquinone*,

$$C_6H_4{:}(CO)_2{:}C_6H_2Cl{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H,$$

obtained by condensing 1 : 4-dichloroanthraquinone and anthranilic acid in hot amyl-alcoholic solution in the presence of potassium acetate and copper acetate for fifteen hours, crystallises from glacial acetic acid (1 in 200) in felted, Bordeaux-red needles, m. p. 262—263° (corr.), and gives a dark green coloration with concentrated sulphuric acid. The acid chloride in the presence of boiling nitrobenzene yields 4-*chloroanthraquinone*-2 : 1-*acridone*  $C_6H_4{:}(CO)_2{:}C_6HCl{<}\begin{smallmatrix}NH\\CO\end{smallmatrix}{>}C_6H_4$, in the form of glistening, violet needles, m. p. 267° (corr.), which dye cotton reddish-violet.

4-p-*Toluenesulphonamidoanthraquinone*-2 : 1-*acridone*,

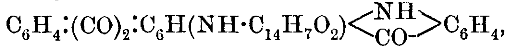


$$C_6H_4{:}(CO)_2{:}C_6H(NH{\cdot}SO_2{\cdot}C_7H_7){<}\begin{smallmatrix}NH\\CO\end{smallmatrix}{>}C_6H_4,$$

crystallises from nitrobenzene in small, bluish-black needles, m. p. 295°. Its solubility in boiling glacial acetic acid is 1 in 3000. 4-*Aminoanthraquinone*-2 : 1-*acridone*, $C_{21}H_{12}O_3N_2$, obtained by hydrolysing the toluenesulphonamido-derivative with sulphuric acid, crystallises from nitrobenzene in dark blue needles, which are not molten at 410°, and dyes cotton blue.

4-p-*Toluidinoanthraquinone*-2 : 1-*acridone*, $C_{28}H_{18}O_3N_2$, crystallises from nitrobenzene in glistening, bluish-green needles, m. p. 300°.

4-a-*Aminoanthraquinoylanthraquinone*-2 : 1-*acridone*,



$$C_6H_4{:}(CO)_2{:}C_6H(NH{\cdot}C_{14}H_7O_2){<}\begin{smallmatrix}NH\\CO\end{smallmatrix}{>}C_6H_4,$$

forms felted, violet needles, insoluble in organic solvents, and dyes cotton a bluish-green.

3 : 4- or 5 : 6-Dichlorobenzoylbenzoic acid has m. p. 216°. 1 : 2-*Dichloroanthraquinone* crystallises from glacial acetic acid in golden-yellow needles, m. p. 208°.

4 : 5-*Dichlorobenzoylbenzoic acid* crystallises from benzene in glistening, colourless needles, m. p. 209°, and with concentrated sulphuric acid yields 2 : 3-*dichloroanthraquinone*, which crystallises from glacial acetic acid in long, pale yellow needles, m. p. 267° (corr.).

J. J. S.

Preparation of 5-Methyl*iso*oxazole from the Acetals of Tetrolaldehyde. Ludwig Claisen (*Ber.*, 1911, **44**, 1161—1169).—Starting from crotonaldehyde, the author has synthesised 5-methyl*iso*-

oxazole, and finds that it is identical in all respects with the compound previously described (Abstr., 1909, i, 185).

αβ-Dibromobutaldehyde has b. p. 75—82°/14 mm., and is converted by sodium acetate into *α*(?)-bromocrotonaldehyde (compare Viguier, Abstr., 1910, i, 461). When methylated by means of methylorthoformate in methyl-alcoholic solution, this gives *β(?)-bromo-αα-dimethoxy-Δ^{β}-butylene*, $C_3H_4Br\cdot CH(OMe)_2$, a colourless liquid, b. p. 175°, under ordinary pressure, or 59°/10 mm., D^{15} 1·357, having an odour of camomile. The diethoxy-compound may be prepared in a similar manner.

αα-Dimethoxybutinene, $CMe{:}C\cdot CH(OMe)_2$, prepared by heating the preceding bromodimethoxy-derivative with methyl-alcoholic potassium hydroxide, is a colourless liquid with a penetrating odour, b. p. 144—145°, D^{15} 0·954. It is converted by continued heating with sodium methoxide in methyl-alcoholic solution into an oil, b. p. 160—166°, consisting probably of *ααγ-trimethoxy-Δ^{β}-butylene*, $OMe\cdot CMe{:}CH\cdot CH(OMe)_2$.

Tetrolaldehyde, $CMe{:}C\cdot CHO$, obtained in small yield by hydrolysing dimethoxybutinene with mineral acids, is a colourless liquid, with an intolerably sharp odour, resembling acraldehyde; it is decomposed by cold aqueous sodium hydroxide into allylene and sodium formate. The *oxime*, C_4H_5ON, obtained together with 5-methyl*iso*oxazole by shaking dimethoxybutinene with aqueous hydroxylamine hydrochloride and a small quantity of hydrochloric acid, crystallises in large needles, m. p. 103°. On treatment with excess of sodium hydroxide or of alcoholic sodium ethoxide, it is transformed with explosive violence into cyanoacetone. With minute quantities of sodium hydroxide, it yields 5-methyl*iso*oxazole. The transformation into the latter compound is, however, best effected with aqueous sodium carbonate.

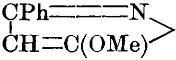
F. B.

Esterification of the *iso*Oxazolones with Diazomethane.

E. Oliveri-Mandalà and A. Coppola (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 244—249).—To ascertain if the *iso*oxazolones can behave tautomerically, like their analogues the pyrazolones, the authors have investigated the esters obtainable from them by the action of diazomethane.

γ-Methyl*iso*oxazolone yields an *N*-methyl derivative, m. p. 74°, identical with that prepared by Uhlenhuth (Abstr., 1897, i, 444), and a *C*-methyl *derivative*, $C_9H_{10}O_3N_2$, m. p. 163—164°, which may be separated from the former by reason of its insolubility in light petroleum; it crystallises in very small needles. Both substances are obtained in the form of a condensation product of one molecule of the ester with one molecule of the methyl*iso*oxazolone, and Uhlenhuth observed a similar behaviour in the case of the salts.

γ-Phenyl*iso*oxazolone gives an *N*-methyl derivative, m. p. 77—78°, identical with that of Uhlenhuth (*loc. cit.*), and also an *O-ester*,



$\left.\begin{array}{l}\mathrm{CPh{=\!=\!=}N}\\ \mathrm{CH{=}C(OMe)}\end{array}\right>\mathrm{O}$, m. p. 70°, which crystallises in silky needles and contains one methoxyl group.

R. V. S.

[Preparation of Methyl-2 : 4-diaminoanisole.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 230630).—*Methyl-2 : 4-diaminoanisole*, a colourless oil, b. p. 180°/15 mm., and very sparingly soluble in water, is prepared by the action of methyl sulphate on an aqueous solution of 2 : 4-diaminoanisole at 40—50°.

F. M. G. M.

[Preparation of Dichlorodinitrobenzidine.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 229029).—2 : 2′-*Dichloro*-5 : 5′-*dinitrobenzidine*, a yellow powder, m. p. 255°, is obtained by the nitration and subsequent hydrolysis of 2 : 2′-dichlorodiacetylbenzidine; when tetrazotised and combined with 2 mols. of β-naphthol, it yields 2 : 2′-*dichloro*-5 : 5′-*dinitrodiphenylbisazo*-β-*naphthol*, a red substance which (being soluble in oils) is suitable for employment as a pigment.

F. M. G. M.

***holo*- and *meri*-Quinonoid Salts of Benzidine.** JEAN PICCARD (*Ber.*, 1911, **44**, 959—960. Compare this vol., i, 323).—Polemical. Madelung claims to have proved the existence of strongly-coloured *holo*-quinonoid imonium salts of benzidine. When a *meri*-quinonoid salt is precipitated and a further amount of bromine added to the filtered salt, a *meri*-quinonoid salt of a brominated benzidine and not a *holo*-quinonoid salt is formed. Benzidine with less than two atoms of halogen yields bluish-violet, blue or green *meri*-quinonoid salts, whereas the *holo*-quinonoid imonium salt with two atoms of halogen is only yellow in colour.

E. F. A.

Resolution of Asymmetric Diammonium Compounds into Optical Antipodes. EMIL FRÖHLICH (*Ber.*, 1911, **44**, 1057—1070).—The author has prepared substances of the type $Y(NR'R'')_2$, where $Y = CH_2$, C_2H_4, or C_3H_6, and R′ and R″ are various alkyl or aryl groups (Abstr., 1907, i, 346). By the addition of alkyl or aryl halogenides, R‴X, asymmetric diammonium compounds should be formed. This happens, however, only when Y is C_3H_6; thus Wedekind has obtained two series of isomeric trimethylenebisphenylmethylethylammonium derivatives, which, however, he was unable to resolve into optically active components (Abstr., 1910, i, 834). The author attributes the failure to the presence of impurities, and has therefore prepared other series of the di-tertiary bases in a pure state. First he obtained NN′-*dimethyl*-NN′-*diethylbenzidine*, $NMeEt\cdot C_6H_4\cdot C_6H_4\cdot NMeEt$, m. p. 110°, by oxidising methylethylaniline with concentrated sulphuric acid, but found that it formed only a *mono-allyloiodide*, $NMeEt\cdot C_6H_4\cdot C_6H_4\cdot NMeEt(C_3H_5)I$, m. p. 154—155° (decomp.), and *monobenzylobromide*,

$$NMeEt\cdot C_6H_4\cdot C_6H_4\cdot NMeEtBr\cdot CH_2Ph,$$

m. p. 146—147° (decomp.). Better results, however, have been obtained with derivatives of pp′-diaminodiphenylmethane. NN′-*Dimethyl*-NN′-*diethyl*-pp′-*diaminodiphenylmethane*, $CH_2(C_6H_4\cdot NMeEt)_2$, m. p. 40°, b. p. 282°/40 mm., obtained by boiling methylethylaniline with concentrated hydrochloric acid and 34% formaldehyde for three to four hours, forms additive compounds with 2 mols.

of allyl iodide or of benzyl bromide. Theoretically two isomerides belonging to the *para*- and the *meso*-series respectively should be produced in each case, but experience shows that the *as*-diammonium salts are individual and belong to the *para*-series (since the allyl derivative has been resolved into its active components). Thus p-*methylenebisphenylenebisallylmethylethylammonium iodide*,

$$CH_2(C_6H_4{\cdot}NMeEtI{\cdot}C_3H_5)_2,$$

m. p. 174° (decomp.), obtained from *NN'*-dimethyl-*NN'*-diethyl-*pp'*-diaminodiphenylmethane and allyl iodide (2 mol.) in alcohol, is resolved by silver *d*-camphorsulphonate in alcohol-acetone solution. The less soluble *dicamphorsulphonate*, as first precipitated, has m. p. 159—160° and $[M]_D$ $+89{\cdot}32°$. It is purified by solution in alcohol and precipitation by ether. After twenty-four repetitions of this operation a fraction is obtained having m. p. 159—160° and $[M]_D$ $+34{\cdot}06°$, from which the value $[M]_D$ $-69{\cdot}34°$ is calculated for the active diammonium ion. From the active dicamphorsulphonate the active *di-iodide* is obtained by addition of potassium iodide; it has m. p. 174° and $[M]_D$ $-68{\cdot}66°$ in alcoholic solution. The alcohol-acetone mother liquor, from which the active dicamphorsulphonate has been precipitated, is concentrated and treated with ether, the oil obtained is dissolved in warm water and treated with potassium iodide, whereby d-p-*methylenebisphenylenebisallylmethylethylammonium iodide*, m. p. 174°, is obtained; the maximal value of $[M]_D$ is $+29{\cdot}93°$. p-*Methylenebisphenylenebisallylmethylethylammonium bromide*, m. p. 205° (decomp.), can also be resolved by silver *d*-camphorsulphonate, but in consequence of the slight difference in the solubilities of the two dicamphor sulphonates the fractionation has not been continued.

An alcoholic solution of *NN'*-dimethyl-*NN'*-diethyl-*pp'*-diaminodiphenylmethane reacts with benzyl iodide (2 mols.) to form p-*methylenebisphenylenebisbenzylmethylethylammonium iodide*, m. p. 129—130° (decomp.), and with benzyl bromide (2 mols.) to form the corresponding *dibromide*, m. p. 145° (decomp.); the latter yields with silver *d*-camphorsulphonate a *dicamphorsulphonate*, $C_{53}H_{70}O_8N_2S_2$, m. p. 130—140°, which has $[M]_D$ $+97{\cdot}07°$, and therefore shows practically no indication of being resolved ($[M]_D = +103{\cdot}4°$ for two *d*-camphorsulphonic ions).

NN-*Dimethyl*-NN'-*dipropyl*-pp'-*diaminodiphenylmethane*,

$$CH_2(C_6H_4{\cdot}NMePr^{\alpha})_2,$$

b. p. 295—297°/40 mm., obtained from methylpropylaniline, hydrochloric acid, and formaldehyde, combines with alcoholic allyl iodide to form p-*methylenebisphenylenebisallylmethylpropylammonium iodide*, $C_{27}H_{38}N_2I_2$, m. p. 140° (decomp.), and with allyl bromide to form the corresponding *dibromide*, m. p. 135° (decomp.); the *di*-d-*camphorsulphonate*, $C_{47}H_{70}O_8N_2S_2$, has m. p. 130° (decomp.) and $[M]_D$ $+102{\cdot}3°$, and cannot be resolved into its two components. C. S.

The Oxidation and Auto-reduction of Hydrazines.

FREDERICK D. CHATTAWAY (*Chem. News*, 1911, **103**, 217—218. Compare Trans., 1911, **99**, 404).—Phenylhydrazine readily absorbs oxygen with development of heat, gives off nitrogen, and forms benzene. The reaction is found to be general for all aromatic hydrazines: $2RHN-NH_2+O_2=2RH+2N_2+2H_2O$. The author supposes that a hydrogen atom of the $-NH_2$-group is first attacked with production of a hydroxy-hydrazine, which, being unstable, undergoes a disruption analogous to the typical diazonium decomposition. Potassium hydroxide, and to a less extent sodium hydroxide, very much accelerates the rate of oxidation; indeed, on exposing to the air a solution of phenylhydrazine in alcoholic potash the temperature rises, and nitrogen is rapidly given off with vigorous effervescence. Potassium chromate in alkaline solution acts in the same way; the reaction is quantitative, so that the evolved nitrogen can be used as a measure of the amount of hydrazine present. The reaction further affords the most satisfactory method known of replacing an amino-group by hydrogen; the amino-group is converted through the diazonium salt into the hydrazine group, which is then oxidised as above. E. J. R.

Experiments on the Preparation of Derivatives of Hydroxyhydrazines. HEINRICH WIELAND and HANS FRESSEL (*Ber.*, 1911, **44**, 898—904).—Attempts have been made to synthesise derivatives of hydroxyhydrazine by the action of Grignard reagents on nitrosoamines, according to the scheme:

$$NR_2\cdot NO + R'MgX \longrightarrow NR_2\cdot NR'\cdot OH,$$

but so far without success.

Diethylnitrosoamine reacts with magnesium ethyl iodide, yielding ethane and a liquid consisting mainly of acetaldehydediethylhydrazone. The latter compound is produced from the initial additive product, $NEt_2\cdot NEt\cdot O\cdot MgI$ by the loss of $MgI\cdot OH$, which then reacts with a second molecule of magnesium ethyl iodide to form ethane. For the purpose of comparison, *acetaldehydediethylhydrazone*,

$$CHMe\colon N\cdot NEt_2,$$

was prepared by the interaction of acetaldehyde and diethylhydrazine in aqueous solution. It has b. p. 123—126°, and is readily decomposed by dilute mineral acids into its components.

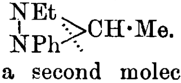
Dimethylnitrosoamine, on treatment with magnesium methyl iodide, yields methane, the reaction apparently proceeding in a similar manner to that already described in the case of diethylnitrosoamine.

When diphenylnitrosoamine is treated with magnesium ethyl iodide, ethane and acetaldehydediphenylhydrazone are produced.

The interaction of diethylnitrosoamine and magnesium phenyl bromide leads to the formation of *α-phenyl-β(α)-phenylethyl-β-ethylhydrazine*, $NHPh\cdot NEt\cdot CHMePh$, and *α-phenyl-ββ-diethylhydrazine*, $NEt_2\cdot NHPh$. The latter compound is a light yellow, viscid oil, b. p. 110—112°/14 mm., having a geranium-like odour, and forms a yellow, oily *nitroso*-compound, a crystalline *hydrochloride*, and a yellow *picrate*, m. p. 131°. When reduced with zinc dust and glacial acetic acid it yields aniline and diethylamine.

α-Phenyl-β(α)-phenylethyl-β-ethylhydrazine is a greenish-yellow, viscid oil, b. p. 177°/10 mm. It forms an oily *nitroso*-compound, which decomposes when kept, yielding benzenediazonium chloride; its salts were all obtained in the form of oils. When reduced with zinc and glacial acetic acid, it yields aniline and *a-phenylethylethylamine*, NHEt·CHMePh. The last-mentioned compound, which, for the purpose of comparison, was also prepared by the interaction of *a*-phenylethylamine and ethyl sulphate, has b. p. 125—127°/94 mm., and forms a *hydrochloride*, crystallising in slender needles, m. p. 196—197°; the *nitrosoamine* is a yellow oil.

The formation of phenyldiethylhydrazine by the action of magnesium phenyl bromide on diethylnitrosoamine is due to the reduction of the initial additive product, $NEt_2·NPh·O·MgBr$, whilst the formation of *a*-phenyl-*β*(*a*)-phenylethyl-*β*-ethylhydrazine is referred by the authors to the intermediate production of a cyclic hydrazi-compound:



$$\begin{array}{l} NEt \\ | \\ NPh \end{array} \!\!\!> CH·Me.$$

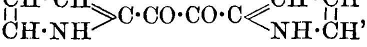
Under the influence of a second molecule of magnesium phenyl bromide, the ring of the latter compound is opened with the formation of phenyl-*a*-phenylethylethylhydrazine, the addition of C_6H_5 and H taking place at the position indicated by the dotted line.

F. B.

Syntheses in the Pyrrole Group. III. Dipyrroyl and its Derivatives.

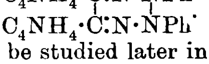
Bernardo Oddo (*Gazzetta*, 1911, 41, i, 248—255).—Since ketonic compounds are readily formed from magnesium pyrryl iodide and acyl chlorides corresponding with monocarboxylic acids (compare Abstr., 1910, i, 426), the author has investigated the reaction in the case of the chlorides of dibasic acids, the *a*-, *β*-, *γ*-, etc., diketones with pyrrole nuclei, which should be formed, being unknown. It is found that these compounds are actually formed, the reaction being apparently of general applicability, although Lemaire (*Rec. trav. chim.*, 1910, 39) was unable to obtain either an alcoholic or a ketonic compound by the action of malonyl chloride on the ordinary Grignard compounds; further, it has not been found possible to prepare aromatic ortho-diketones or the chlorides of *a*-keto-acids from oxalyl chloride by means of Friedel and Craft's reaction, this chloride being decomposed quantitatively by aluminium chloride into carbon monoxide and carbonyl chloride.

[With Gerolamo Andò.]—*Dipyrroyl* (*dipyrroyl-a:a-diketone*),



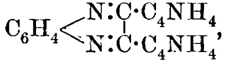
$$\begin{array}{l} CH·CH \\ \| \\ CH·NH \end{array} \!\!\!> C·CO·CO·C < \!\!\! \begin{array}{l} CH·CH \\ \qquad \| \\ NH·CH \end{array},$$

pale yellow crystals, m. p. 199·5—200°, is prepared from oxalyl chloride and magnesium pyrryl iodide, the reaction proceeding violently unless cooling with a freezing mixture and dilution with ether are resorted to. It exhibits normal cryoscopic behaviour in acetic acid and forms a *diphenylosazone*, $C_4NH_4·C(N_2HPh)·C(N_2HPh)·C_4NH_4$, yellowish-red needles, m. p. 146°, which, when heated with alcohol and ferric chloride, yields a reddish-brown compound, probably



$$\begin{array}{l} C_4NH_4·C{:}N·NPh \\ \qquad\quad | \qquad\quad | \\ C_4NH_4·C{:}N·NPh \end{array}.$$

It forms also a dioxime, to be studied later in its relation to dibenzoyl, which gives three stereoisomeric dioximes. It does not give Bamberger's colour reaction for 1 : 2-diketones (compare Abstr., 1885, 807), but with *o*-phenylenediamine it yields *dipyrrylquinoxaline*,



$$C_6H_4<\begin{matrix}N{:}C{\cdot}C_4NH_4\\ |\\ N{:}C{\cdot}C_4NH_4\end{matrix},$$

which forms chrome-yellow, twinned crystals, m. p. 158°, and gives the general reactions of the quinoxalines.

Dipyrroyl yields a *silver* derivative, $C_4NH_3Ag{\cdot}CO{\cdot}CO{\cdot}C_4NH_3Ag$, as a yellow precipitate, and, on oxidation with permanganate, gives ketopyrrolic acid (compare Holleman, Abstr., 1904, i, 474).

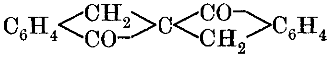
T. H. P.

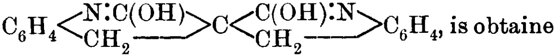
Preparation of Indigotin from Indole. GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P. 230542).—The partial conversion of indole into indigotin by oxidation with ozonised air has previously been recorded; it is now found that the reaction is complete, and a pure product obtained if the indole is converted into *β*-indolecarboxylic acid, purified, dissolved in a mixture of acetone and sodium hydroxide, and treated with ozonised air until the separation of indigotin is complete.

F. M. G. M.

Theory of Indigo Dyeing. ARTHUR BINZ and K. MANDOWSKY (*Ber.*, 1911, **44**, 1225—1229).—It is well known that the dyes of the indigo group readily form additive compounds with sodium hydroxide; indigotin itself reacts slowly on account of its insolubility, but readily forms an additive compound with sodium ethoxide. The addition does not occur, however, when the indigotin has been applied to the (vegetable) fibre by the vat process. This suggests that the usual theory that the dye is fixed on the fibre by mere mechanical enclosure is insufficient; the union between the dye and the fibre must be of a more intimate character. It is impossible to say what is the nature of this union. It is determined, however, to some extent by the conditions under which the vat process is conducted. Thus when calico is printed with a mixture of indigo paste, flour thickening, and olive oil (no alkali or reducing agent), and is steamed for three-quarters of an hour, the dye is fixed as the dull blue "indigo grey"; the colour is not fast like that of the ordinary vat blue, and the indigo reacts at once with sodium ethoxide. The same is true when the dye is used in the form of an alcoholic solution of indigo white (without alkali) or in colloidal solution; in both cases the dye on the fibre is attacked by sodium ethoxide. The theory of a union of some kind between the dye and the fibre also serves to explain the fact that indigo on the fibre loses its fastness to scouring by prolonged steaming. The usual explanation, that the loss depends on sublimation, must be incorrect, since indigotin sublimes at about 290° and is not volatile with steam. The author suggests that the union between the dye and the fibre is loosened by steaming; after six hours the separation is complete and the dye readily forms the yellow additive compound with sodium ethoxide.

C. S.

Nomenclature of the Spirans. DAN RADULESCU (*Ber.*, 1911, **44**, 1023—1026. Compare Baeyer, Abstr., 1901, i, 135).—Spirans or dispirans are homo- or hetero-cyclic compounds containing two rings with a carbon atom common to both; trispirans contain three such rings. Stereochemically the planes of the two rings may be imagined as cutting at right angles. Each ring retains its usual name and the position which the carbon atom common to both rings occupy is indicated. Thus  $C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>C<\begin{matrix}CO\\CH_2\end{matrix}>C_6H_4$ is bishydrindone-(2:2-) spiran.

By the reduction of ethyl di-*o*-nitrobenzylmalonate, biscarbostyrilspiran,  $C_6H_4<\begin{matrix}N{:}C(OH)\\CH_2\text{———}\end{matrix}>C<\begin{matrix}C(OH){:}N\\CH_2\text{———}\end{matrix}>C_6H_4$, is obtained in lustrous, snow-white plates, m. p. above 400° (compare Lellmann and Schleich, Abstr., 1887, 490). It partly sublimes and dissolves in alcoholic potassium hydroxide, being precipitated unchanged by acids. The *chloride* was obtained by the action of phosphorus pentachloride and oxychloride in crystalline flakes; on reduction with hydrogen iodide, 2-*hydroxydihydroquinoline-dihydroquinoline*-(3 : 3)-*spiran* is formed as a greenish-yellow, crystalline powder.

By condensation of dibenzylmalonyl chloride (colourless needles, m. p. 69°, b. p. 225—227°/13 mm.), *bis*-1-*hydrindone*-(2 : 2)-*spiran* is formed. This crystallises in colourless, short, well-formed prisms from benzene or in long needles from amyl alcohol, m. p. 173°. E. F. A.

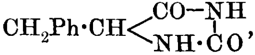
Preparation of Salt-like Compounds from Toluenesulphonamides and 1-Phenyl- or 1-*p*-Tolyl-2 : 3-dimethyl-5-pyrazolone.

ARNOLD VOSWINKEL (D.R.-P. 229814).—When *o*- or *p*-toluenesulphonamide and 1-phenyl- or 1-tolyl-2 : 3-dimethyl-5-pyrazolone are fused together in molecular proportions, crystalline salt-like substances of therapeutic value are obtained.

The *product* from *o*-toluenesulphonamide and 1-phenyl-2 : 3-dimethyl-5-pyrazolone has m. p. 102°, whilst that from *p*-toluenesulphonamide forms prismatic crystals, m. p. 95°. These substances are sparingly soluble in cold, and are rapidly decomposed by boiling water (or alkali) into their components. F. M. G. M.

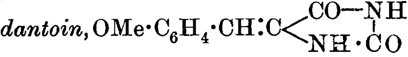
Hydantoins. Synthesis of Phenylalanine and of Tyrosine. I.

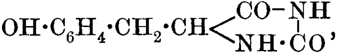
HENRY L. WHEELER and CHARLES HOFFMAN (*Amer. Chem. J.*, 1911, 45, 368—383).—This investigation was undertaken with the object of studying various hydantoin derivatives for synthetical purposes. It has been found that hydantoin condenses readily with aldehydes, and that excellent yields of the products are obtained by boiling hydantoin with aldehydes in presence of glacial acetic acid and anhydrous sodium acetate. Benzylidenehydantoin (Ruhemann and Stapleton, Trans., 1900, 77, 246) can be thus obtained in a yield of 70—80% of the theoretical.

When benzylidenehydantoin is reduced with hydriodic acid, 4-*benzylhydantoin* (*phenylalaninehydantoin*),  $CH_2Ph{\cdot}CH<\begin{matrix}CO\text{—}NH\\NH{\cdot}CO\end{matrix}$, m. p. 188—190°, is obtained, which forms flat, lancet-shaped crystals; a small quantity of phenylalanine is simultaneously produced. Benzylhydantoin can also be prepared by evaporating a solution of phenylalanine and potassium cyanate, and warming the residue with dilute hydrochloric acid. On reducing benzylidenehydantoin with aluminium amalgam, an amorphous *aluminium* compound,

$$C_{10}H_{12}O_3N_2,3Al(OH)_3,$$

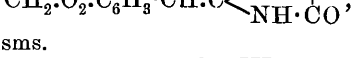
is produced, together with benzylhydantoin and benzylhydantoic acid. 4-Benzylhydantoic acid (α-carbamido-β-phenylpropionic acid) (Dakin, Abstr., 1909, ii, 685) can be readily obtained by boiling benzylhydantoin with dilute sodium hydroxide. When 4-benzylhydantoin is reduced with hydriodic acid or boiled with barium hydroxide and water, phenylalanine is produced; in one experiment with barium hydroxide, 73% of the hydantoin was converted into phenylalanine and 23·7% into benzylhydantoic acid.

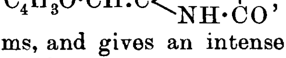
Anisylidenehydantoin,  $OMe\cdot C_6H_4\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 243—244° (decomp.), forms brownish-yellow prisms, and, when boiled with alkali hydroxide, yields methyl *p*-hydroxyphenylpyruvate; its *bromo*-derivative, m. p. 247°, crystallises in long, pale yellow needles. When anisylidenehydantoin is boiled for several hours with hydriodic acid, it is converted into tyrosine, together with a small quantity of 4-*p*-hydroxybenzoylhydantoin, but if the mixture is boiled for only one hour, the latter compound is produced in a yield of about 80% of the theoretical. 4-p-*Hydroxybenzylhydantoin* (*tyrosinehydantoin*),



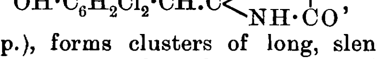
$$OH\cdot C_6H_4\cdot CH_2\cdot CH<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix},$$

m. p. 257—258° (decomp.), forms small, colourless prisms. A tyrosinehydantoin has been obtained by Blendermann (Abstr., 1883, 818), which has m. p. 275—280°, and crystallises in yellow needles; it is suggested that this substance may be an optically active isomeride of the compound now described. 4-*p*-Hydroxybenzylhydantoic acid (tyrosinehydantoic acid) can be obtained by boiling tyrosinehydantoin with dilute alkali hydroxide, but is best prepared by the action of potassium cyanate on tyrosine. The latter method was employed by Jaffé (*Zeitsch. physiol. Chem.*, 1882, **7**, 310), but he failed to obtain a pure product. The pure compound has m. p. 172° (decomp.), crystallises in prisms, and when boiled with dilute hydrochloric acid is converted into tyrosinehydantoin. If tyrosinehydantoin is boiled with barium hydroxide and water, tyrosine is produced.

Piperonylidenehydantoin,  $CH_2{:}O_2{:}C_6H_3\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 245°, forms clusters of yellow prisms.

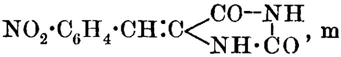
Furfurylidenehydantoin,  $C_4H_3O\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix}$, m. p. 232°, crystallises in dark yellow prisms, and gives an intense green coloration with concentrated sulphuric acid.

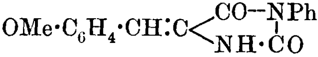
3 : 5-*Dichloro-4-hydroxybenzylidenehydantoin*,



$$OH\cdot C_6H_2Cl_2\cdot CH{:}C<\begin{matrix}CO-NH\\ NH\cdot CO\end{matrix},$$

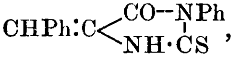
m. p. 300° (decomp.), forms clusters of long, slender, pale yellow needles, and yields an orange-coloured *ammonium* salt.

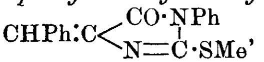
p-*Nitrobenzylidenehydantoin*,  $NO_2\cdot C_6H_4\cdot CH:C<\begin{array}{l}CO-NH\\ NH\cdot CO\end{array}$, m. p. 254° (decomp.), crystallises in lemon-yellow prisms, and dissolves in *N*-potassium hydroxide to form a blood-red solution.

1-Phenylhydantoin condenses with anisaldehyde with formation of 1-*phenyl*-4-*anisylidenehydantoin*,  $OMe\cdot C_6H_4\cdot CH:C<\begin{array}{l}CO-NPh\\ NH\cdot CO\end{array}$, m. p. 251°, which crystallises in small, yellow prisms. When 3-phenylhydantoin and 1 : 3-diphenylhydantoin are treated in the same way, condensation does not take place. E. G.

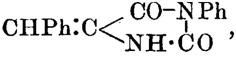
Hydantoins. II. Aldehyde Condensation Products of Phenylthiohydantoins. Henry L. Wheeler and Charles A. Brautlecht

(*Amer. Chem. J.*, 1911, **45**, 446—458).—It has been shown (preceding abstract) that hydantoin condenses readily with aldehydes in presence of glacial acetic acid and anhydrous sodium acetate, and that 1-phenylhydantoin behaves in a similar manner, whilst 3-phenyl- and 1 : 3-diphenyl-hydantoin do not undergo condensation. Since it seemed probable that the presence of the 3-phenyl group prevented condensation from taking place, a study has been made of the behaviour of 2-thio-1-phenylhydantoin, 2-thio-3-phenylhydantoin, and 2-thio-1 : 3-diphenylhydantoin with aldehydes under similar conditions. It has been found that all these compounds yield condensation products, and that 2-thio-1-phenylhydantoin reacts more readily than hydantoin or 1-phenylhydantoin. The compounds obtained from 2-thio-1-phenylhydantoin and 2-thio-3-phenylhydantoin yield 2-alkylthiol derivatives when warmed with an alkyl halide in presence of sodium alkyloxide.

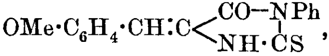
2-*Thio*-1-*phenyl*-4-*benzylidenehydantoin*,  $CHPh:C<\begin{array}{l}CO-NPh\\ NH\cdot CS\end{array}$, m. p. 204°, forms yellow prisms, and is soluble in about 60 parts of boiling alcohol. 2-*Methylthiol*-1-*phenyl*-4-*benzylidenehydantoin*,



$$CHPh:C<\begin{array}{l}CO\cdot NPh\\ N{=\!=}C\cdot SMe\end{array},$$

m. p. 150°, crystallises in cream-coloured needles or octahedral pyramids. The corresponding 2-*ethylthiol* derivative, m. p. 123°, forms straw-coloured needles; the 2-*benzylthiol* derivative, m. p. 178—179°, crystallises in nearly colourless needles, and is soluble in about 890 parts of alcohol at 22° and in 137 parts of boiling alcohol. When these thiol derivatives are boiled with hydrochloric acid and alcohol, mercaptan is evolved, and 1-*phenyl*-4-*benzylidenehydantoin*,  $CHPh:C<\begin{array}{l}CO-NPh\\ NH\cdot CO\end{array}$, m. p. 243°, is produced, which forms cream-coloured prisms or diamond-shaped blocks.

2-*Thio*-1-*phenyl*-4-*anisylidenehydantoin*,

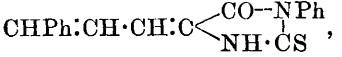


$$OMe\cdot C_6H_4\cdot CH:C<\begin{array}{l}CO-NPh\\ NH\cdot CS\end{array},$$

m. p. 214°, crystallises in long, lemon-yellow needles, and is soluble in about 124 parts of boiling alcohol; its *sodium* salt has m. p. about

280° (decomp.). 2-*Ethylthiol*-1-*phenyl*-4-*anisylidenehydantoin*, m. p. 138—139°, forms yellow needles, and, when boiled with hydrochloric acid and alcohol, yields mercaptan and 1-phenyl-4-anisylidenehydantoin.

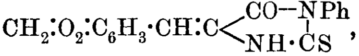
2-*Thio*-1-*phenyl*-4-*cinnamylidenehydantoin*,



$$\mathrm{CHPh{:}CH{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO-NPh}\\ \mathrm{NH\cdot CS}\end{array},$$

m. p. 272—273°, forms long, flat, orange-coloured prisms, and is soluble in about 305 parts of boiling alcohol.

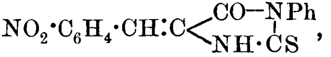
2-*Thio*-1-*phenyl*-4-*piperonylidenehydantoin*,



$$\mathrm{CH_2{:}O_2{:}C_6H_3{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO-NPh}\\ \mathrm{NH\cdot CS}\end{array},$$

m. p. 222—223°, crystallises in yellow plates; its *potassium* salt forms long, yellow needles.

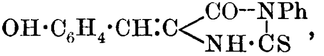
2-*Thio*-1-*phenyl*-4-p-*nitrobenzylidenehydantoin*,



$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO-NPh}\\ \mathrm{NH\cdot CS}\end{array},$$

m. p. 278—279°, crystallises in flat, yellow prisms.

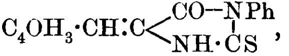
2-*Thio*-1-*phenyl*-4-*salicylidenehydantoin*,



$$\mathrm{OH{\cdot}C_6H_4{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO-NPh}\\ \mathrm{NH\cdot CS}\end{array},$$

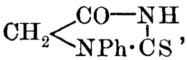
m. p. 224—225°, forms pale yellow prisms.

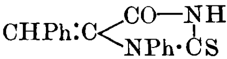
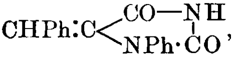
2-*Thio*-1-*phenyl*-4-*furfurylidenehydantoin*,



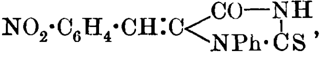
$$\mathrm{C_4OH_3{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO-NPh}\\ \mathrm{NH\cdot CS}\end{array},$$

m. p. 233—234°, forms yellow, prismatic blocks.

When ethyl phenylaminoacetate *hydrochloride*, m. p. 119°, is boiled with an alcoholic solution of potassium thiocyanate, 2-*thio*-3-*phenylhydantoin*,  $\mathrm{CH_2}<\begin{array}{l}\mathrm{CO-NH}\\ \mathrm{NPh\cdot CS}\end{array}$, m. p. 179—180°, is produced, which forms colourless, transparent prisms.

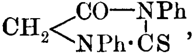
2-*Thio*-3-*phenyl*-4-*benzylidenehydantoin*,  $\mathrm{CHPh{:}C}<\begin{array}{l}\mathrm{CO-NH}\\ \mathrm{NPh\cdot CS}\end{array}$, m. p. 207—208°, crystallises in yellow plates. 2-*Ethylthiol*-3-*phenyl*-4-*benzylidenehydantoin*, m. p. 165—166°, forms yellow prisms, and, when boiled with hydrochloric acid and alcohol, is converted into mercaptan and 3-*phenyl*-4-*benzylidenehydantoin*,  $\mathrm{CHPh{:}C}<\begin{array}{l}\mathrm{CO-NH}\\ \mathrm{NPh\cdot CO}\end{array}$, m. p. 223—224° which crystallises in pale yellow plates.

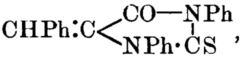
2-*Thio*-3-*phenyl*-4-p-*nitrobenzylidenehydantoin*,



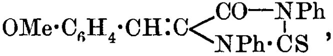
$$\mathrm{NO_2{\cdot}C_6H_4{\cdot}CH{:}C}<\begin{array}{l}\mathrm{CO-NH}\\ \mathrm{NPh\cdot CS}\end{array},$$

m. p. 236—237°, forms orange-red prisms.

2-*Thio*-1 : 3-*diphenylhydantoin*,  $\mathrm{CH_2}<\begin{array}{l}\mathrm{CO-NPh}\\ \mathrm{NPh\cdot CS}\end{array}$, m. p. 212°, obtained by heating phenylaminoacetic acid or its ethyl ester with phenylthiocarbimide, crystallises in flat, yellow prisms.

2-*Thio*-1 : 3-*diphenyl*-4-*benzylidenehydantoin*,  $CHPh{:}C{<}\begin{array}{l}CO{-}NPh\\ NPh{\cdot}CS\end{array}$, m. p. 193—194°, forms yellow needles.

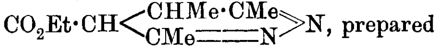
2-*Thio*-1 : 3-*diphenyl*-4-*anisylidenehydantoin*,



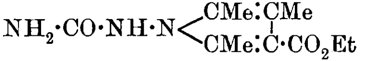
$$OMe{\cdot}C_6H_4{\cdot}CH{:}C{<}\begin{array}{l}CO{-}NPh\\ NPh{\cdot}CS\end{array},$$

m. p. 221—222°, crystallises in yellow needles. E. G.

Interaction of Ethyl Diacetylbutyrate and Hydrazine.

Georg Korschun and C. Roll (*Gazzetta*, 1911, **41**, i, 186—190. Compare Paal and Kühn, Abstr., 1908, i, 57 ; Bülow and Filchner, Abstr., 1908, i, 578).—*Ethyl* 3 : 5 : 6-*trimethyl*-4 : 5-*dihydropyridazine*-4-*carboxylate*,  $CO_2Et{\cdot}CH{<}\begin{array}{l}CHMe{\cdot}CMe\\ CMe{=\!=}N\end{array}{>}N$, prepared by the action of hydrazine on ethyl $\alpha\beta$-diacetylbutyrate (compare Korschun, Abstr., 1905, i, 373), has m. p. 112·5—113·5°, b. p. about 200°/18 mm., and has the normal molecular weight in freezing benzene.

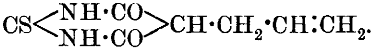
Ethyl 1-*carbamido*-2 : 3 : 5-*trimethylpyrrole*-4-*carboxylate*,

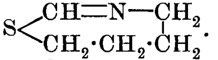


$$NH_2{\cdot}CO{\cdot}NH{\cdot}N{<}\begin{array}{l}CMe{:}CMe\\ CMe{:}C{\cdot}CO_2Et\end{array}$$

(compare Bülow, Riess, and Sautermeister, Abstr., 1905, i, 660), prepared by the interaction of semicarbazide and ethyl $\alpha\beta$-diacetylbutyrate, forms crystals which do not melt at 210°, and remains unchanged on prolonged boiling with 10% alcoholic potassium hydroxide solution. T. H. P.

Pyrimidines. L. Condensation of Thiocarbamide with Esters of Allylmalonic Acid and Some Alkyl-substituted Allylmalonic Acids.

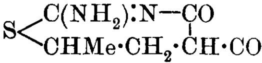
Treat B. Johnson and Arthur J. Hill (*Amer. Chem. J.*, 1911, **45**, 356—367).—The γ- and $\gamma\delta$-halogen-substituted propylmalonic acids are unstable (compare Hjelt, Abstr., 1882, 946), and are therefore of limited value for synthetical purposes. The present work was undertaken with the object of obtaining a derivative of allylmalonic acid in which the carboxyl groups would be so linked that lactone formation would not occur after the addition of halogen hydrides or halogens. It was expected that ethyl allylmalonate would react with thiocarbamide to form allylthiobarbituric acid,  $CS{<}\begin{array}{l}NH{\cdot}CO\\ NH{\cdot}CO\end{array}{>}CH{\cdot}CH_2{\cdot}CH{:}CH_2$. It has been found, however, that, instead of this compound, a stable, cyclic substance is obtained which is representative of a new class of compounds, the tetrahydrohexathiazoles, of which the simplest member would be



$$S{<}\begin{array}{l}CH{=}N{-}CH_2\\ CH_2{\cdot}CH_2{\cdot}CH_2\end{array}.$$

Ethyl benzylallylmalonate and ethyl diallylmalonate do not behave in this way, but condense with thiocarbamide to form the sodium salts of the corresponding acylthiocarbamides, which on treatment with acids are converted into γ-lactones.

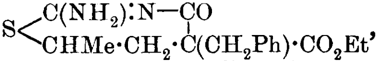
Ethyl 2-*amino*-4-*keto*-7-*methyltetrahydrohexathiazole*-5-*carboxylate*,



$\mathrm{S}<\begin{array}{l}\mathrm{C(NH_2){:}N{-}CO}\\ \mathrm{CHMe{\cdot}CH_2{\cdot}CH{\cdot}CO_2Et}\end{array}$, m. p. 88—89°, forms pink prisms; it is not desulphurised when warmed with mercuric oxide or lead acetate, and is remarkably stable towards alkali hydroxides. When a solution of this compound in concentrated hydrochloric acid is evaporated to dryness on the water-bath, *γ-thiol-*n*-valerylcarbamide*,

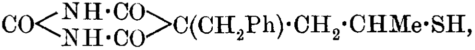
$\mathrm{SH{\cdot}CHMe{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2}$,

m. p. 186°, is produced. If the hexathiazole compound is heated with benzyl chloride in presence of sodium ethoxide, *ethyl 2-amino-5-benzyl-7-methyltetrahydrohexathiazole-4-one-5-carboxylate*,



$$\mathrm{S}<\begin{array}{l}\mathrm{C(NH_2){:}N{-}CO}\\ \mathrm{CHMe{\cdot}CH_2{\cdot}C(CH_2Ph){\cdot}CO_2Et}\end{array}$$

m. p. 221°, is obtained, which crystallises in colourless prisms, and, when heated with concentrated hydrochloric acid, gives a quantitative yield of *5-benzyl-5-thiolpropylbarbituric acid*,



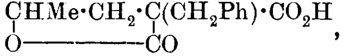
$$\mathrm{CO}<\begin{array}{l}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CO}\end{array}>\mathrm{C(CH_2Ph){\cdot}CH_2{\cdot}CHMe{\cdot}SH},$$

m. p. 236°, which forms colourless prisms. On heating the latter compound with 50% potassium hydroxide solution in a sealed tube at 130° and adding excess of hydrochloric acid to the reaction product, *potassium hydrogen benzyl-β-thiolpropylmalonate*,

$\mathrm{SH{\cdot}CHMe{\cdot}CH_2{\cdot}C(CH_2Ph)(CO_2H){\cdot}CO_2K}$,

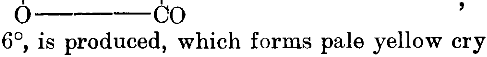
is produced, and separates in a crystalline form.

Ethyl benzylallylmalonate, $\mathrm{CH_2{:}CH{\cdot}CH_2{\cdot}C(CH_2Ph)(CO_2Et)_2}$, b. p. 228—230°/60—65 mm., prepared by the action of allyl iodide on ethyl sodiobenzylmalonate or of benzyl chloride on ethyl sodioallylmalonate, is a colourless, viscous oil. On hydrolysis with potassium hydroxide, it yields *α-benzyl-γ-valerolactone-α-carboxylic acid*,



$$\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}C(CH_2Ph){\cdot}CO_2H}\\ \mathrm{O{-\!-\!-\!-\!-}CO}\end{array},$$

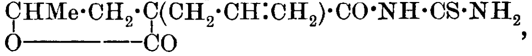
in the form of a thick syrup; the *silver* salt is described. When this compound is heated with 50% potassium hydroxide solution at 130—150°, it is converted into *benzyl-β-hydroxypropylmalonic acid*, $\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}C(CH_2Ph)(CO_2H)_2}$, which was obtained as an oil; its *silver* salt was prepared. By the action of thiocarbamide on ethyl benzylallylmalonate in presence of sodium ethoxide, *α-benzyl-γ-valerolactone-α-carbonylthiocarbamide*,



$$\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}C(CH_2Ph){\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2}\\ \mathrm{O{-\!-\!-\!-\!-}CO}\end{array},$$

m. p. 145—146°, is produced, which forms pale yellow crystals.

α-Allylvalerolactone-α-carbonylthiocarbamide,



$$\begin{array}{l}\mathrm{CHMe{\cdot}CH_2{\cdot}C(CH_2{\cdot}CH{:}CH_2){\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH_2}\\ \mathrm{O{-\!-\!-\!-\!-}CO}\end{array},$$

m. p. 134—135°, obtained by the condensation of thiocarbamide with ethyl diallylmalonate, crystallises in cream-coloured plates. When hydrolysed with potassium hydroxide, it yields *β-hydroxypropylallylmalonic acid*, $\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}C(CH_2{\cdot}CH{:}CH_2)(CO_2H)_2}$, m. p. 120—122° (decomp.), which forms rosettes of small prisms; its *silver* salt was prepared. E. G.

Preparation of Nitrogen Derivatives of Anthraquinones. FRITZ ULLMANN (D.R.-P. 230454).—The patent contains an account of some compounds, certain of which have previously been described (Ullmann and Schalk, this vol., i, 165) *N*-Phenylpyridazonanthrone (*loc. cit.*) forms yellow needles, m. p. 286°. By the interaction of the chloride of anthraquinone-1-carboxylic acid and phenylhydrazine-*p*-sulphonic acid, a *substance* is obtained which crystallises in yellow leaflets. F. M. G. M.

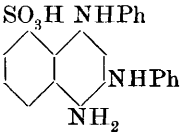
The Halogenation of Indanthren. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 229166).—It is found that indanthren can be readily chlorinated by treatment with aromatic acid chlorides. Indanthren (10 parts) suspended in nitrobenzene is treated with benzoyl chloride (20 parts) and copper powder (0·5 part) and heated at 200—205°, when crystals of *dichloroindanthren* separate from the clear solution; it is very sparingly soluble in organic solvents, but dissolves in concentrated sulphuric acid with an olive-brown colour.

The *compound* obtained from *p*-dihydroxyindanthren and benzoyl chloride is a crystalline powder with metallic lustre and a high chlorine content. F. M. G. M.

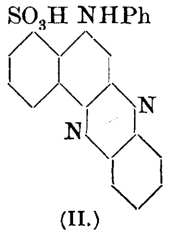
Preparation of 3 : 6-Diaminoacridine. LEOPOLD CASSELLA & Co. (D.R.-P. 230412).—3 : 6-*Diaminoacridine* is prepared by nitrating a cooled sulphuric acid solution of *pp*-diaminodiphenylmethane, and after some hours pouring on to ice; the separated oo′-*dinitro*-pp′-*diaminodiphenylmethane* is reduced with tin and hydrochloric acid, and subsequently heated at 135° during four hours; the diaminoacridine stannichloride is decomposed in the ordinary manner, and the required base extracted with hot water, from which it crystallises in glistening, orange to brown leaflets. F. M. G. M.

Preparation of Azines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 230456).—Important azine derivatives can be prepared by the action of diazotised aniline on 1 : 3-diarylnaphthylenediamines and their 6-sulphonic or 6 : 8-disulphonic acids.

Aniline is diazotised and coupled with 1 : 3-diphenylnaphthylenediamine-8-sulphonic acid, the *azo*-compound reduced with iron or zinc dust, and the crystalline paste of the reduction *product* (I) treated with ammonium hydroxide and oxidised with a current of air; after some time the *azine* (II) is deposited from the deep green solution in the form of a black powder. F. M. G. M.

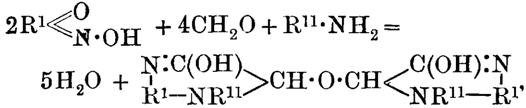


(I.)



(II.)

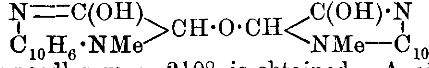
Preparation of Pyrazine Derivatives. MARTIN LANGE (D.R.-P. 229127).—The interaction of *o*-oxynitroso-compounds with formaldehyde and primary aliphatic amines yields strongly basic pyrazine derivatives according to the general formula:



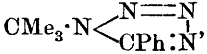
$$2R^{1}\!<\!\begin{matrix}O\\ N\cdot OH\end{matrix} + 4CH_2O + R^{11}\cdot NH_2 =$$

$$5H_2O + \begin{matrix}N{:}C(OH)\\ | \qquad\quad \\ R^{1}\text{—}NR^{11}\end{matrix}\!\!>\!CH\cdot O\cdot CH\!<\!\!\begin{matrix}C(OH){:}N\\ \qquad\quad | \\ NR^{11}\text{—}R^{1}\end{matrix},$$

where R^1 is aryl and R^{11} alkyl or substituted alkyl groups.

By the interaction of α-nitroso-β-naphthol, methylamine hydrochloride, and formaldehyde in alkaline solution, the *compound*, (I)  $\begin{matrix}N\!\!=\!\!=C(OH)\\ | \qquad\qquad \\ C_{10}H_6\cdot NMe\end{matrix}\!\!>\!CH\cdot O\cdot CH\!<\!\!\begin{matrix}C(OH)\cdot N\\ \qquad\qquad | \\ NMe\text{—}C_{10}H_6\end{matrix}$, crystallising in colourless needles, m. p. 210°, is obtained. A similar compound, m. p. 228°, in which the group $\cdot CH_2\cdot CO_2H$ replaces the group Me in the above formula, is formed when glycine is substituted for methylamine in the above reaction. Disulphonic and dicarboxy-*derivatives* of (I) are prepared similarly from α-nitroso-β-naphthol-6-sulphonic and -3-carboxylic acids, and by employing α-nitroso-2 : 7-dihydroxynaphthalene, a compound, m. p. 304°, is obtained. F. M. G. M.

Thio-derivatives of Homoantipyrine. FRITZ VON KONEK-NORWALL (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV A I, 234—236).—Antipyrine disulphide, when shaken with mercury in chloroform solution, forms a crystalline compound of the composition $C_{22}H_{22}O_2N_4S_2Hg$. Benzyl, benzoyl, and *p*-nitrophenyl disulphides do not react with mercury. Homoantipyrine (1-phenyl-3-methyl-2-ethylpyrazolone) reacts with sulphur chloride, forming a *monosulphide*, $C_{24}H_{26}O_2N_4S$, which crystallises from benzene in white crystals, m. p. 219—220°, and a *disulphide*, $C_{24}H_{26}O_2N_4S_2$, which forms very pale yellow crystals, m. p. 200°. When the disulphide is shaken in chloroform solution with mercury, a little mercuric sulphide separates, and glistening, pale green crystals of the mercuric *compound*, $C_{24}H_{26}O_2N_4S_2Hg$, are obtained, m. p. 230—231°. The structure of these compounds has not been determined. C. H. D.

Rearrangements. III. GEORG SCHROETER (*Ber.*, 1911, **44**, 1201—1209. Compare Abstr., 1909, i, 617, 773).—In extension of his investigations of the reactions by which the chlorides of aromatic ketones are converted through the ketonediazoimide into substituted tetrazoles, the author has examined the behaviour of an aromatic-aliphatic ketone in order to discover whether the aryl or the alkyl group migrates during the reactions. Ketonediazoimides cannot be suitably obtained from the chlorides of aliphatic-aromatic ketones of the type Ar·CO·CH⁚, since such chlorides too readily lose hydrogen chloride. Pivalophenone (trimethylacetophenone), however, with phosphorus pentachloride at 140—160°, yields *pivalophenone chloride*, $CMe_3\cdot CCl_2Ph$, b. p. 118—120°/10 mm., which reacts with silver azoimide in boiling amyl ether to form 5-*phenyl*-1-tert.-*butyl*-1 : 2 : 3 : 4-*tetrazole*,  $CMe_3\cdot N\!<\!\begin{matrix}N\!=\!=N\\ \qquad | \\ CPh{:}N\end{matrix}$, white needles, m. p. 102°. The constitution of this tetrazole is proved by heating it with 88—90% sulphuric acid at 130° for about two minutes, whereby *iso*butylene and 5-phenyl-1 : 2 : 3 : 4-tetrazole are produced. Consequently the tertiary butyl group has migrated, a result which is rather unexpected, since it is the phenyl group which wanders when acetophenoneoxime experiences the Beckmann transformation and is eliminated when phenyl *tert.*-alkyl ketones are warmed with sodamide (Haller and Bauer, Abstr., 1909, i, 131). Experiments show, however, that when pivalophenoneoxime undergoes the Beckmann change either the alkyl or the aryl group migrates according to the nature of the transforming reagent. Thus in ether with phosphorus pentachloride, the oxime yields products from which benzonitrile can be isolated. Probably the transformation proceeds according to the scheme : $CMe_3\cdot CPh\!:\!NOH \rightarrow CMe_3\cdot NH\cdot CPhCl_2 \rightarrow HCl + C_4H_9Cl + C_6H_5\cdot CN$, a view which is supported by the fact that *benz*-tert.-*butylamide*, $CMe_3\cdot NHBz$, m. p. 135·5°, obtained from benzoyl chloride and *tert.*-butylamine, is decomposed by phosphorus pentachloride, yielding hydrogen chloride, *tert.*-butyl chloride, and benzonitrile. When, however, pivalophenoneoxime in glacial acetic acid is heated with hydrogen chloride, it is converted into the *anilide*, $CMe_3\cdot CO\cdot NHPh$, m. p. 132°, of pivalic acid. These results show that caution is necessary in determining the configuration of an oxime from its products of transformation. The author discusses Montagne's criticisms (Abstr., 1910, i, 623) of Schroeter's theory of the course of the Beckmann transformation.

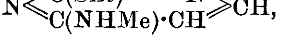
C. S.

1-Methyldeoxyxanthine. JULIUS TAFEL and AUGUST HERTERICH (*Ber.*, 1911, **44**, 1033—1034).—The acid properties of the deoxyxanthines are due to the iminazole ring, and persist so long as this is not methylated ; the susceptibility towards acids is connected with the imino-group in position 3, and disappears when this is methylated. This behaviour is now confirmed in the case of 1-*methyldeoxyxanthine* prepared by electrolytic reduction from 1-methylxanthine (Engelmann, Abstr., 1909, i, 192). This crystallises in reniform aggregates, becomes brown at 240° (decomp 260°). The aqueous solution is neutral. The *sulphate* forms needles in stellate aggregates ; the *oxalate* is a fine crystalline powder ; the *picrate* is obtained in hair-like bent needles.

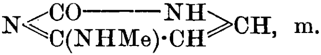
E. F. A.

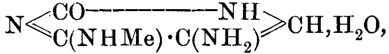
Purines. III. 2-Oxy-9-methylpurine and 2 : 8-Dioxy-9-methylpurine. CARL O. JOHNS (*J. Biol. Chem.*, 1911, **9**, 161—167).—In earlier papers (Abstr., 1909, i, 192 ; this vol., i, 242), 2 : 8-dioxy-6-methylpurine, 2-oxy-6-methylpurine, and 2 : 8-dioxypurine have been described. In continuation of this work, an account is now given of 2-oxy-9-methylpurine and 2 : 8-dioxy-9-methylpurine.

When 6-chloro-2-ethylthiolpyrimidine (Wheeler and Johnson, Abstr., 1903, i, 526) is heated at 100° with an aqueous solution of methylamine, 6-*methylamino*-2-*ethylthiolpyrimidine*,



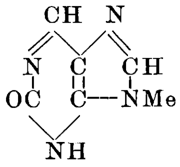
$$\mathrm{N}\!\left<\begin{matrix}\mathrm{C(SEt)}=\!=\mathrm{N}\\ \mathrm{C(NHMe)\cdot CH}\end{matrix}\right>\!\mathrm{CH},$$

m. p. 55°, is produced, which forms small, stout prisms. On boiling this substance with concentrated hydrochloric acid, it is converted into 6-*methylamino*-2-*pyrimidone*,  $N\lessgtr\begin{array}{l}CO\text{———}NH\\C(NHMe)\cdot CH\end{array}\gtrless CH$, m. p. 270° (decomp.), which crystallises in small, stout prisms, and yields a 5-*nitro*-derivative, which forms minute prisms and turns black above 300°. 5-*Amino*-6-*methylamino*-2-*pyrimidone*,

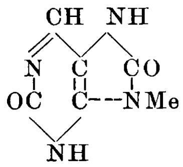


$$N\lessgtr\begin{array}{l}CO\text{—————}NH\\C(NHMe)\cdot C(NH_2)\end{array}\gtrless CH,H_2O,$$

obtained by reducing the 5-nitro-compound with ferrous hydroxide, forms slender prisms, darkens at 210°, and decomposes at about 225°. When this compound is heated for an hour with formic acid, the solution evaporated to dryness, and the residue heated at 130—140°, 2-*oxy*-9 *methylpurine* (annexed formula) is produced, which forms long, slender prisms containing $1H_2O$, turns brown at about 290°, decomposes at about 310°, and gives a brilliant murexide reaction.



If a mixture of 5-amino-6-methylamino-2-pyrimidone and carbamide is heated for an hour at 150—160°, 2 : 8-*dioxy*-9-*methylpurine* (annexed formula) is obtained, which crystallises in minute prisms, does not melt below 315°, and yields the murexide reaction.



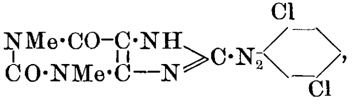
E. G.

Action of Nitriles on Cyanoguanidine. ADRIANO OSTROGOVICH (*Atti. R. Accad. Lincei*, 1911, [v], 20, i, 249—252. Compare this vol., i, 332).—The 4 : 6-diamino-2-methyl-1 : 3 : 5-triazine previously described may also be obtained (yield about 60%) by heating together cyanoguanidine and acetonitrile in a sealed tube for three hours at 225—230°; ammeline is also formed as a secondary product. The corresponding phenyl derivative is obtained by heating cyanoguanidine with benzonitrile for four or five hours in a sealed tube at 190—200°; in this case also some ammeline is produced.

It appears likely that the reaction can be extended to other cases, and further, diguanide may be employed instead of cyanoguanidine, although the yields obtained in this case are poor.

R. V. S.

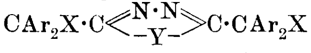
Preparation of 8-Aminopurine Derivatives. KALLE & Co. (D.R.-P. 230401. Compare Burian, Abstr., 1904, i, 354).—8-Amino-2 : 6-dioxypurine derivatives have previously been prepared by treating the 8-chloro-derivatives with ammonia at a high temperature; it is now found that purines which are unsubstituted in positions 7 and 8 will couple energetically with diazonium salts, and by subsequent reduction yield the corresponding aminopurines. The *compound*,



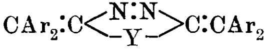
glistening, red needles, is prepared by diazotising 2 : 5-dichloroaniline and coupling it in alkaline solution with theophylline; on reduction a quantitative yield of 8-aminotheophylline is obtained.

F. M. G. M.

New Method of Preparation of Azo-compounds. ROBERT STOLLÉ and J. LAUX (*Ber.*, 1911, **44**, 1127—1134).—Halogen compounds of the types: $CAr_2X\cdot CX{:}N\cdot N{:}CX\cdot CArX$ and



$$CAr_2X\cdot C{<}\genfrac{}{}{0pt}{}{N\cdot N}{-Y-}{>}C\cdot CAr_2X$$

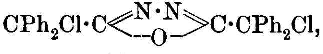
(where X = halogen, and Y = S, :NH, :NR or ·N:N·) when shaken with mercury lose halogen from the $\alpha:\zeta$-positions, with the formation of $CAr_2{:}CX\cdot N{:}N\cdot CX{:}CAr_2$ and  $CAr_2{:}C{<}\genfrac{}{}{0pt}{}{N{:}N}{-Y-}{>}C{:}CAr_2$ respectively. The azo-compounds thus obtained readily combine with halogens, the addition taking place in the $\alpha:\zeta$-position.

s-*Bi-diphenylacetylhydrazide*, $CHPh_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot CHPh_2$, prepared by the addition of an ethereal solution of diphenylacetyl chloride to a mixture of hydrazine hydrate and sodium carbonate in aqueous solution, crystallises in slender needles, m. p. 297°. It reacts with phosphorus pentachloride in carbon tetrachloride solution, yielding *bis-diphenylacetylhydrazide chloride*, $CHPh_2\cdot CCl{:}N\cdot N{:}CCl\cdot CHPh_2$, which forms slender, colourless needles, and, when heated with phosphorus pentachloride at 120—130°, is transformed into *bis-diphenylchloroacetylhydrazide chloride*, $CPh_2Cl\cdot CCl{:}N\cdot N{:}CCl\cdot CPh_2Cl$, crystallising in colourless leaflets, m. p. 164°.

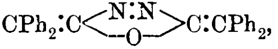
Azodiphenylchloroethylene (*bisdiphenylchlorovinyldi-imide*),

$$CPh_2{:}CCl\cdot N{:}N\cdot CCl{:}CPh_2,$$

prepared by shaking a benzene solution of the last-named compound with mercury, forms lustrous, brick-red crystals, m. p. 236°; it combines with chlorine, yielding the original hydrazide chloride, and with bromine to form *bisdiphenylbromoacetylhydrazide chloride*, m. p. 175°; the *additive* compound with hydrochloric acid has m. p. 145°.

2 : 5-*Dibenzhydryl*-1 : 3 : 4-*oxadiazole*, $CHPh_2\cdot C{<}\genfrac{}{}{0pt}{}{N\cdot N}{-O-}{>}C\cdot CHPh_2$, is obtained by heating s-bisdiphenylacetylhydrazide with phosphoryl chloride for several days in benzene solution; it crystallises in slender needles, m. p. 162°, and, when heated with phosphorus pentachloride in benzene solution, yields *di-ω-chloro*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*oxadiazole*,  $CPh_2Cl\cdot C{<}\genfrac{}{}{0pt}{}{N\cdot N}{-O-}{>}C\cdot CPh_2Cl$, which forms stout, octahedral crystals, m. p. 165°.

2 : 5-*Didiphenylmethylenedihydro*-1 : 3 : 4-*oxadiazole*,



$$CPh_2{:}C{<}\genfrac{}{}{0pt}{}{N{:}N}{-O-}{>}C{:}CPh_2,$$

obtained by shaking bisdiphenylchloromethyl-1 : 3 : 4-furazan with mercury in benzene solution for several days, forms dark brownish-red crystals, having a green fluorescence, m. p. 174°; it combines with chlorine, forming the original di-ω-chloro-1 : 3 : 4-oxadiazole, and with bromine, yielding *di-ω-bromo*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*oxadiazole*, $C_{28}H_{20}ON_2Br_2$, which forms colourless crystals, m. p. 179°, and is also obtained by the bromination of dibenzhydryl-1 : 3 : 4-oxadiazole in the presence of phosphorus pentabromide; the *additive* product with hydrochloric acid has m. p. 130°.

1-*Phenyl*-2 : 5 -*dibenzhydryl*-1 : 3 : 4-*triazole*,

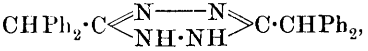
$$\mathrm{CHPh_2\cdot C}\left\langle\begin{matrix}\mathrm{N\cdot N}\\ \mathrm{NPh}\end{matrix}\right\rangle\mathrm{C\cdot CHPh_2},$$

prepared by heating bisdiphenylacetylhydrazide chloride with aniline at 150°, crystallises in slender needles, m. p. 215°; on chlorination this yields *di-ω-chloro*-1-*phenyl*-2 : 5-*dibenzhydryl*-1 : 3 : 4-*triazole*,

$$\mathrm{CPh_2Cl\cdot C}\left\langle\begin{matrix}\mathrm{N\cdot N}\\ \mathrm{NPh}\end{matrix}\right\rangle\mathrm{C\cdot CPh_2Cl},$$

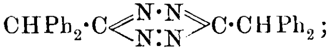
which crystallises in colourless cubes, m. p. 204° (decomp.), and gives a deep bluish-violet coloration when shaken with mercury in benzene solution.

3 : 6-*Dibenzhydryldihydro*-1 : 2 : 4 : 5 *tetrazine*,



$$\mathrm{CHPh_2\cdot C}\left\langle\begin{matrix}\mathrm{N\text{——}N}\\ \mathrm{NH\cdot NH}\end{matrix}\right\rangle\mathrm{C\cdot CHPh_2},$$

is obtained by the interaction of bisdiphenylacetylhydrazide chloride and hydrazine hydrate in benzene solution; it melts at 190°, becoming red in colour, and is oxidised with amyl nitrite in alcoholic solution to 3 : 6-*dibenzhydryl*-1 : 2 : 4 : 5-*tetrazine*,



$$\mathrm{CHPh_2\cdot C}\left\langle\begin{matrix}\mathrm{N\cdot N}\\ \mathrm{N{:}N}\end{matrix}\right\rangle\mathrm{C\cdot CHPh_2};$$

this crystallises in slender, violet needles, m. p. 172°. F. B.

Preparation of Naphtha-anthraquinoneazines. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 230005).—It is found that the azo-derivatives of anthraquinonyl-β-naphthylamine are converted by condensing agents (such as sulphuric acid) into the corresponding naphtha-anthraquinoneazines. Benzeneazo-α-anthraquinonyl-β-naphthylamine (prepared from α-chloroanthraquinone and benzeneazo-β-naphthylamine) is dissolved in 80% sulphuric acid and heated during several hours at 100°; on dilution with water the *azine* separates in crystalline form. F. M. G. M.

Preparation of Arylsulphodiazoimino-derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 229247).—Arylsulphodiazoimino-derivatives are prepared by coupling diazotised aniline, *p*-nitroaniline, and *o* : *o*-dianisidine with *p*-toluenesulphonylaniline-*m*- or -*p*-sulphonic acids respectively. The *sodium* salts (two series owing to the replacability of the iminic hydrogen by metals) are colourless, crystalline needles or powders, the free acids are sparingly soluble in water, but the introduction of two or more sulphonic groups in the molecule yields soluble and readily crystallisable compounds.

The *products* from *p*-nitroaniline, and from *o* : *o*-dianisidine with *p*-toluenesulphonylaniline-*m*-sulphonic acid separate in brown nodules, whilst benzeneazo-α-naphthylamine when diazotised and coupled in the same manner yields a similar product. Treatment with concentrated sulphuric acid removes the *p*-toluenesulphonyl residue. F. M. G. M.

Diazoamino- and Aminoazo-derivatives Obtained from Aminomethylenedioxybenzene. Efisio Mameli (*7th Intern. Congr. App. Chem.*, 1909, Sect. IV B, 101—107. Compare Abstr., 1909, i, 854).—The diazo-compound of aminomethylenedioxybenzene yields with aniline a mixture of aminoazo- and diazoamino-derivatives, whilst from diazobenzene and aminomethylenedioxybenzene only the aminoazo-derivative is formed. Aminomethylenedioxybenzene reacts with the diazonium salts prepared from α- and β-naphthylamine, giving aminoazo-derivatives, and aminoazo-derivatives are also obtained from the diazo-compound of aminomethylenedioxybenzene and α- and β-naphthylamine. Finally, the diazo-compound of aminomethylenedioxybenzene reacts with aminomethylenedioxybenzene, yielding an aminoazo-derivative identical with that formed by the action of nitrous acid on an excess of aminomethylenedioxybenzene.

*Benzeneazo-*4*-amino-*1 : 2*-methylenedioxybenzene*,

$$CH_2{:}O_2{:}C_6H_2(NH_2)\cdot N_2Ph,$$

has m. p. 130°.

4*-Amino-*1 : 2*-methylenedioxybenzene-α-azonaphthalene*,

$$CH_2{:}O_2{:}C_6H_2(NH_2)\cdot N_2\cdot C_{10}H_7,$$

has m. p. 151°, whilst the analogous derivative of *β-diazonaphthalene* has m. p. 175°.

1 : 2*-Methylenedioxybenzenediazoaminobenzene*,

$$CH_2{:}O_2{:}C_6H_3\cdot N_3H\cdot Ph,$$

has m. p. 148—149°. Along with it a small quantity of an *aminoazo-compound* is formed,

*α-Aminonaphthalene-*4*-azo-*1 : 2*-methylenedioxybenzene*,

$$CH_2{:}O_2{:}C_6H_3\cdot N_2\cdot C_{10}H_6\cdot NH_2,$$

has m. p. 189—190°, and the *β-derivative*, m. p. 142—144°.

*Aminoazo-*1 : 2*-methylenedioxybenzene*,

$$CH_2{:}O_2{:}C_6H_2(NH_2)\cdot N_2\cdot C_6H_3{:}O_2{:}CH_2,$$

has m. p. 210—215°.

The aminoazo-derivatives yields salts, some of which are fairly stable, and acetyl and benzoyl compounds have also been prepared. Both aminoazo- and diazoamino-derivatives dye wool and silk, and cotton when mordanted; in most cases the colours are fast to washing and to light. R. V. S.

Yeast Nucleic Acid. IV. Phoebus A. Levene and Walter A. Jacobs (*Ber.*, 1911, **44**, 1027—1032. Compare Abstr., 1909, i, 620, 686; this vol., i, 96).—Compounds analogous to inosic and guanylic acid of the type $PO(OH)_2\cdot O\cdot C_5H_8O_4,C_5H_4ON_5$, are termed nucleotides, and the molecule of yeast-nucleic acid is composed of four such nucleotides. By boiling nucleic acid with 2% sulphuric acid for two hours a mixture of the pyrimidine nucleotides was obtained, namely, cytidine nucleotide, $PO(OH)_2\cdot O\cdot C_9H_{12}O_4N_3$, and uridine nucleotide, $PO(OH)_2\cdot O\cdot C_9H_{11}O_5N_2$. This was hydrolysed with ammonia and cytidine isolated as nitrate; the filtrate from this was evaporated to dryness and benzoylated, when dibenzoyluridine was obtained. Uridine was also isolated after hydrolysis from the residues without the addition of nitric acid, which can conceivably bring about its formation from cytidine. A comparison of uridine obtained as above with that prepared by the action of nitrous acid on cytidine showed them to be identical. E. F. A.

Comparative Observations on the Composition and Cleavage of Different Kinds of Silk. XII. The Monoamino-acids from the "Gelatin" of Indian Tussore Silk. FRIEDRICH WILHELM STRAUCH (*Zeitsch. physiol. Chem.*, 1911, **71**, 365—366).—The gelatin obtained from Indian tussore silk contained 25% of ash. One hundred grams of ash-free substance yielded: glycine, 1·5; alanine, 9·8; leucine, 4·8; serine, 5·4; aspartic acid, 2·8; glutamic acid, 1·8; phenylalanine, 0·3; tyrosine, 1·0; and proline, 3·0 grams.
W. D. H.

Action of Pepsin and Hydrochloric Acid on Elastin and other Proteins. III. EMIL ABDERHALDEN and FRANZ WACHSMUTH (*Zeitsch. physiol. Chem.*, 1911, **71**, 339—364).—Further details as to time, etc., are given in relation to the action of elastin and pepsin. Some forms of horny structure behave like elastin in adsorbing pepsin. W. D. H.

Action of the Enzymes of Gastric Juice. II. EMIL ABDERHALDEN and FRIEDRICH W. STRAUCH (*Zeitsch. physiol. Chem.*, 1911, **71**, 315—338. Compare Abstr., 1910, i, 795).—Elastin takes up pepsin from gastric juice, and when then placed in distilled water at 37°, undergoes digestion; if pancreatic juice replaces the water, it is more rapidly digested, and the same occurs if sodium hydroxide solution is employed. The adsorbed pepsin appears to be protected and able to work in an unusual medium. Water removes some of the adsorbed enzyme from the elastin. Elastin also adsorbs propepsin, rennet, and trypsin. Both the peptic and rennetic activities of the gastric juice are destroyed by shaking, but the lessening of the two actions does not appear to be quite parallel. By the elastin method a proteolytic enzyme can be extracted from fæces.
W. D. H.

The Stimulating Effect of Chloride of Calcium and of Intestinal Mucous Membrane Extract on the Action of Trypsin. EBEL HEKMA (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1002—1012).—Calcium chloride increases the activity of trypsin which contains no trypsinogen, and this action is to be distinguished from the activating effect on the latter. Extracts of mucous membrane also increase the activity by trypsin, even after they have been boiled. In addition, therefore, to enterokinase, which activates trypsinogen and is not heat stable, another substance is present in the extract of mucous membrane which promotes tryptic digestion by accelerating the action on the activated trypsin. S. B. S.

Bacterial Proteases. KURT MEYER (*Biochem. Zeitsch.*, 1911, **32**, 274—279).—The proteases obtained from *Bacillus prodigiosus* and *B. pyocyaneus* exhibit their maximum action in faintly alkaline solution (hydrogen ion concentration $=10^{-7 \cdot 2}$), and these enzymes are therefore classed with the tryptases.

These enzymes are not destroyed when their solutions are boiled, but are rendered completely inactive when heated between 56° and 85°, and the activity is not restored by further heating to 100°, as happens in the case of staphylolysin. The proteases will not bring about the digestion of protein at 100°. W. J. Y.

Bacterial Anti-proteases. KURT MEYER (*Biochem. Zeitsch.*, 280—286).—By immunising rabbits with solutions of the proteases from *Bacillus prodigiosus* and *B. pyocyaneus*, sera were obtained which contained anti-substances to these enzymes. These anti-substances withstood heating for half an hour at 75°, but were destroyed at 100°, so that a mixture of protease and antiprotease was rendered active again by heating at 100°. They were precipitated with the globulin fraction of the serum, and were weakened by extraction with light petroleum.

When the protease was added fractionally to the anti-substance, the Danysz effect was not observed. The proteases were not completely bound by the anti-substance, since the enzyme was able to bring about digestion to a slight extent even in the presence of excess.

These anti-substances would not inhibit the action of other bacterial proteases nor of pancreatic trypsin; they are therefore specific.

W. J. Y.

Action of Invertase on Polysaccharides Derived from Lævulose. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1911, **152**, 1060—1062).—Sucrose, raffinose, gentianose, and stachyose have the property in common of yielding lævulose and dextrose as products of hydrolysis when acted on by invertase. The order in which these sugars are placed indicates the relative rates at which lævulose is liberated, the first-mentioned being most rapidly decomposed. The marked difference in the rates of hydrolysis suggests that the ferment has to bring about disruption, not only between a single dextrose and lævulose residue, but also, in the case of raffinose, gentianose, and stachyose, between lævulose and the rest of the molecule. In other words, it would appear that the lævulose complex is not the terminal member of a chain of hexoses in these three polysaccharides.

W. O. W.

Organic Chemistry.

New Method for Esterification of Alcohols by Halogen Acids. GEORGES DARZENS (*Compt. rend.*, 1911, **152**, 1314—1317).—A general method for replacing the hydroxyl group by a halogen consists in treating the substance with thionyl chloride or bromide (2 mols.) in presence of a tertiary base (1 mol.). There is but little development of heat, and the reaction is complete in half an hour. Sulphur dioxide may be removed by heating at 80—110°, but this is not always necessary. The process gives yields exceeding 95%, and is stated to be free from the disadvantages associated with the use of a halogen hydride or the employment of phosphorus pentachloride. Dimethyl- and diethyl-aniline are the most suitable bases to use. As examples of its application, the conversion of *iso*amyl alcohol, dichlorohydrin, benzyl carbinol, and cinnamyl carbinol into the corresponding chloro-derivatives is mentioned. The method cannot be applied to phenols. *cyclo*Hexanol is converted into *cyclo*hexene through removal of hydrogen chloride from the unstable chloro-compound.

W. O. W.

Boiling Point of Mixtures of Water and [Ethyl] Alcohol. C. MARILLER (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 768—770).—The boiling point of mixtures of ethyl alcohol and water, containing 8 to 100% of alcohol, can be represented by means of the formula $t = 78{\cdot}4 + \sqrt{0{\cdot}22\ a.e/a}$, in which e and a denote respectively the percentages of water and alcohol in the mixture boiling at t° under atmospheric pressure.

H. M. D.

Synthesis of Tertiary α-Keto-alcohols. D. GAUTHIER (*Compt. rend.*, 1911, **152**, 1259—1261. Compare this vol., i, 415).—An extension of the reaction previously described to the cyanohydrins of ketones. *β-Methylbutanone-β-ol*, $OH{\cdot}CMe_2{\cdot}COMe$, prepared by the action of magnesium methyl iodide on acetone cyanohydrin (cyano*iso*propyl alcohol), has b. p. 79°/730 mm., and forms a *semicarbazone*, m. p. 180°. This substance is not identical with the compound to which Schmidt and Austin (Abstr., 1903, i, 2) have ascribed the above constitution.

β-Methylpentan-γ-one-β-ol, $OH{\cdot}CMe_2{\cdot}COEt$, has b. p. 96—98°/725 mm. *γ-Methylpentanone-γ-ol*, $OH{\cdot}CMeEt{\cdot}COMe$, has b. p. 94°/729 mm.

W. O. W.

Chemical Action of Light. XIX. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, **44**, 1280—1289. Compare Abstr., 1910, i, 299).—A mixture of acetone (1 part) and methyl alcohol (2 parts), after being exposed to the action of light for over one year, was found to contain *iso*propyl alcohol, formaldehyde, ethylene glycol, and *iso*butylene glycol, $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$. The two substances first-named are formed by the interaction of acetone and methyl alcohol:

$$COMe_2 + Me{\cdot}OH = CHMe_2{\cdot}OH + CH_2O,$$

whilst the formation of ethylene glycol and *iso*butylene glycol is due to a condensation of methyl alcohol with formaldehyde and acetone respectively.

Similar results have been obtained by replacing the methyl alcohol by ethyl alcohol. A mixture of acetone and ethyl alcohol, after exposure to light for nine months, gave the following products: (1) diacetyl, which was identified by means of its oxime, m. p. 244° (Fittig, Abstr., 1889, 490, gives 234·5°); (2) *iso*propyl alcohol; (3) *β-methylbutylene βγ-glycol*, $OH·CMe_2·CHMe·OH$; (4) an oil, containing, amongst other substances, trimethylethylene glycol and butylene-βγ-glycol, OH·CHMe·CHMe·OH. In order to separate the latter compound, advantage was taken of the fact that it undergoes the pinacolin rearrangement when heated with dilute sulphuric acid at 130° less readily than methylbutylene glycol, which is converted under the same conditions into methyl *iso*propyl ketone. The distillate, after this treatment, was found to contain, besides methyl *iso*propyl ketone, a *liquid*, b. p. 149°, having the composition $C_4H_{10}O_2$. This substance is probably formed from methylbutylene glycol and butylene glycol by the loss of water: $C_5H_{12}O_2 + C_4H_{10}O_2 = 2H_2O + C_9H_{18}O_2$, but whether it is contained in the original mixture or is subsequently produced by the action of sulphuric acid has not been decided.

The βγ-butylene glycol, isolated from the mixture, gave, on treatment with phenylcarbimide, two isomeric *phenylurethanes*, the less soluble one having m. p. 175°, the other, m. p. 201—202°. These have the composition NHPh·CO·O·CHMe·CHMe·O·CO·NHPh, and are considered by the authors to be the phenylurethanes of racemic and inactive butylene βγ-glycol. Two *dibenzoyl* derivatives,

OBz·CHMe·CHMe·OBz,

were also obtained: a solid, crystalline form, m. p. 77° (monoclinic: $a:b:c = 0·4170:1:0·3337$; $\beta = 69°6'$), and a liquid modification, b. p. 217—218°/16 mm.

With *iso*propyl alcohol and acetone the reaction is much simpler; the only product formed by exposing a mixture of these substances, in equal parts, to the action of light for nine months consists of pinacone.

With the object of discovering if a condensation of alcohol with aromatic ketones takes place under the influence of light, similar to that found in the case of acetone, the behaviour of benzophenone in ethyl-alcoholic solution has been re-investigated (compare Abstr., 1901, i, 329), but no evidence of such a condensation has been obtained.

F. B.

Basic Properties of the Oxygen of Ethers. DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1911, [iv], 9, 519—523).—Determinations of the viscosities and densities of mixtures of (1) ethyl ether and acetic acid, and (2) ethyl ether and trichloroacetic acid, indicate that the first two substances do not form additive compounds with each other, whilst the second two form at least one (compare Tsakalotos and Guye, Abstr., 1910, ii, 826). The conclusion is drawn that ethereal oxygen is weakly basic and can only unite with strong acids.

T. A. H.

Catalytic Decomposition of Formic Acid. PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, **152**, 1212—1215).—Substances which bring about catalytic decomposition of formic acid may be divided into three classes: (1) Those capable of effecting dehydrogenation; the products in this case contain only traces of formaldehyde. The following act in this way: palladium, platinum, rhodium, reduced copper, nickel and cadmium, zinc and stannous oxides; (2) catalysts effecting dehydration, namely, the oxides of titanium, tungsten, zirconium, aluminium, uranium and silicon; (3) substances acting in the same way as the foregoing, but in addition giving more or less formaldehyde, such as ferrous, manganous, chromic, magnesium, molybdenum, vanadium and glucinum oxides, lime, carbon and Jena glass. Since the nature of the products and their relative proportions depend on the catalyst employed, it is evident that these substances do not act merely by lowering the temperature at which the reactions become possible. W. O. W.

Direct Synthesis of Glycerides. ITALO BELLUCCI and R. MANZETTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 503—504).—In reply to Gianoli's claim for priority (Sixth Congress of Applied Chemistry, Rome, 1906; this vol., i, 349) to the authors (this vol., i, 259), the latter point out that Scheij (Abstr., 1899, i, 667) was the first to synthesise glycerides under reduced pressure. T. H. P.

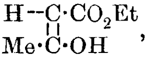
The Systems: Fat–Alcohol. ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1911, **25**, 210—216).—Butter-fat, cocoanut oil, and olive oil were separately brought into contact with different proportions of 94% alcohol at 37° until equilibrium was attained, and the composition of the fatty and alcoholic layers was then determined. Similar experiments were also made with a mixture of butter-fat and cocoanut oil. H. M. D.

Action of Ultra-violet Light on Lactic Acid. MARC LANDAU (*Compt. rend.*, 1911, **152**, 1308—1309. Compare Berthelot and Gaudechon, this vol., ii, 170; Euler, *ibid.*, ii, 452).—In addition to the liberation of gases when lactic acid is exposed to ultra-violet light, other changes occur involving the production of ethyl alcohol, pyruvic acid, and traces of an unidentified substance which reduces ammoniacal silver nitrate in the cold. W. O. W.

Oxidation of Higher Acetylenic Aliphatic Acids. ALBERT ARNAUD and V. HASENFRATZ (*Compt. rend.*, 1911, **152**, 1603—1606. Compare Abstr., 1902, i, 342—343).—In the oxidation of stearolic and tariric acids by nitric acid, the chain is broken between the two carbonyl groups of the diketonic acid which represents the first stage of oxidation. When potassium permanganate is employed, however, one carbonyl group is eliminated as carbon dioxide. This follows from the observation that on treatment with alkaline permanganate, stearolic acid gives nonoic and octoic acids (38%) with suberic and azelaic acids (53%), whilst tariric acid yields lauric and undecoic acids (55%) with glutaric and adipic acids (25%). W. O. W.

Studies on Tautomerism. IV. Desmotropy of Acetoacetic Ester. LUDWIG KNORR, O. ROTHE, and H. AVERBECK (*Ber.*, 1911, **44**, 1138—1157).—The ketonic and enolic forms of ethyl acetoacetate have been isolated in a pure condition and their transformations studied. The ketonic ester is sparingly soluble in organic solvents at a low temperature, and therefore crystallises when its solutions are strongly cooled. It was isolated by cooling its solution in alcohol or a mixture of alcohol and ether to $-78°$, and washing the crystals thus obtained with light petroleum or methyl ether until free from the enolic form, in a specially constructed apparatus, a sketch of which is given. All operations must be carried out in the complete absence of moisture. The ketonic ester crystallises in prisms or needles, which may be kept for a long time at a low temperature without undergoing any change. At the ordinary temperature it is slowly transformed into the equilibrium mixture, the change in the absence of catalytic influences being complete in the course of several weeks. Small quantities may be distilled in the vacuum of the cathode light practically unchanged. It has b. p. 40—41°/2 mm., n_D^{10} 1·4225, and solidifies at $-39°$, whereas the equilibrium mixture solidifies at $-45°$ to $-43°$, and has b. p. 39—40°/2 mm., n_D^{10} 1·4230 to 1·4232. At the ordinary temperature, it gives the ferric chloride reaction like the equilibrium mixture, but this is ascribed to enolisation induced by the ferric chloride. At low temperatures the enolisation takes place less rapidly, and in these circumstances comparative tests show that the red coloration with ferric chloride is developed much more slowly in the case of the ketonic ester than with the equilibrium mixture.

The enolic ester is obtained by treating a suspension of ethyl sodioacetoacetate in light petroleum with gaseous hydrogen chloride, in quantity just insufficient for complete decomposition, filtering from sodium chloride, and evaporating the filtrate as rapidly as possible under strongly diminished pressure, all operations being carried out at $-78°$ and in the complete absence of moisture. A sketch of the apparatus employed is given.

The enolic ester is a colourless oil, having an agreeable fruity odour; it has D_4^{10} 1·0119, n_D^{10} 1·4480, and solidifies in liquid air to a glassy mass, which soon becomes crystalline. In a high vacuum and in small quantities, it distils at about 33° without undergoing appreciable change. Its enolic nature is shown by a much more rapid development of the ferric chloride reaction than is the case with the ketonic ester. In ethereal solution at $-78°$, it gives at once an intense coloration with ethereal ferric chloride. Reasons are given in favour of the cis-configuration,  $\begin{matrix}\mathrm{H{-}C{\cdot}CO_2Et}\\ \|\\ \mathrm{Me{\cdot}C{\cdot}OH}\end{matrix}$, for the ester.

A large number of mixtures of the ketonic and enolic esters have been prepared, and their refractive indices determined; from the results thus obtained it is found that, at the equilibrium point, ethyl acetoacetate contains 2% of the enolic form (compare Hantzsch, Abstr., 1910, i, 811; K. H. Meyer, this vol., i, 350).

At low temperatures the enolic ester may be kept for a long time unchanged. At the ordinary temperature, it is transformed in the course of ten to fourteen days into the equilibrium mixture, whilst at 100° the transformation is complete in one minute. The velocity of transformation has been determined refractometrically, and it is found to be enormously increased by the catalytic influence of both acids and bases. Contact with gaseous hydrogen chloride, soft alkali glass, and even exposure to air, transform the enolic ester into the equilibrium mixture in the course of a few seconds or minutes. In solution, the velocity of transformation at the ordinary temperature also increases, but diminishes rapidly with fall of temperature.

The influence of temperature on the equilibrium between the ketonic and enolic forms has been investigated by heating ethyl acetoacetate at various temperatures up to 181°, and then rapidly cooling, but no displacement of the equilibrium could be detected. Refractometric measurements showed that all specimens thus treated contained 2% of the enolic modification.

The equilibrium between the ketonic and enolic esters in the form of vapour varies, however, with the temperature and pressure. When ethyl acetoacetate is distilled under ordinary pressure and the vapour rapidly cooled, a distillate containing 10% of the enolic form was obtained, whilst by distilling slowly under diminished pressure and cooling the vapour rapidly to $-78°$, the proportion of enolic ester rises to 27—39%, and remains constant until the end of the distillation. According to the authors, the greater proportion of the enolic form in the distillate is due to its greater vapour pressure; it therefore distils over more rapidly, and since the equilibrium thus disturbed is quickly restored at the temperature of the distillation, the enolic ester is continuously replenished in the distillation flask. The distilled ester is far more rapidly transformed into the equilibrium mixture than the enolic ester, prepared from ethyl sodioacetoacetate. The view is expressed that this is due to the formation during the distillation of the trans-enolic ester, which has a greater velocity of transformation into the ketonic form than the cis-isomeride.

The relative proportions of the ketonic and enolic forms in equilibrium in various solvents have also been determined; the values obtained for the percentage of enolic ester vary from 2% in light petroleum to 31% in hexane.

By strongly cooling solutions of many other tautomeric substances, one of the forms crystallises out, whilst in other cases a separation may be effected by freezing and pressing out. F. B.

Action of Thionyl Chloride in Presence of a Tertiary Base on Esters of Hydroxy-acids. GEORGES DARZENS (*Compt. rend.*, 1911, **152**, 1601—1603. Compare this vol., i, 513).—The method previously described for replacing the hydroxyl group by a halogen has been successfully applied to the esters of hydroxy-acids. Ethyl lactate gave a practically theoretical yield of ethyl α-chloropropionate; pyridine is the best base to employ in this case. Ethyl *l*-malate has been transformed into ethyl *d*-chlorosuccinate; less racemisation takes place than when phosphorus pentachloride is employed, and the product has $[\alpha]_D^{20}$ $+31·20°$, whereas Walden found 27·30°.

In some cases dehydration occurs; thus ethyl *cyclo*hexan-1-ol-1-carboxylate gives ethyl *cyclo*hexenecarboxylate, whilst esters of the type $OH\cdot CRMe\cdot CH_2\cdot CO_2Et$ are converted into the corresponding acrylates. W. O. W.

ψ-Acid Esters in the Mesoxalic Ester Synthesis. Richard S. Curtiss and John A. Kostalek (*J. Amer. Chem. Soc.*, 1911, 33, 962—974).—It has been shown by Curtiss (Abstr., 1906, i, 480) that when the gases evolved by the action of nitric acid on arsenious oxide are allowed to react with ethyl malonate at − 10°, ethyl mesoxalate is produced, together with an oily acid substance which was at first supposed to be ethyl *iso*nitrosomalonate, but has now been found to consist of a mixture of acid esters containing nitrogen. From this mixture, ethyl nitromalonate and ethyl dinitroacetate have been separated by means of their potassium salts. The acid esters are colourless oils, whilst their potassium salts are coloured. Ethyl nitromalonate and its salts have been studied by Hantzsch (Abstr., 1907, i, 556), who explains the variation in colour on the basis of differences in structure.

Ethyl dinitroacetate yields potassium salts of two forms, one yellow, which has been described by Bouveault and Wahl (Abstr., 1903, i, 225), and the other red, the latter being known only in solution. The cold aqueous solution of the yellow form is also yellow, but becomes red when heated, and reverts to its original colour on cooling. The yellow form is dimorphous, crystallising in slender, monoclinic prisms or lustrous plates; it decomposes at 194—195°. On reduction with tin and hydrochloric acid, it yields ethyl glyoxylate and ammonia. When the potassium salt is heated with methyl or ethyl iodide and 50% alcohol in a sealed tube at 100—110°, a yellow, viscous, unstable oil is produced. The salt reacts more readily with ethyl sulphate, and yields potassium sulphate and nitrite and a mixture of oily products. On boiling potassium ethyl dinitroacetate (1 mol.) with alcoholic potassium hydroxide (2 mols.), a brilliant yellow *salt* is formed, which is probably a form of dipotassium *aci*-dinitroacetate; it decomposes violently at 210°. The *ammonium* and *silver* salts of ethyl dinitroacetate are described; the *sodium*, *hydrazine*, and *aniline* salts were also prepared.

Potassium ethyl nitromalonate, m. p. 154°, crystallises in dark yellow needles or hexagonal prisms. Hantzsch (*loc. cit.*) obtained a colourless form of this salt by the action of potassium carbonate on the colourless form of the ammonium salt. The ammonium salt, m. p. 151°, obtained by the action of dry ammonia on ethyl nitromalonate at − 10°, forms pale yellow, prismatic crystals. The white modification dissolves in alcohol or water to form a yellow solution.

If dry ammonia is passed into an ethereal solution of the crude product of the action of nitrogen oxides on ethyl malonate, the salts of ethyl nitromalonate and ethyl dinitroacetate are precipitated. When an excess of ammonia is added, an unstable red oil separates. The filtrate from the ammonium salts yields a crystalline substance, m. p. 50°, which forms flat, colourless needles. E. G.

New Complex Iridium Derivatives: Iridotetrachloro-oxalates and Iridotetrachlorides. ALEXIS DUFFOUR (*Compt. rend.*, 1911, **152**, 1393—1396).—The iridotetrachloro-oxalates are intermediate between the iridichlorides and the iridodichloro-oxalates previously described (Abstr., 1909, i, 762). The *sodium* salt, $Na_3IrCl_4(C_2O_4)_2$, was obtained in solution by heating sodium oxalate with aqueous sodium iridichloride. The *potassium* salt obtained from this by double decomposition crystallises with $1H_2O$ in dark reddish-brown, orthorhombic prisms showing strong dichroism and double refraction. An aqueous solution gives no reaction for chloride or oxalate, but with silver nitrate yields an insoluble *silver* salt. The *rubidium, caesium,* and *ammonium* salts crystallise with $1H_2O$, and appear to be isomorphous with the potassium salt.

Iridotetrachloro-oxalic acid, prepared from the silver salt, is crystalline, but very unstable. In solution it decomposes into oxalic acid and a new acid, $HIrCl_4$, which has not been isolated. The existence of a substance of this constitution is assumed from the fact that the corresponding *barium* salt gives no silver chloride when treated with silver nitrate, but forms a green precipitate of the *silver* salt.

W. O. W.

New Types of Irido-oxalic Acids and Irido-oxalates. ALEXIS DUFFOUR (*Compt. rend.*, 1911, **152**, 1591—1594. Compare preceding abstract).—Gialdini's irido-oxalic acid (Abstr., 1907, i, 1005) is best prepared by the action of hydrochloric acid on the silver salt. When freshly prepared, its aqueous solution is golden-yellow, but on exposure to air becomes brown, and, finally, emerald-green. The solution now contains a new acid arising from the elimination of a molecule of oxalic acid from the original substance. The corresponding *potassium* salt, $KIr(C_2O_4),5H_2O$, obtained by adding potassium hydroxide (1 mol.), occurs in highly refractive, dichroic, green crystals, which lose $3H_2O$ at 110° without changing colour. On further treatment with potassium hydroxide (1 mol.), it forms an orange-red salt, $K_2[Ir(C_2O_4)_2(OH)(H_2O)],2H_2O$. The corresponding *acid,*

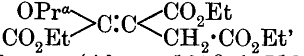
$$H_2[Ir(C_2O_4)_2(OH)(H_2O)],5H_2O,$$

forms monoclinic crystals, losing $3H_2O$ over sulphuric acid and $5H_2O$ at 110°; on treatment with potassium hydroxide (1 mol.), yellow dichroic prisms of the salt, $KH[Ir(C_2O_4)_2(OH)(H_2O)],2H_2O$, are obtained isomeric with the first-mentioned green salt, from which it can also be prepared by the action of heat on the aqueous solution.

W. O. W.

Action of the Oxides of Lead on Potassium Tartrate. FRANCIS C. KRAUSKOPF (*J. Amer. Chem. Soc.*, 1911, **33**, 943—947).—The solubility of litharge in solutions of alkali tartrates (Kahlenberg and Hillyer, Abstr., 1894, i, 275; Kahlenberg, Abstr., 1896, ii, 6) and the supposed insolubility of red lead and lead dioxide in such solutions indicated a method for freeing red lead and lead dioxide from litharge and for estimating the amount of litharge in samples of these oxides. It has been found, however, that both red lead and lead dioxide are soluble to some extent in alkali tartrate solutions.

A study of the action of red lead and lead dioxide on potassium tartrate solutions has shown that these oxides dissolve without causing the evolution of oxygen. In the case of lead dioxide, the tartrate is oxidised and lead carbonate is precipitated, but red lead dissolves without appreciable oxidation of the tartrate. The rotatory power of potassium tartrate solution is diminished by the addition of either litharge or red lead. Red lead causes a slightly greater diminution of the rotation than an equivalent quantity of litharge, and it is therefore evident that red lead is not reduced to litharge before dissolving. E. G.

Dibasic Ketonic Acids. EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. chim.*, 1911, [iv], 9, 451—458, 458—464).—A more detailed account is given of the general method for the preparation of dibasic ketonic acids described already (Abstr., 1908, i, 713; 1909, i, 134, 362; 1910, i, 487, 542), and syntheses of new acids of this type are described. Ethyl oxalylsuccinate, b. p. 170—175°/12—13 mm., is a pale yellow oil which must be distilled rapidly in order to avoid much decomposition. Wislicenus and Nassauer's ester was probably chiefly ethyl ethanetricarboxylate (Abstr., 1895, i, 506). On condensation with propyl iodide, ethyl oxalylsuccinate gives ethyl *O*-propyloxalylsuccinate,  $\genfrac{}{}{0pt}{}{\mathrm{OPr^{\alpha}}}{\mathrm{CO_2Et}}\!>\mathrm{C{:}C}<\!\genfrac{}{}{0pt}{}{\mathrm{CO_2Et}}{\mathrm{CH_2\cdot CO_2Et}}$, b. p. 195—198°/15 mm. or 190—191°/13 mm. (Abstr., 1908, i, 713). On hydrolysis by hydrobromic or hydrochloric acid, this yields as one product (*loc. cit.*) α-ketoglutaric acid, $CO_2H\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, which gives a yellowish-green coloration with ferric chloride and furnishes a *phenylhydrazone*, m. p. 260° (approx. decomp.), separating from dilute alcohol in small, yellow crystals; and a *semicarbazone*, m. p. 220° (approx.), crystallising from warm water. Its reaction with hydrazine hydrate has been described by Gabriel (Abstr., 1909, i, 259). *Ethyl α-ketoglutarate*, b. p. 144°/13 mm., obtained by esterification of the acid in a closed tube at 120°, is a colourless liquid; the *semicarbazone*, m. p. 114°, is crystalline. Attempts to prepare the acid anhydride were unsuccessful.

Ethyl α-oxalyl β-methylsuccinate (Abstr., 1908, i, 713) furnishes a crystalline p-*nitrophenylhydrazone*. On heating, the ester furnishes *propane α-ββ-tricarboxylic acid*, m. p. 170° (decomp.), which on further heating yields methylsuccinic acid. On hydrolysis by acids, ethyl methyloxalylsuccinate furnishes *γ-keto-α′-methylglutaric acid*,

$$CO_2H\cdot CO\cdot CH_2\cdot CHMe\cdot CO_2H,$$

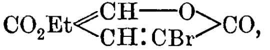
as a viscous liquid which is not volatile without decomposition. It yields an unstable *oxime*, m. p. 162° (approx.), a *semicarbazone*, m. p. 141—142°, a *phenylhydrazone*, m. p. 171—172°, and p-*nitrophenylhydrazone*, m. p. 163°, all of which are crystalline. The acid cannot be regenerated from the semicarbazone; the phenylhydrazone on dehydration, by heating at 140°, furnishes 1-*phenyl*-5-*methylpyridazin*-6-*one*-3-*carboxylic acid*, m. p. 134°, crystallising from water in lamellæ. By the direct action of hydrazine hydrate on methyl ketoglutaric acid, 5-*methylpyridazin*-6-*one*-3-*carboxylic acid*, m. p. 175°, is obtained.

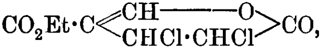
Ethyl ketomethylglutarate, b. p. 144—145°/15 mm., obtained by esterifying the acid in the usual way, is a colourless liquid; it forms a crystalline *additive product* with sodium hydrogen sulphite, and yields a *semicarbazone*, m. p. 98°, and a p-*nitrophenylhydrazone*, m. p. 109—110°, both of which are crystalline. T. A. H.

Ethyl Formylglutaconate and its Isomerides. WILHELM WISLICENUS and MARGARITA VON WRANGELL (*Annalen*, 1911, **381**, 367—384. Compare Wislicenus and Bindemann, Abstr., 1901, i, 361).—The oily product formed by leaving ethyl formylglutaconate dissolved in moist ether for two to three days is shown to be a polymeride, namely, $C_{20}H_{28}O_{10}$, of the original ester. It is characterised by its oily consistency and by the red coloration it gives with ferric chloride. Moisture is essential for its formation; in dry benzene solution the original ester is stable, and can be kept for months; with the dry solid in a desiccator at the ordinary temperature the transformation is extremely slow, but rise of temperature favours the change. Small amounts of acid, on the other hand, retard the transformation. With sodium ethoxide the polymeride yields an orange-yellow salt, but is not so reactive as the original ester, for example, it does not react with bromine, hydrogen bromide, phenylhydrazine, or benzoyl chloride. Its *copper* derivative forms a deep green, slimy mass, which was obtained as a solid, m. p. 97°, on one occasion only. The structure suggested for the oily polymeric form is
$CO_2Et\cdot CH_2\cdot CH{:}C(CO_2Et)\cdot CH(OH)\cdot CH(CO_2Et)\cdot CH{:}C(CO_2Et)\cdot CHO$,
and this formula is in agreement with the fact that when heated at 120° under slight pressure the oil yields ethyl trimesate, formic acid, and ethyl acetate, and also with the formation of an additive compound, $C_{27}H_{33}O_{11}N$, with phenylcarbimide. It is probably that the original ester is first transformed into the tautomeric aldo-form before polymerisation occurs.

The *benzoyl* derivative of ethyl formylglutaconate,
$CO_2Et\cdot CH{:}CH\cdot C(CO_2Et){:}CH\cdot O\cdot COPh$,
crystallises from ether in colourless needles, m. p. 63·5°, and the corresponding p-*nitrobenzoyl* derivative, $C_{17}H_{17}O_8N$, in colourless needles, m. p. 117°.

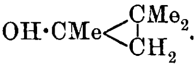
The *phenylcarbimide* additive product, $C_{17}H_{19}O_6N$, forms colourless plates, m. p. 74°. When bromine is added to its chloroform solution, the ester yields a *dibromide*, $C_{10}H_{14}O_5Br_2$, as an oil which does not react with ferric chloride. When distilled under 14 mm. pressure, it loses hydrogen bromide and yields an oily *ethyl bromoformylglutaconate*. $CO_2Et\cdot C({:}CH\cdot OH)\cdot CH{:}CBr\cdot CO_2Et$, which gives an intense red coloration with ferric chloride. Potassium ethoxide transforms the oily bromo-ester into an *isomeric* solid, which crystallises from ether in colourless needles, m. p. 55—56°, and gives a violet coloration with ferric chloride. The *copper* derivative, $(C_{10}H_{12}O_5Br)_2Cu$, crystallises from benzene in small prisms, m. p. 144—145°.

Ethyl bromocoumalate,  $CO_2Et\left\langle\begin{matrix}CH\text{——}O\\CH{:}CBr\end{matrix}\right\rangle CO$, obtained by distilling ethyl bromoformylglutaconate, crystallises from alcohol in colourless prisms, m. p. 94—95°, and on hydrolysis with the theoretical amount of potassium hydroxide solution yields Feist's furan-2 : 4-dicarboxylic acid (Abstr., 1901, i, 557).

Ethyl formylglutaconate dichloride forms a colourless oil, and when distilled under reduced pressure yields ethyl dichlorodihydrocoumalate,  $CO_2Et{\cdot}C\left<\begin{matrix}CH\text{———}O\\ CHCl{\cdot}CHCl\end{matrix}\right>CO$, as an oil with b. p. 175—180°/18—20 mm. J. J. S.

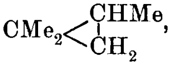
Tetrolaldehyde (**Δ^{a}-Butinal**). Paul L. Viguier (*Compt. rend.*, 1911, **152**, 1490—1493. Compare Abstr., 1909, i, 691).—Diethoxybutinene is best prepared by the action of ethyl orthoformate on magnesium allylene bromide. When the acetal is hydrolysed with 10% aqueous oxalic acid, *tetrolaldehyde*, CMe⋮C·CHO, is produced, and may be isolated by distillation in steam and extraction with ether. This substance is a colourless, mobile liquid with an intensely irritating odour, m. p. $-26°$, b. p. 27—28°/34 mm., 106·5—107° under ordinary pressure, D^{0} 0·944, D^{17} 0·9265, n_D^{17} 1·4467. It shows the usual reactions of an aldehyde and forms a very soluble compound with sodium hydrogen sulphite. The *semicarbazone* has m. p. 158°. The *oxime* crystallises in long needles, subliming at about 100°, m. p. 108—109°; at the ordinary temperature it changes slowly into methyl*iso*oxazolone (compare Claisen, this vol., i, 491).

Tetrolaldehyde reacts with hydrazine hydrate to give a *hydrazone*, b. p. 63—65°/15 mm., $D^{18.5}$ 0·9768, $n_D^{18.5}$ 1·530; the corresponding *azine* forms yellow needles, m. p. 123—124°. The hydrazone unites with phenylthiocarbimide, producing a *phenylthiosemicarbazone*, m. p. 114—116° (decomp.). 5-Methylpyrazole is formed when the aldehyde is heated with potassium hydroxide. W. O. W.

The Pinacolin Transformation. I. J. Lindner (*Monatsh.*, 1911, **32**, 403—426).—The researches of previous investigators leave little doubt that pinacones and pinacolins have respectively the constitutions, for example, $OH{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH$ and $CMe_3{\cdot}COMe$. During the conversion of the former into the latter by dilute acids, therefore, a methyl group has shifted from the one tertiary carbon atom to the other. The author hopes to show that the change is explicable by Erlenmeyer's theory of the intermediate production of a *cyclo*propane derivative, despite Montagne's criticism (Abstr., 1905, i, 445, 524). A suggestion is advanced to counter Montagne's objection that in the conversion to 4 : 4′ : 4″ : 4‴-tetrachlorobenzopinacone into the corresponding pinacolin, the halogen atoms are still in the para-position, whereas by Erlenmeyer's theory they should be in the ortho- or meta-positions, to the tertiary carbon atom. A serious objection to Erlenmeyer's theory, however, is Lieben's statement (Abstr., 1905, i, 167) that the pinacolin transformation is possible only with (purely aliphatic) pinacones which contain the group ⁚CMe·OH. Attention is drawn to the mobility of aromatic groups in glycols; thus Thörner and Zincke have shown that acetophenonepinacone yields only the pinacolin, $CMePh_2{\cdot}COMe$ (compare also Tiffeneau, Abstr., 1907, i, 130). This mobility, which may be due to the unsaturated character of the aromatic nucleus and its consequent ability to enter into ring formation, is in favour of Erlenmeyer's theory. The theory would be proved by the isolation of the intermediately formed *cyclo*propanol derivative, for example,  $\mathrm{OH{\cdot}CMe}{<}\begin{array}{l}\mathrm{CMe_2}\\ \mathrm{CH_2}\end{array}$.

With this end in view the author has prepared the two methyl ethers of acetonepinacone. An intimate mixture of the pinacone (1 mol.) and sodium is carefully warmed, and the resulting sodium derivative is heated for several days with methyl iodide. The separation of the two ethers is very difficult. The *methyl ether*, $OMe{\cdot}CMe_2{\cdot}CMe_2{\cdot}OH$, has b. p. 148—149°; the *dimethyl ether* has b. p. 144°; both are colourless liquids, with a pleasant odour recalling that of the pinacone.

A preliminary experiment with boric anhydride having shown that acetonepinacone can be thereby transformed into the pinacolin, the two ethers have been separately heated at 140° with this oxide, but in both cases the pinacolin, not the desired *cyclo*propanol derivative, is formed. The methyl ether is recovered unchanged after being heated with sodium acetate at 120—140°, or with barium oxide at 200°, but is partly converted into the pinacolin after being shaken with 25% sulphuric acid and kept for two weeks. The *acetate*, $OMe{\cdot}CMe_2{\cdot}CMe_2{\cdot}OAc$, b. p. 179—180°, of the methyl ether, obtained by the action of acetic anhydride and 3 drops of concentrated sulphuric acid for twelve days, has also been heated with boric anhydride at 110°, but methyl acetate and pinacolin are the only products which have been identified.

Dimethyl*iso*propylcarbinol, which is most conveniently prepared from methyl *iso*propyl ketone and magnesium methyl iodide, has also been examined in the hope that it might yield a *cyclo*propane derivative,  $\mathrm{CMe_2}{<}\begin{array}{l}\mathrm{CHMe}\\ \mathrm{CH_2}\end{array}$, under the influence of acids. However, 20% sulphuric acid at 120° converts it almost quantitatively into $\beta\gamma$-dimethyl Δ^{β}-butylene, whilst the action of boric anhydride, which is different, has not yet been fully examined. The preceding experiments, although not fulfilling the author's hopes, indicate that the formation of esters plays an important part in the pinacolin transformation, which is a specific action of acids. C. S.

Ethyl Derivatives of Acetone. Ernst Zerner (*Compt. rend.*, 1911, **152**, 1599—1601).—Using Haller and Bauer's method (Abstr., 1910, i, 219—300), the author has prepared the tri-, tetra-, penta-, and hexa-ethyl derivatives of acetone.

$\gamma\gamma\epsilon$-*Triethylheptan*-δ-*one*, $CEt_3{\cdot}CO{\cdot}CHEt_2$, has b. p. 237·5—238·5°/761 mm. $\gamma\gamma\epsilon\epsilon$-*Tetraethylheptan*-$\delta$-*one*, $CEt_3{\cdot}CO{\cdot}CEt_3$, m. p. 44°, b. p. 274—275°/759 mm., has an apple-like odour, and does not undergo the usual scission when treated with sodamide. W. O. W.

Action of Hydrogen Peroxide on α-Diketones. Jacob Böeseken, (Mlle.) Lichtenbelt, Milo, and van Marlen (*Rec. trav. chim.*, 1911, **30**, 142—147).—The normal course of the oxidation of α-ketonic acids, such as pyruvic, phenylglyoxylic, *p*-chlorophenylglyoxylic, and thienyl-glyoxylic acids, by hydrogen peroxide results in the elimination of the ketonic group. The presence of a methyl group near the ketonic group, however, induces by-reactions; thus trimethylpyruvic acid is partly converted into *iso*butyric acid, and 2 : 4 : 6-trimethylphenylglyoxylic acid into phthalic acid.

Diacetyl is oxidised by hydrogen peroxide, yielding acetic acid, but not carbon dioxide; oxalic acid is only slowly and partly oxidised, yielding carbon dioxide, whilst oxamide, oxanilide, and oxanilic acid are almost unattacked, showing that the hydroxyl group largely, and the amino-group almost entirely, prevents the oxidation of the α-diketones.

β-Naphthaquinone is oxidised by hydrogen peroxide, yielding an unsaturated dibasic acid, m. p. 173—175° (*o*-carboxycinnamic acid ?), whilst stearoxylic acid is quantitatively converted into azelaic and pelargonic acids; the latter oxidation furnishes another proof of the constitution of oleic acid. C. S.

The Destruction of Dextrose by Light. ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, **33**, 252. Compare Mayer, this vol., i, 423).—The author reiterates his statement, that in alkaline solutions of dextrose when kept, the polarisation sinks to zero. The reaction must be carried out in well-closed flasks. S. B. S.

Action of Ultra-violet Light on Sucrose. HENRI BIERRY, VICTOR HENRI, and ALBERT RANC (*Compt. rend.*, 1911, **152**, 1629—1632. Compare Abstr., 1910, i, 625; this vol., i, 255).—The first action on sucrose of the light from a quartz-mercury lamp is to hydrolyse the sugar, and then to effect profound decomposition of the two hexoses, leading ultimately to the formation of formaldehyde and carbon monoxide. W. O. W.

Inversion of Sucrose in Ultra-violet Radiation. HANS VON EULER and H. OHLSÉN (*J. Chim. Phys.*, 1911, **9**, 416—422).—Aqueous solutions of sucrose were exposed in a quartz cell to the radiation from a quartz-mercury lamp. The solutions became heated to about 79° in twenty minutes, and were maintained at that temperature. The rate of hydrolysis appeared to be independent of the quantity of sugar present, and did not follow the unimolecular law. An acidic substance was progressively formed in the solutions, and the inversion was not greater than could be attributed to the action of this acid.
R. J. C.

Action of Alkalis on Chloraloses. MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1911, **152**, 1398—1399. Compare Abstr., 1910, i, 95).—Chloralose suffers decomposition when treated with aqueous alkalis, but if heated in sealed tubes with ammonia and methyl alcohol, it forms a *dichloro*-derivative, $C_7H_{11}O_6{\cdot}CHCl_2$, needles, m. p. 156—157°; the *tribenzoyl* derivative of this substance crystallises in needles, m. p. 192°. On hydrolysis, it yields dichloroacetaldehyde and dextrose, whilst nitric acid oxidises it to an *amide*, $C_7H_9O_5Cl_2{\cdot}CO{\cdot}NH_2$, m. p. 161—162°. The corresponding *acid* is obtained in needles, m. p. 129—130°, by treating this with nitrous acid; it very readily forms a *lactone*, from which well defined salts are prepared by the action of alkalis. W. O. W.

Action of Ammonia on Chloraloses. MAURICE HANRIOT and ANDRÉ KLING (*Compt. rend.*, 1911, **152**, 1596—1599. Compare preceding abstract).—The reaction previously described is general for chloraloses. Ammonia withdraws an atom of chlorine from α-chloralose, replacing it by hydrogen, forming a *compound*, $C_8H_{12}O_6Cl_2$, long needles, m. p. 165°, in aqueous solution $[\alpha]_D$ +9·96°; the *dibenzoyl* derivative has m. p. 146°. When the substance is treated with nitric acid, it forms a vitreous, feebly acidic *lactone*.

Galactochloralose and ammonia yield a *compound* isomeric with the foregoing, but existing in two modifications; one separates from water in crystals, m. p. 96°, but is changed in the second modification, m. p. 133°, on crystallisation from chloroform. The *dibenzoyl* derivative has m. p. 116°. Nitric acid oxidises the compound to mucic acid, whilst hydrochloric acid converts it into dichloroacetaldehyde and probably galactose.

The *compound*, $C_7H_{10}O_5Cl_2$, obtained from arabinochloralose has m. p. 88—89°, $[\alpha]_D$ −19·72°; the *dibenzoyl* derivative has m. p. 90·5°. Nitric acid converts it into an *acid*, $C_7H_8O_6Cl_2$, m. p. 215°, and possibly this is accompanied by trihydroxyglutaric acid.
W. O. W.

An Experiment to Demonstrate the Reducing Properties of Cellulose. ROLAND SCHOLL (*Ber.*, 1911, **44**, 1312—1314. Compare Scholl and Berblinger, Abstr., 1904, i, 110; Scholl, *ibid.*, 1907, i, 540).—A simple experiment which demonstrates the reducing properties of cellulose in a few minutes is as follows: The specimen to be tested is digested for a few seconds with a dilute solution obtained by boiling flavanthren with water, dilute sodium hydroxide solution, and solid sodium hyposulphite. After washing, the yellow dye is developed by exposing the fabric to the air for a few minutes, or by treatment with hypochlorite solution. By heating the yellow fabric to boiling with a 2*N*-sodium hydroxide solution, the blue colour is restored. The length of time required for the reduction depends upon the amount of hydrocelluloses and oxycelluloses present in the original specimen. Oxycelluloses give an immediate blue colour, but when the oxycelluloses are removed by previous boiling with dilute sodium hydroxide solution, a longer time is required for the development of the blue colour, and the alkaline extract produces the coloration more rapidly than does pure alkali. Other vat dyes, such as pyranthrones or anthraquinoneazine, can be used in place of flavanthren. In the ordinary process of printing without specific reducing agents, the reduction is brought about by the dextrin, gum, etc., used. J. J. S.

Partial Hydrolysis of Tunicate Cellulose. Formation of Cellobiose. EMIL ABDERHALDEN and GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1911, **72**, 58—62).—The mere obtaining of dextrose from tunicin, the cellulose of tunicate animals, does not establish its identity with vegetable cellulose. Further proofs of the identity or close relationship are now adduced, namely: (1) by the action of acetic anhydride in the presence of sulphuric acid, an acetyl compound (octa-acetylcellobiose) was obtained with the same melting point, solubility, composition, and optical activity as the product similarly obtained from filter paper; (2) the osazones of the cellobioses are also identical; (3) by saponification of the acetyl compound by means of barium hydroxide in the cold, crystallised cellobiose was obtained.

W. D. H.

Phosphates of Uranyl and of Amines. LÉONCE BARTHE (*Compt. rend.*, 1911, **152**, 1396—1397).—Double phosphates of the type $B'HUO_2PO_4$ have been prepared by saturating an aqueous solution of phosphoric acid with an amine, and adding a solution of uranyl acetate drop by drop. The compounds are precipitated in a pale yellow colloidal condition, and when dried in a vacuum become horny. They are very stable, and are not decomposed at 100°.

Methylamine uranyl phosphate, $NH_3Me{\cdot}UO_2PO_4$, has been obtained in this way, and also the corresponding *ethylamine* and *trimethylamine* salts.

W. O. W.

Preparation of Tetramethylenediamine [αδ-Diaminobutane]. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 232072).—A method for the technical preparation of αδ-diaminobutane has not previously been known; it is now found that a satisfactory yield can be obtained by treating adipodiamide, $NH_2{\cdot}CO{\cdot}[CH_2]_4{\cdot}CO{\cdot}NH_2$, with a halogen in aqueous alkaline solution; the amide dissolves, and the temperature rises to 70°; the reaction is completed by heating on the water-bath.

F. M. G. M.

Syntheses of Polypeptides. Derivatives of α-Aminobutyric Acid and their Behaviour towards Peptolytic Ferments. EMIL ABDERHALDEN, HSING LANG CHANG, and ERICH WURM (*Zeitsch. physiol. Chem.*, 1911, **72**, 24—36).—dl-*α-Formylaminobutyric acid*, $CH_2Me{\cdot}CH(CO_2H){\cdot}NH{\cdot}CHO$, obtained by the action of formic acid on α-aminobutyric acid, crystallises from water in colourless plates, m. p. 153°, and can be resolved into its optically active components by means of brucine. The brucine salt, which is less soluble, is that of formyl-*l*-aminobutyric acid, although the formyl acid is dextrorotatory. On crystallisation the m. p. of the acid falls, probably owing to the removal of the formyl group.

When *dl*-α-aminobutyric acid is fermented with yeast in the presence of sucrose, the *d*-acid is destroyed before the *l*-acid, so that the product isolated by Fischer's esterification method is lævorotatory.

The action of active yeast extract on the three dipeptides, glycyl-*d*-aminobutyric acid and the corresponding *l*- and *dl*-compounds, has been investigated. The *l*-compound is not affected, but both the *d*- and *dl*-compounds are attacked.

From these results the conclusion is drawn that the α-aminobutyric acid which occurs in nature is the *d*-acid, as almost invariably it is the naturally-occurring acid which is more readily attacked by ferments.

Chloroacetyl-dl-*α-aminobutyric acid*, $CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CHEt{\cdot}CO_2H$, crystallises from ethyl acetate and light petroleum in pointed plates, m. p. 130° (corr.), and $[\alpha]_D^{20}$ $-18\cdot14°$. The corresponding *d*-compound has m. p. 119° (corr.) after sintering at 112°. *Glycyl*-dl-*a-aminobutyric acid*, $NH_2\cdot CH_2\cdot CO\cdot NH\cdot CHEt\cdot CO_2H$, crystallises from dilute alcohol in pointed needles, m. p. 231° (corr.), and the corresponding d-*acid* forms long needles, m. p. 223° (corr.), and has $[\alpha]_D^{20}$ $-12\cdot24°$.

Glycyl-l-*a-aminobutyric acid* has m. p. 222° (corr.) and $[\alpha]_D^{20}$ $+18\cdot29°$.

l-Alanine is best prepared from *d*-alanine from silk. The *d*-alanine is transformed into *l*-*a*-bromopropionic acid, and this on treatment with 10% aqueous ammonia at the ordinary temperature yields an alanine with $[\alpha]_D^{20}$ $-10\cdot3°$ (in form of the hydrochloride). J. J. S.

The Walden Inversion. VI. β-Aminobutyric Acid. EMIL FISCHER and HELMUTH SCHEIBLER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911 566—586. Compare Abstr., 1910, i, 622).—β-Aminobutyric acid has been resolved into the optically active components by the crystallisation of the camphorsulphonate of its methyl ester. The active amino-acid may be converted into hydroxy-acid by means of nitrous acid or by treatment with nitrosyl chloride and subsequent boiling of the chlorobutyric acid formed with water. The two methods result in the formation of optically opposed hydroxy-acids, although the reactions are not so simple as with the *a*-amino-acids. In at least one of them a Walden inversion takes place, and this phenomenon is therefore extended to the β-series.

dl-Aminobutyric acid is prepared in quantity by heating crotonic acid with ammonia in an autoclave for twenty-four hours at 130—140°. The *methyl* ester, prepared by esterification with methyl alcohol and hydrogen chloride and decomposition of the hydrochloride so formed with ammonia, is a colourless, odorous liquid, b. p. 54—55°/13 mm., D^{20} 0·993.

dl-β-Aminobutyric acid has m. p. 191—192° (corr.). The copper salt is best prepared by repeated evaporation with copper acetate.

β-Naphthalenesulphonyl-dl-*β-aminobutyric acid*,

$$C_{10}H_7\cdot SO_2\cdot NH\cdot CHMe\cdot CH_2\cdot CO_2H,$$

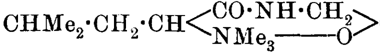
crystallises in prisms, which sinter at 163°, m. p. 166—167° (corr.). *Methyl-β-iminodibutyrate* has b. p. 135°/12 mm., 144—145°/17 mm., D^{20} 1·044.

l-*β-Aminobutyric acid* crystallises in well-formed, thick prisms, decomp. about 220°, $[\alpha]_D^{20}$ $-35\cdot2°$ ($\pm0\cdot2°$); the d-*isomeride* is very similar, $[\alpha]_D^{20}$ $+35\cdot3°$ ($\pm0\cdot2°$); in *N*-hydrochloric acid it has $[\alpha]_D^{20}$ $+29\cdot7°$; in *N*-sodium hydroxide, $[\alpha]_D^{20}$ $+14\cdot7°$.

By the action of nitrous acid on *l*-β-aminobutyric acid, *d*-β-hydroxybutyric acid is obtained, the product being about 62% racemised. Nitrous acid acts in the same way optically on the methyl ester, methyl-*d*-β-hydroxybutyrate being formed.

By the action of nitrosyl chloride on *d*-β-aminobutyric acid, *l*-β-chlorobutyric acid is obtained, but little racemisation taking place.

d-β-Chlorobutyric acid crystallises in large prisms, m. p. 43—44·5°, $[\alpha]_D$ $+49\cdot8°$ ($\pm0\cdot2°$). E. F. A.

Methylated Polypeptides. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1911, **72**, 44—49).—*Trimethylleucylglycine*, $CHMe_2{\cdot}CH_2{\cdot}CH(NMe_3{\cdot}OH){\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2H$ or  $CHMe_2{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CO{\cdot}NH{\cdot}CH_2\\ NMe_3\text{———}O\end{matrix}{>}CO$, may be obtained by methylating *dl*-leucylglycine with methyl iodide in the presence of methyl alcohol and *N*-potassium hydroxide at the ordinary temperature, and is best isolated as the *platinichloride*, $(C_{11}H_{23}O_3N_2)_2PtCl_6$, which crystallises from water in brilliant orange-red prisms or plates. The *aurichloride*, $C_{11}H_{23}O_3N_2AuCl_4$, also crystallises from water in orange-yellow prisms, m. p. 170—172°, after softening at a lower temperature. The *picrate* crystallises from dilute alcohol in brilliant lemon-yellow prisms, m. p. 228—229° (corr.), and decomposing at 240—250°. J. J. S.

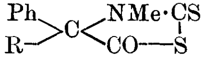
Salts and Esters of Alkylaminodithiocarbamic Acids. ERNEST FOURNEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 532—536).—Methylaminoacetic acid reacts in ether with carbon disulphide to form the corresponding *dithiocarbamate*,

$$CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S{\cdot}NH_2Me{\cdot}CH_2{\cdot}CO_2Et,$$

m. p. 77°, which crystallises in colourless, inodorous, hexagonal tablets, and is very soluble in alcohol or water. On adding mercuric chloride to the aqueous solution, the *mercury* derivative,

$$(CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS_2)_2Hg,$$

m. p. 148°, is formed. It crystallises from boiling alcohol in slender, yellow needles, and is soluble in acetone. The corresponding *mercury* derivative of the *propyl* ester, $(CO_2Pr^{\alpha}{\cdot}CH_2{\cdot}NMe{\cdot}CS_2)_2Hg$, m. p. 86°, resembles its lower homologue. On adding sodium hydroxide to an alcoholic solution of either of these substances, the unstable *compound*, $(CO_2Na{\cdot}CH_2{\cdot}NMe{\cdot}CS_2)_2Hg$, is precipitated in the form of small, colourless needles.

Similar series of derivatives are formed from the ethyl esters of ethylaminoacetic and methylaminohydroxy*iso*butyric acids, whilst ethyl phenylmethylaminoacetate reacts with carbon disulphide to form the *dithiazolone*,  $\begin{matrix}Ph\\ R\end{matrix}{>}C{<}\begin{matrix}NMe{\cdot}CS\\ CO\text{—}S\end{matrix}$. T. A. H.

Derivatives of *s*-Diaminoacetone. ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Rec. trav. chim.*, 1911, **30**, 177—182).—The reaction of *s*-diaminoacetone hydrochloride with ethyl chloroformate under the conditions employed by Franchimont and Friedmann (Abstr., 1907, i, 832) yields *ethyl acetone-αγ-diurethane*,

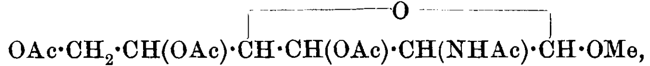
$$CO(CH_2{\cdot}NH{\cdot}CO_2Et)_2,$$

m. p. 136—137°. This substance is not attacked by boiling acetic anhydride alone, but in the presence of a little zinc chloride yields the *diacetyl* derivative, $CO(CH_2{\cdot}NAc{\cdot}CO_2Et)_2$, m. p. 61—62°. It nitrates readily, forming the *αγ-dinitro*-compound, $C_9H_{14}O_9N_4$, m. p. 56—57°.

Tetra-acetyl-1 : 3-*diaminoacetone*, $CO(CH_2{\cdot}NAc_2)_2$, obtained by boiling 1 : 3-diacetylaminoacetone (*loc. cit.*) for three hours with a large excess of acetic anhydride, forms large needles, which soften at 98°, and have m. p. 108°. C. S.

A Tetra-acetyl Aminoglucoside. MARSTON L. HAMLIN (*J. Amer. Chem. Soc.*, 1911, **33**, 766—769).—The work described in this paper has been forestalled by the publication of Irvine, McNicoll, and Hynd's paper on new derivatives of *d*-glucosamine (Trans., 1911, **99**, 250). These authors' results are confirmed, but it is found that bromotriacetylglucosamine hydrobromide does not melt, but darkens at 138—148°, and chars at 153° (uncorr.).

When a solution of bromotriacetylglucosamine hydrobromide in methyl alcohol is shaken with silver carbonate and filtered, the filtrate boiled with acetic anhydride, the methyl alcohol and acetic anhydride removed by distillation in a vacuum, and the residue boiled with a further quantity of acetic anhydride, *tetra-acetylglucosamine methylglucoside*,



$$\mathrm{OAc{\cdot}CH_2{\cdot}CH(OAc){\cdot}\overset{\lceil\text{———}O\text{———}}{CH{\cdot}CH(OAc){\cdot}CH(NHAc){\cdot}CH}{\cdot}OMe},$$

m. p. 150·5° (uncorr.), is obtained, which forms a white, crystalline powder. This compound is not a derivative of the aminoglucoside prepared by Fischer and Zach (this vol., i, 117), since the latter on hydrolysis yields the hydrochloride of an amino-sugar which is not identical with glucosamine hydrochloride. E. G.

Preparation of Acetamide. MARTIN A. ROSANOFF, LOUISE GULICK, and HERBERT K. LARKIN (*J. Amer. Chem. Soc.*, 1911, **33**, 974—977).—Acetamide can be prepared in good yield by the following method.

Dry ammonium acetate is prepared by neutralising glacial acetic acid with powdered ammonium carbonate at about 50°, allowing the product to cool, draining the crystals, and pressing them between filter paper. A mixture of this ammonium acetate (1 mol.) and glacial acetic acid (1·5 mols.) is boiled for five hours under a reflux condenser. The product is rapidly distilled, and the distillate is submitted to slow fractional distillation, using a two-bulb Wurtz dephlegmator. Three fractions are collected : (1) below 180° ; (2) between 180° and 213°, and (3) above 213°. The second fraction is redistilled, and the portion passing over above 213° is added to fraction 1. The portion with high-boiling point, after it has solidified, is pressed between filter paper, and the dry crystals thus obtained consist of almost pure acetamide (b. p. 214—216°). The yield from 100 grams of ammonium acetate amounts to over 60 grams, or about twenty grams more than can be obtained by the Hoffmann-Gattermann method. The yield cannot be increased by carrying out the reaction in sealed tubes. E. G.

Acetylation of Substituted Acetamides. ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Rec. trav. chim.*, 1911, **30**, 183—185). —The formation of tetra-acetyldiaminoacetone (this vol., i, 528) is merely an instance of a general reaction, whereby mono- and di-substituted amines are acetylated by boiling with a large excess of acetic anhydride. Thus acetmethylamide is converted into diacetylethylamine, acetethylamide into diacetylethylamine, and *s*-diacetylethylenediamine into *tetra-acetylethylenediamine*, $NAc_2{\cdot}CH_2{\cdot}CH_2{\cdot}NAc_2$, m. p. 156—157°. C. S.

Ammonium Cyanate and Carbamide. RICHARD ESCALES (*Chem. Zeit.*, 1911, **35**, 595).—The author (with H. KÖPKE) has found that when carbamide is sublimed in a vacuum at 160—190°, the sublimate consists of ammonium cyanate. He remarks that if Wöhler had endeavoured to purify his synthetical urea by sublimation, his famous discovery might never have been made. L. DE K.

Catalytic Action of Ferric Thiocyanate. H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1911, **152**, 1586—1587).—The authors consider that ferric thiocyanate is not strictly speaking a specific peroxydase. Its action in bringing about oxidation of phenols in presence of hydrogen peroxide is partly due to decomposition of the salt, whereby peroxy-acids of sulphur are formed. Potassium thiocyanate acts in the same way as the iron salt, but not to such a marked extent. W. O. W.

Aliphatic Nitro-compounds. X. Hydroxamyl Chlorides. WILHELM STEINKOPF and BORIS JÜRGENS (*J. pr. Chem.*, 1911, [ii], **83**, 453—470. Compare Abstr., 1910, i, 280).—The substance, previously recorded as β-oximino-oxalimino-chloride from its reactions and methods of formation, may be chloro-oximinoacetamide, produced, for example, from nitroacetonitrile and hydrogen chloride in dry ether, by the following series of reactions: $NO_2\cdot CH_2\cdot CN \xrightarrow{HCl} NOH{:}C(OH)\cdot CN \longrightarrow NOH{:}CCl\cdot CN + H_2O \longrightarrow NOH{:}CCl\cdot CO\cdot NH_2$. At first sight the explanation appears improbable, because it is unlikely that the water formed in the second reaction can convert the nitrile into the amide in the presence of the large excess of ether. However, the discovery that hydrogen chloride converts ethyl nitroacetate in dry ether into ethyl chloro-oximinoacetate shows that the first two phases of the series above can occur. The fact that the third phase does occur, and that the so-called β-oximino-oxalimino-chloride is really chloro-oximinoacetamide, is proved by the action of aqueous sodium carbonate on the substance in the cold, whereby an odour of a nitrile oxide is observed, and furoxandicarboxylamide (dinitrosoperoxide of succinamide) is formed.

From analogy to the preceding, the so-called α-oximino-oxalimino-chloride, m. p. 173—174° (decomp.), produced from methazonic acid and hydrogen chloride in ether (*loc. cit.*), must be chloro-oximinoacetaldoxime (chloroglyoxime), $NOH{:}CCl\cdot CH{:}NOH$. This is so, because not only is the substance converted by thionyl chloride in dry ether into *chloro-oximinoacetonitrile*, $CN\cdot CCl{:}NOH$ (which is too unstable to be analysed, but yields with aniline, *anilino-oximinoacetonitrile*, $NHPh\cdot C(CN){:}NOH$, m. p. 138—139°), but also the identity of the substance with Hantzsch's chloro*anti*glyoxime, m. p. 161° (Abstr., 1892, 693) (the m. p. can be raised to 168° by repeated crystallisation), is proved by the fact that the two substances form the same acetyl derivative, m. p. 163—164°, and diacetyl derivative, m. p. 90·5°. Moreover, a moist ethereal solution of the chloro-oximinoacetonitrile is hydrolysed by hydrogen chloride, yielding chloro-oximinoacetamide. *Chloro-oximinoacetic acid*, $NOH{:}CCl\cdot CO_2H$, decomp. 129°, is obtained by keeping for three weeks a suspension of potassium nitroacetate in dry ether saturated with hydrogen chloride in the cold.

In Nägeli's chloro*amphi*glyoxime (Abstr., 1883, 728) the chlorine atom and one of the hydroxyl groups have the *anti*-configuration, because the substance is insensitive to alkalis and does not yield a nitrile oxide with sodium carbonate. Now an aqueous solution of this *anti*chloro*amphi*glyoxime reacts with aniline to form a *salt*, $NOH{:}CCl{\cdot}CH{:}NOH,NH_2Ph$, m. p. 114° (decomp.). This behaviour not only illustrates the stability of the halogen atom in *anti*hydroxamyl chlorides, but may also serve for the characterisation of such substances, because other hydroxamyl chlorides, in which the chlorine atom and the hydroxyl group have the *syn*-configuration, react with aniline to form anilino-derivatives by substitution of the halogen atom. The authors deduce from the preceding that the α- and the β-oximinohydroxamic acids previously described (*loc. cit.*) have the *anti*- and the *syn*-configurations respectively.

By chlorinating a cold solution of chloro*anti*glyoxime in dilute hydrochloric acid, anti*dichloroglyoxime* (*αβ-dichloro-αβ-dioximinoethane*), $NOH{:}CCl{\cdot}CCl{:}NOH$, m. p. 201°, is obtained, which yields the odour of a nitrile oxide by heating or by treatment with sodium carbonate, forms a *dibenzoyl* derivative, m. p. 217°, and reacts with aniline to form αβ-dianilino-αβ-dioximinoethane.

Ethyl iodo-oximinoacetate, $CO_2Et{\cdot}CI{:}NOH$, m. p. 95—96°; *iodo-oximinoacetamide*, $NOH{:}CI{\cdot}CO{\cdot}NH_2$, yellow crystals, decomp. 154—155°; *iodo*anti*glyoxime*, $NOH{:}CI{\cdot}CH{:}NOH$, m. p. 136°, and anti*di-iodoglyoxime*, $NOH{:}CI{\cdot}CI{:}NOH$, decomp. 172°, are obtained by heating the corresponding chloro-compounds with a solution of sodium iodide in acetone. *anti*Chloro*amphi*glyoxime does not react with sodium iodide in acetone, another instance of the stability of the chlorine atom in *anti*chloro-oximino-compounds. C. S.

Friedel and Crafts' Reaction. JACOB BÖESEKEN (*Rec. trav. chim.*, 1911, 30, 148—150).—The formation of *as*-heptachloropropane from tetrachloroethylene and chloroform in the presence of aluminium chloride (this vol., i, 173) is typical of the reactions between trichloroethylene and chloroform, trichloroethylene and carbon tetrachloride, dichloroethylene and chloroform, and dichloroethylene and carbon tetrachloride; in every case the initial reaction is the simple addition of the two molecules.

The preceding explains the nature of the Friedel and Crafts' reaction. Three molecules must be present: (*a*) an unsaturated molecule, (*b*) a molecule which can be so activated that it can combine with the unsaturated molecule, (*c*) a catalyst which activates the molecules in (*a*) and (*b*). The possibility of the reaction is determined by the loss of free energy. The initial action is due to the encounter of the two molecules with the catalyst; in the case of benzene and other unsaturated cyclic systems the initial additive product, a derivative of dihydrobenzene, etc., cannot be isolated, because by elimination of hydrogen chloride or the like it is converted into a system containing less free energy. C. S.

Friedel and Crafts' Reaction. XI. Action of Sulphur Monochloride on Benzene, Chlorobenzene, and Toluene. JACOB BOESEKEN and D. A. WITTOP KONING (*Rec. trav. chim.*, 1911, **30**, 116—136).—The reaction between benzene and sulphur monochloride in the presence of aluminium chloride is more complex than that previously recorded (Abstr., 1905, i, 583), since diphenyl disulphide is always formed. The formation of the disulphide, if produced by a primary reaction, indicates that sulphur monochloride may have a symmetrical constitution.

The authors have examined quantitatively the action of sulphur monochloride on an excess of benzene, chlorobenzene, or toluene in the presence of an excess of aluminium chloride. When the reaction is completed, the sulphur monochloride has been entirely destroyed. Estimations are made of the sulphur present in the free state or combined as hydrogen sulphide, aromatic sulphide, aromatic disulphide, thianthren, or in the side-chain (in the case of toluene).

The reaction is simplest in the case of chlorobenzene; hydrogen sulphide and a thianthren are not formed, the products consisting of sulphur, di-*p*-chlorophenyl sulphide, and di-*p*-chlorophenyl disulphide (identified by oxidising it to chloronitrobenzenesulphonic acid by nitric acid, D 1·5). The reaction with benzene yields sulphur, hydrogen sulphide, diphenyl sulphide, diphenyl disulphide, thianthren, and a trace of phenyl mercaptan.

The reaction is still more complicated in the case of toluene; in addition to substances corresponding with the preceding, a small amount of dibenzyl sulphide (and disulphide?) is formed by substitution in the side-chain.

Despite these quantitative examinations, a clear picture of the reaction of sulphur monochloride and benzene (or chlorobenzene or toluene) cannot be drawn, because the primary reaction is obscured by secondary reactions due to the action, in the presence of the catalyst, of the liberated sulphur on the benzene and the diphenyl sulphide, and to the decomposition of the disulphide. C. S.

The System Propylbenzene–Antimony Trichloride. BORIS N. MENSCHUTKIN (*J. Chim. Phys.*, 1911, **9**, 314—322).—Propylbenzene, b. p. 157°/765 mm., becomes viscous on cooling, and solidifies below $-100°$ to an isotropic mass, which has no definite melting point. When small proportions of antimony chloride are present, crystals of an additive compound separate on cooling. The compound usually has the formula $SbCl_3,C_6H_5Pr$, m. p. $+1·5°$, but sometimes consists of $2SbCl_3,C_6H_5Pr$, m. p. $+9°$ to $+10°$, which is less soluble.

There are two distinct liquidus curves, representing the stable and labile compounds respectively. These curves cut the antimony trichloride liquidus at $+1°$ and $+8·5°$, representing two distinct eutectics. The two liquidus curves are practically parallel, the difference being 8° near the eutectic points, and about 11° at 3% antimony trichloride concentration. The less fusible compound was not obtained spontaneously above 15% of antimony chloride, but could be easily obtained by sowing the more concentrated solutions.

According to the phase rule, the more soluble, more fusible compound should be labile, whereas in the experiments the more fusible compound was the more readily obtainable. R. J. C.

Bromination of Some Hydroaromatic Compounds. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1911, **152**, 1252—1254; *Bull. Soc. chim.*, 1911, [iv], **9**, 595—601).—*cyclo*Hexane is converted into an oily monobromo-derivative when treated with bromine in sunlight; further treatment with bromine changes this into 1 : 2-dibromo*cyclo*hexane. The bromination of *cyclo*hexane, menthene, and thymomenthene in presence of aluminium bromide leads to the production of viscous liquids. Dibromo*cyclo*hexane and *cyclo*hexene under the same conditions give hexabromobenzene. Methyl*cyclo*hexane and Δ^2- and Δ^4-methyl*cyclo*hexenes yield pentabromotoluene amongst other products. 1 : 3-Dimethyl*cyclo*hexane furnishes a mixture of isomeric tetrabromoxylenes. W. O. W.

Action of Sulphur on Aromatic Sulphones. JACOB BÖESEKEN (*Rec. trav. chim.*, 1911, **30**, 137—141).—When heated with rather more than 1 atom of sulphur at 250—275° in a current of dry carbon dioxide, the following sulphones do not yield sulphides, as does diphenylsulphone (Krafft and Vorster, Abstr., 1894, i, 88), but decompose in a characteristic manner. 4 : 4′-Dichlorodiphenylsulphone yields *p*-dichlorobenzene and sulphur dioxide; 4 : 4′-dibromodiphenylsulphone decomposes similarly, but less readily. 4-Chloro-4′-bromodiphenylsulphone yields *p*-chlorobromobenzene. 4-Bromophenyl-*p*-tolylsulphone yields hydrogen sulphide, water, hydrogen bromide, and a little red oil. C. S.

Action of Dichloromethane on Di-*p*-tolylmethane. JAMES LAVAUX (*Compt. rend.*, 1911, **152**, 1400—1402. Compare Abstr., 1905, i, 43, 125, 640, 698; 1906, i, 25; 1907, i, 150, 256).—To solve the problem of the constitution of the supposed 1 : 6- and 2 : 7-dimethylanthracenes previously obtained by the action of dichloromethane and aluminium chloride on a mixture of isomeric ditolylmethanes, the condensation has been repeated on a pure specimen of di-*p*-tolylmethane. The latter prepared by the action of trioxymethylene on toluene in presence of sulphuric acid, occurs in needles, m. p. 28° (Ador and Rillet give 22—23°; Weiler, below $-15°$). It was found, however, that the pure hydrocarbon gave the same mixture of dimethylanthracenes, indicating that aluminium chloride has brought about a transposition similar to that which it effects in converting *n*-propyl into *iso*propyl derivatives. W. O. W.

Hydrogenation by means of (1) Spongy Palladium and Sodium Hypophosphite, (2) Nickel and Sodium Hypophosphite. PIERRE BRETEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 515—517, 518—519. Compare this vol., i, 123).—Spongy palladium, precipitated from a solution of the chloride by sodium hypophosphite, decomposes water in presence of sodium hypophosphite, forming hydrogen and sodium hydrogen phosphite, and this mixture is useful as a reducing agent. In boiling alcohol, it reduces phenanthrene to the tetrahydride, and nitro- or dinitro-derivatives to the corresponding amines.

In the second paper it is shown that nickel in powder form, prepared by adding sodium hypophosphite to a hot solution of nickel sulphate, also decomposes water in presence of sodium hypophosphite. This mixture does not reduce phenanthrene, although it converts nitro-derivatives into the corresponding amines. T. A. H.

Compounds which Cause the Red Coloration of Aniline. II. Effect of Sunlight in the Absence of Oxygen and Oxidising Influences and a Comparison with the Behaviour of Mono- and Di-methylaniline. HARRY D. GIBBS (*Philippine J. Sci.*, 1910, **5**, 419—435. Compare Abstr., 1910, i, 550).—Aniline purified by various processes is sealed in glass tubes either in a vacuum or in an atmosphere of hydrogen, and exposed to sunlight for many (51—60) days during the summer months. The liquid acquires a very deep red, almost black, colour. The products are azophenine, benzene, and ammonia. The rate of coloration appears to increase with the pressure of the hydrogen in the tube. Aniline in tubes containing carbon dioxide colours very much less rapidly, the rate of coloration being greatest when the pressure of the gas is least. Methylaniline in an atmosphere of hydrogen also becomes red in sunlight (methylamine is present among the products), whilst dimethylaniline is only slightly coloured, the coloration probably being due to impurities.

From these and the previous experiments on aniline (*loc. cit.*) and phenol (Abstr., 1909, i, 221, 640), it seems that the fixation of the labile hydrogen atom destroys the sensibility of the molecule to chemical change produced by sunlight. Attention is called to the fact that the introduction of methyl or ethyl groups into certain dyes to produce methyl or ethyl ethers, increases the fastness of the dye to light. C. S.

Mechanism of the Elimination of Halogens by Aromatic Amines. IWAN OSTROMISSLENSKY and PAWEL ALABÉEFF (*J. pr. Chem.*, 1911, [ii], **83**, 506—512).—Hitherto an explanation has not been attempted of the fact that certain aromatic amines (aniline, phenylhydrazine, quinoline, pyridine) eliminate the halogen from various olefine dihalogenides with the regeneration of the original olefine. Thus the authors show that when stilbene dibromide is heated with dry pyridine for twelve hours on the water-bath, about 87% of the halogen is eliminated as hydrogen bromide, stilbene itself being formed. Consequently, in such reactions the hydrogen of the halogen acid must have been withdrawn from the aromatic amine, and, furthermore, must have been withdrawn from the aromatic nucleus, since the elimination in question can be effected by tertiary amines. It follows, therefore, that unstable groups, such as $\cdot C_6H_4\cdot NH_2$, must be formed. From these groups, by intramolecular change, polymerisation, etc., probably are formed the resinous substances which are almost invariably produced in the reactions in question. The formation of benzidine itself has never been observed in such reactions.

The authors' explanation accounts for the formation of tetramethyldiaminodiphenylethane observed by Schoop when dimethylaniline and ethylene dibromide are heated for eight days in the water-bath.

C. S.

Catalytic Hydrogenation of Cyclic Oximes. Synthesis of Arylamines. ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1911, [iv], **9**, 464—468).—The reduction of aliphatic oximes to amines by means of finely divided metals has been described already (Abstr., 1905, i, 571, 635), and this work has now been extended to cyclic oximes. These are reduced less easily than the aliphatic oximes. The normal reaction is the formation of a mixture of the corresponding primary and secondary amines, the latter predominating, but in addition other reactions occur. The water formed leads to the regeneration of the parent ketone, and a part of the primary amine formed is decomposed, forming ammonia and olefinic hydrocarbons, the latter being in part reduced to the saturated hydrocarbons by the action of the metal; thus aminophenylbutane furnishes with hot, finely-divided nickel, ammonia, phenylbutylene, and phenylbutane. Except in the case of benzophenoneoxime this decomposition of the primary amine formed occurs to a large extent in all the cases tried.

The following new compounds were obtained: Acetophenoneoxime gave the *secondary amine*, $NH(CHMePh)_2$, b. p. 295—298° (approx.), D^{13} 1·018, n_D 1·573. Propiophenoneoxime gave the *secondary amine*, $NH(CHEtPh)_2$, b. p. 310—315°, the *hydrochloride* of which has m. p. 200° (approx. decomp.). Butyrophenoneoxime, m. p. 49°, b. p. 248°, furnished the *primary amine*, $CHPrPh·NH_2$, b. p. 240°, D^{13} 0·9813, n_D 1·534, and a small quantity of *secondary amine*, b. p. 320° (approx.). Benzophenoneoxime gave a 70% yield of benzhydrylamine with some *dibenzhydrylamine*, m. p. 126°, the *hydrochloride* of which melts at 300° (approx. decomp.).

o-Methyl*cyclo*hexanoneoxime furnished the *primary amine*, b. p. 150°, and the *secondary amine*, b. p. 260° (approx. decomp.), the *hydrochloride* of which has m. p. 225° (approx. decomp.). The isomeric meta-*secondary amine* has b. p. 265° (decomp.), whilst the para-*secondary amine* has b. p. 265° (approx. decomp.).

Menthoneoxime yields *dimenthylamine*, b. p. 305°, the *hydrochloride* of which has m. p. 207° (approx. decomp.). T. A. H.

Quantitative Examination of the Introduction of One Atom of a Halogen into Phenol. ARNOLD F. HOLLEMAN and I. J. RINKES (*Rec. trav. chim.*, 1911, **30**, 48—100).—The authors have plotted the freezing-point curve of mixtures of *o*- and *p*-bromophenol, using specially purified materials; the eutectic point is at −11·7°.

By brominating phenol with exactly the calculated amount (1 mol.) of bromine, either as vapour diluted with air or carbon dioxide or in a solvent, it is possible to conduct the operation quantitatively in such a way that no phenol remains unattacked and no dibrominated products are formed. After the bromination is complete and the solvent, if such has been used, has been removed by suitable methods (which are described), the product is distilled as completely as possible in a vacuum and the freezing point of the distillate is determined; reference to the freezing-point curve then gives the composition of the mixture, providing it consist only of *o*- and *p*-bromophenols. That the meta-isomeride is never produced is proved in the following way. The brominated product is nitrated by nitric acid, D 1·52, at −5°, the resulting nitrated bromophenols are treated with methyl-alcoholic sodium methoxide (1 mol.), the alcoholic solution is added to water acidified with nitric acid after twenty minutes, the phenolic substances are removed by ether, and the aqueous solution is tested with silver nitrate; the absence of a precipitate of silver bromide proves that no halogen has been eliminated from the nitrated bromophenols by the sodium methoxide, and therefore that no *m*-bromophenol was originally present, since this is the only bromophenol which yields by nitration a product containing nitro-groups in the ortho- and para-positions to the bromine atom. A distinct turbidity of silver bromide was produced when a mixture of *o*- and *p*-bromophenols containing 1% of the meta-isomeride was examined by the preceding process.

The presence of only *o*- and *p*-bromophenols in the product of the bromination of phenol is also proved by adding to the product (the composition of which has been ascertained from its freezing point) the amount of *o*-bromophenol required to bring its composition to that of the eutectic mixture; the freezing point is then found to be that, or very nearly that, of the eutectic mixture, −11·7°.

The percentages of *p*-bromophenol obtained are as follows: 97·4% at −30°, 92·8% at 0°, 86·2% at 30°, with carbon disulphide as solvent; 91·2% at 15°, 87·5% at 30°, 86·8% at 60°, with glacial acetic acid as solvent; 88·6% at 30°, with carbon tetrachloride as solvent; 90·2% at 60°, 90·7% at 90°, 81·6% at 131°, 79·4% at 153°, and 77% at 180°, without a solvent. The increase with the temperature in the percentage of *o*-bromophenol is much less than might be expected from references in the literature; also, for example at 30°, the composition of the mixture apparently is almost independent of the nature of the solvent.

o-Bromophenol has been prepared by brominating phenol without a solvent at 170° and fractionating the product; in addition to the usual form, m. p. 5·5°, a second modification of *o*-bromophenol has been discovered which solidifies at −10° (compare Ostromisslensky, Abstr., 1907, i, 120).

The chlorination of phenol without a solvent has been performed at 40°, 90°, and 155°, the percentages of *p*-chlorophenol, determined from the freezing-point curve of *o*- and *p*-chlorophenols, being 47·3, 50·2, and 48·8 respectively. It should be noted that the percentage of the para-isomeride is much less than that obtained by bromination, and remains nearly constant between 40° and 155°.

The quantitative conversion of phenol into iodophenols by direct iodination cannot be performed; even with a large excess of phenol the product contains unchanged substance and polyiodophenols. The main product, however, is *p*-iodophenol, the following method being very convenient for obtaining this substance. A solution of iodine in potassium iodide is added to an excess of aqueous phenol. Sodium hydroxide is added until the mixture is decolorised, and finally concentrated hydrochloric acid. The resulting oil is distilled at 76°/0·8 mm., whereby unchanged phenol is almost entirely removed. The residue is finally recrystallised from petroleum. C. S.

Dyeing with Picric Acid. GEORG VON GEORGIEVICS (*Monatsh*, 1911, **32**, 319—327).—The rule that the presence of sulphuric or other acid is essential for the adsorption of an acid dye by the fibre does not hold for picric acid at concentrations between about 0·008 and 0·017%, for the author finds that the amount of picric acid adsorbed from aqueous solutions of these concentrations is almost the same when an amount of sulphuric acid approximately equal to that of the picric acid is added to the bath.

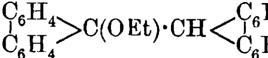
Walker and Appleyard (Trans., 1896, **69**, 1334) have shown that the adsorption of picric acid by silk at 60° is such that the expression $C/\sqrt[2\cdot7]{C'}$ = constant, where C and C' are the concentrations of the dye in the fibre and in the bath respectively. The partition is independent of the temperature, the author's experiments at the ordinary temperature yielding the same result with the exception that the root exponent is 2·64 instead of 2·7. In the author's experiments the concentration of the picric acid varies from 0·02 to 0·4%. At the former concentration the value of the expression $C/\sqrt[2\cdot64]{C'}$ is very much below the mean value, a result which possibly may be due to the prolonged time requisite for equilibrium to be attained in very dilute solutions. The colour can be removed from the dyed silk by repeated treatment with acetone at the ordinary temperature.

The dyeing of animal fibres by acid dyes is often attributed to the formation of molecular compounds between the dye and the fibre. This explanation appears doubtful in the light of the following experiments. When the molecular compound naphthalene picrate is washed with water, the washings soon contain a constant amount, 0·08%, of picric acid; naphthalene, introduced into a solution of 0·08% picric acid, does not form any picrate. Silk containing 3% of picric acid is washed with water, and the washings contain about 0·003% of picric acid. If the dyeing of the silk is due to the formation of a molecular compound analogous to naphthalene picrate, it is to be expected that silk will not adsorb any dye from a 0·003% solution of picric acid; experiment shows, however, that at this or even smaller concentrations the silk removes almost the whole of the picric acid from the solution.

Experiments are described which seem to indicate that the darkening of picric acid by exposure to the air is due to salt formation (ammonium picrate?). Also the fact that wool, dyed by picric acid in the cold, acquires a deeper tone by boiling with water (Abstr., 1906, i, 420) may be due to the formation of picrates of the basic decomposition products of the wool. It is still unexplained, however, why aqueous solutions of picric acid darken by boiling, even in the presence of a little hydrochloric acid. C. S.

The Separation of *p*-Chloro-*m*-cresol ($CH_3 : OH : Cl = 1 : 3 : 6$) from Mixtures of *m*- and *p*-Cresol. FRITZ RASCHIG (D.R.-P. 232071).—The action of sulphuryl chloride (or chlorine) on a cooled solution of the technical mixture of *m*- and *p*-cresols is selective; if only sufficient chlorine is introduced to react with the *m*-cresol this alone is attacked, and on subsequent distillation (at atmospheric pressure) the *p*-cresol will pass over at 200°, followed at 235° by pure *p*-chloro-*m*-cresol. A certain amount of *o-chloro-*m*-cresol*, b. p. 196°/760 mm., is also formed, and passes over with the *p*-cresol, from which it is subsequently separated; it is a colourless liquid with a camphor-like odour, and D^{15} 1·215. F. M. G. M.

Magnesium Derivative of Fluorene. VICTOR GRIGNARD and CHARLES COURTOT (*Compt. rend.*, 1911, **152**, 1493—1495).—Fluorene forms a magnesium derivative when heated at 135° with magnesium ethyl bromide in xylene. In addition to fluorenecarboxylic acid, the following substances have been obtained from it by the usual methods.

tert.-*Fluorenylfluorenol*, rose-coloured crystals, m. p. 195—196°; the corresponding *ethyl ether*,  $\genfrac{}{}{0pt}{}{C_6H_4}{|\;\;C_6H_4}\!>C(OEt)\cdot CH<\!\genfrac{}{}{0pt}{}{C_6H_4}{C_6H_4\;|}$, crystallises in yellow needles, m. p. 174°; the *chloride* forms pale yellow crystals, m. p. 157—158°. *Fluorenyldiphenylcarbinol* was prepared in the same way as the corresponding indenyl derivative (this vol., i, 193).

tert.-1-*Indenylfluorenol* forms a *methyl ether*, m. p. 115—116°, when its solution in methyl alcohol is treated with hydrogen chloride; under the same conditions diphenyl-1-indenylcarbinol undergoes dehydration. In general, the *tert.*-fluorenols are more stable than the corresponding diphenylcarbinols. W. O. W.

Chlorides and Bromides of Diphenyl Sulphide. KARL FRIES and WILHELM VOGT (*Annalen*, 1911, **381**, 337—346. Compare Böeseken, this vol., i, 41; Fromm and Raiziss, Abstr., 1910, i, 554).—Diphenyl sulphide combines with chlorine when the dry gas is led into a benzene solution of the sulphide; the *dichloride*, SPh_2Cl_2, thus obtained forms pale yellow, flat prisms, which decompose when warmed, yielding mono- and di-chloro-substituted derivatives of diphenyl sulphide. In contact with atmospheric moisture, they yield hydrogen chloride and diphenylsulphoxide.

4 : 4'-*Dichlorodiphenylsulphide dichloride*, $SCl_2(C_6H_4Cl)_2$, obtained from either diphenyl sulphide or its 4 : 4'-dichloro-derivative, forms compact, yellow, prismatic crystals, m. p. 95° (decomp.), and on treatment with water yields 4 : 4'-*dichlorodiphenylsulphoxide*, $SO(C_6H_4Cl)_2$, which crystallises from light petroleum in compact prisms, m. p. 143°. The sulphoxide yields a pale violet-coloured solution in concentrated sulphuric acid, and is readily reduced to the sulphide by means of hydrobromic acid.

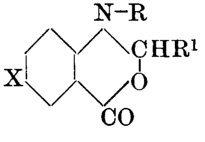
Diphenyl sulphide dibromide, SPh_2Br_2, obtained by the action of bromine on a well-cooled solution of diphenyl sulphide in hexane, forms orange-coloured needles, and even at the ordinary temperature passes over into substituted derivatives of diphenyl sulphide.

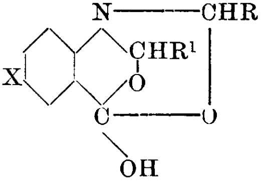
4 : 4'-*Dibromodiphenyl sulphide dibromide*, $C_{12}H_8Br_4S$, forms glistening, dark red plates, and yields a *perbromide*, $C_{12}H_8Br_6S$, in the form of brownish-red prisms.

4 : 4'-*Dibromodiphenylsulphoxide*, $SO(C_6H_4Br)_2$, separates from alcohol in compact, glistening, lance-shaped crystals, m. p. 152°, which dissolve readily in concentrated sulphuric acid, yielding a pale violet solution. J. J. S.

Preparation of Anthranilic Acid Esters Containing a Substituted Group in the para-Position to the Amino-group.

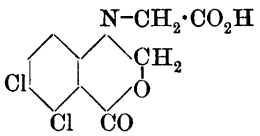
Badische Anilin- & Soda-Fabrik (D.R.-P. 231687).—When the aldehydo-condensation products of para-substituted anthranilic acids with the constitution I or II (where R and R_1 are hydrogen, alkyl,


(I.)

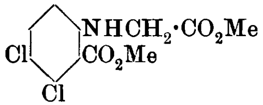

(II.)

aryl, or alkylaryl groups) are treated with esterifying agents, the aldehydo-groups are eliminated and the corresponding anthranilic ester obtained.

Anhydromethylene - 3 : 4 - dichlorophenylglycine - 2 - carboxylic acid (annexed formula), m. p. 246° (decomp.), separates in long needles when a warm methyl - alcoholic solution of 3 : 4-dichlorophenylglycine-2-carboxylic acid (264 parts) is treated with 30% formaldehyde solution (105 parts).



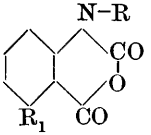
Methyl 3 : 4-dichlorophenylglycine-2-carboxylate (annexed formula), m. p. 76—78°, is prepared by heating the foregoing anhydro-base in methyl-alcoholic solution with concentrated sulphuric acid at 70° during twelve to fifteen hours, any acid ester which is simultaneously produced being removed subsequently by careful treatment with an alkali hydroxide.



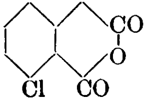
Methyl tetrachloroanthranilate, $NH_2 \cdot C_6Cl_4 \cdot CO_2Me$, needles, m. p. 120—121°, is obtained by heating tetrachloroanthranilic acid with a mixture of methyl alcohol, methylal, and sulphuric acid at 40—50° during twenty-four hours. F. M. G. M.

Preparation of Substituted Anthranilic Acid Esters.

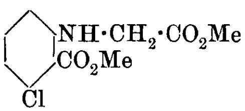
Badische Anilin- & Soda-Fabrik (D.R.-P. 231962. Compare Abstr., 1889, i, 996; 1899, i, 939).—It is found that substituted anthranilic acid esters may be obtained in quantitative yield by treating the isatoic acids of the annexed general formula (where R is hydrogen, alkyl, aryl, or alkylaryl groups, and R_1 is a halogen) with esterifying agents.



3-*Chlorophenylglycine-2-carboxylic acid*, leaflets, m. p. 175° (prepared from 6-chloroanthranilic acid), when treated with carbonyl chloride in alkaline solution yields 6 - *chloroisatoacetic acid* (annexed formula), a colourless, insoluble powder, which when allowed to remain several days in methyl alcohol with concentrated sulphuric



acid slowly dissolves and is converted into *dimethyl 3-chlorophenylglycine-2-carboxylate* (annexed formula), prisms, m. p. 55—56°.



6-Chloroanthranilic acid on treatment with carbonyl chloride yields *6-chloroisatoic anhydride*, sparingly soluble leaflets, decomposing at about 280°, which on esterification is converted into *methyl 6-chloroanthranilate*, $NH_2\cdot C_6H_3Cl\cdot CO_2Me$, a pale yellow oil, b. p. 156—159°/10 mm.
F. M. G. M.

Mono- and Di-ethyl Esters of Diphenylitaconic Acid. HANS STOBBE (*Ber.*, 1911, **44**, 1297—1300).—*α-Ethyl β-hydrogen γ-diphenylitaconate*, $CPh_2{:}C(CO_2H)\cdot CH_2\cdot CO_2Et$, prepared by boiling diphenylitaconic anhydride with alcohol, has m. p. 130—131°; when treated with bromine, it yield *β-bromo-γ-diphenylparaconic acid*. It differs from the corresponding α-ester (Abstr., 1899, i, 900) in being more sparingly soluble in water, and in crystalline form; the α-ester forms rhomboidal plates, whilst the β-ester crystallises in monoclinic needles.

Improvements in the method of preparation of the α-ester and of ethyl γ-diphenylitaconate are also described.
F. B.

Methyl Phenyliminomalonate and its Reactions. RICHARD S. CURTISS and F. GRACE C. SPENCER (*J. Amer. Chem. Soc.*, 1911, **33**, 985—992).—It has been shown in an earlier paper (Abstr., 1909, i, 764) that when methyl anilinotartronate is treated with phosphoric oxide, it is converted into methyl phenyliminomalonate,

$$NPh{:}C(CO_2Me)_2.$$

The compound is thus obtained as a thick, yellow oil; it reacts vigorously with water, alcohols, ammonia, hydrogen chloride, amines, and acids, with formation of colourless, substituted anilinomalonates. The reactivity of this substance is shown to be analogous to that of phenylcarbimide.

When methyl phenyliminomalonate is treated with aniline, methyl dianilinomalonate (Conrad and Reinbach, Abstr., 1902, i, 211) is produced. This compound can also be obtained by the action of aniline on methyl dihydroxymalonate.

Methyl phenyliminomalonate absorbs water from the air, thereby becoming converted into a mixture of methyl dianilinomalonate and methyl dihydroxymalonate.

It has been shown previously (Curtiss, Abstr., 1897, i, 556) that when a solution of ethyl anilinomalonate in light petroleum is heated with freshly precipitated mercuric oxide, the latter undergoes reduction and ethyl dianilinomalonate is produced. It has now been found that when methyl anilinomalonate is treated similarly, the reduction of the mercuric oxide proceeds more slowly and less completely, and a mixture of methyl dihydroxymalonate and dianilinomalonate is produced.

When dry ammonia is passed into an ethereal solution of methyl phenyliminomalonate, a white, crystalline compound and a red, gummy substance are formed. The former is very unstable, and seems readily to undergo polymerisation. Hydrogen chloride reacts with methyl phenyliminomalonate with production of an unstable, crystalline compound, which rapidly loses hydrogen chloride on exposure to the air, and changes into gummy polymerisation products. This polymerisation of methyl phenyliminomalonate appears to be analogous to that of phenylcarbimide.

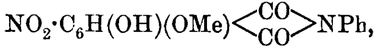
By the action of ethyl alcohol on methyl phenyliminomalonate, a colourless, crystalline *compound*, m. p. 88° (uncorr.), probably $OEt\cdot C(CO_2Et)_2\cdot NHPh$, is produced, which gradually becomes yellow when left in a desiccator. E. G.

Position of the Substituents in α-Resodicarboxylic Acid. PAUL WAITZ (*Monatsh.*, 1911, 32, 427—434).—The identification of Senhofer and Brunner's α-resodicarboxylic acid as 2 : 6-dihydroxybenzene-1 : 3-dicarboxylic acid has been achieved : (1) by heating β- and γ-resorcylic acids separately with ammonium carbonate and water at 130° in closed vessels, whereby α-resodicarboxylic acid is obtained in each case ; (2) by heating α-resodicarboxylic acid with water in sealed tubes, whereby it is decomposed into carbon dioxide and β- and γ-resorcylic acids. C. S.

Derivatives of Nitrohemipinic Acid. RUDOLF WEGSCHEIDER and ALFONS KLEMENC (*Monatsh.*, 1911, 32, 377—401).—Since boiling aniline hydrolyses nitrated phenolic ethers (Abstr., 1910, i, 670), its action on nitrohemipinic acid has been examined. After one hour methylaniline and a substance insoluble in concentrated potassium hydroxide are obtained as by-products, the chief product being 6-*nitromethylnorhemipin*-2-*anilic acid* (6-*nitro*-3-*hydroxy*-4-*methoxyphthal*-2-*anilic acid*), $CO_2H\cdot C_6H(NO_2)(OH)(OMe)\cdot CO\cdot NHPh$, microscopic prisms, m. p. 183—184° (decomp.) ; occasionally the substance merely darkens at 180°, and melts without decomposition at 214°, due probably to the formation of the anil (see below). The anilic acid behaves as a dibasic acid, forms blood-red solutions in alkalis, and does not give a colour reaction with ferric chloride. It yields nitromethylnorhemipinic acid when boiled with water, and forms a disilver *salt*, which is converted by methyl iodide into *methyl* 6-*nitrohemipin*-2-*anilate*, $C_{17}H_{16}O_7N_2$, m. p. 148—149°.

A moist ethereal solution of acetylnitromethylnorhemipinic anhydride (see below) and aniline, after two hours' boiling, yields yellow needles of a mixture, m. p. 197—198°, of the aniline salts of 6-nitromethylnorhemipin-1-anilic acid and its acetyl derivative. The same mixture, which is also produced by working in benzene or without a solvent, yields 6-*nitromethylnorhemipin*-1-*anilic acid* by treatment with potassium hydroxide and subsequent acidification of the red solution. The acid has m. p. 192° (decomp.), resolidifies, and melts again at 213°, the m. p. of the anil below. It differs from the preceding isomeride in behaving as a monobasic acid, and in developing a ruby-red coloration with ferric chloride, a sign that the hydroxyl and carboxyl groups are in the ortho-position to one another. 6-Nitromethylnorhemipin-1-anilic acid forms a sparingly soluble *ammonium* salt, m. p. 229—230° (decomp.), a *silver* salt, and a *disilver* salt ; from the two silver salts methyl iodide produces *methyl* 6-*nitromethylnorhemipin*-1-*anilate*, m. p. 192—193° (decomp.), and *methyl* 6-*nitrohemipin*-1-*anilate*, m. p. 170°

(decomp.), respectively, neither of which gives a colour reaction with ferric chloride.

The following facts prove that 6-nitromethylnorhemipin-1-anilic acid and 6-nitromethylnorhemipin-2-anilic acid are derived from the same nitromethylnorhemipinic acid. (i) Both yield the same *6-nitromethylnorhemipinanil*,  $NO_2\cdot C_6H(OH)(OMe)<\substack{CO\\CO}>NPh$, m. p. 214—215°, when heated in boiling xylene. The anil, which does not give a ferric chloride reaction, is also obtained by heating methyl 6-nitromethylnorhemipin-1-anilate at 198°, or by boiling nitromethylnorhemipinic acid with aniline. (ii) Both react with acetic anhydride and two drops of sulphuric acid on the water-bath to form nitromethylnorhemipinic acid and the acetylated *anil*, $C_{17}H_{12}O_7N_2$, m. p. 212—213°, the latter of which is also produced by acetylating nitromethylnorhemipinanil under the preceding conditions. The hydrolysis of the acetylated anil by aqueous potassium hydroxide (2 mols.) yields 6-nitromethylnorhemipin-2-anilic acid (this is evidently a method whereby 6-nitromethylnorhemipin-1-anilic acid can be converted through the acetylated anil into the isomeric 2-anilic acid, and yields a purer product than the method described above); when hydrolysed by 1 mol. of potassium hydroxide, the acetylated anil yields 6-nitromethylnorhemipinic acid identical with that obtained from nitromethylnoropianic acid by Elbel or by the nitration of methylnorhemipinic acid.

6-Nitromethylnorhemipinic acid is obtained best by passing hydrogen chloride for fifteen hours through a mixture of nitrohemipinic acid and concentrated hydrochloric acid on the water-bath. It has m. p. 205—206° (decomp.) (Elbel gives 220°), and its silver salt and methyl iodide yield *dimethyl 6-nitromethylnorhemipinate*, m. p. 145—146°, which contains a free hydroxyl group, but does not give a coloration with ferric chloride. The acid is not acetylated by acetic anhydride and sodium acetate or 2 drops of sulphuric acid, but is converted by boiling acetyl chloride into *acetylnitromethylnorhemipinic anhydride*, $C_{11}H_7O_8N$, m. p. 165—166°, which is easily hydrolysed to nitromethylnorhemipinic acid by boiling water. C. S.

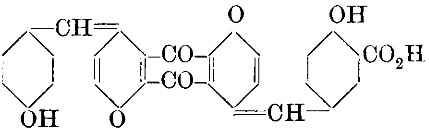
Methylenedisalicylic Acid [Methanedisalicylic Acid] and its Reaction with Bromine and Iodine. ERIK CLEMMENSEN and ARNOLD H. C. HEITMAN (*J. Amer. Chem. Soc.*, 1911, **33**, 733—745).—Methanedisalicylic acid was first prepared by Geigy (D.R.-P. 49970) by heating salicylic acid with a large excess of formaldehyde in presence of concentrated hydrochloric acid, and was afterwards studied by Kahl (Abstr., 1898, i, 259) and Madsen (Abstr., 1907, i, 424). It is now shown that the acid can be obtained in good yield by the interaction of formaldehyde (1 mol.) with salicylic acid (1 mol.) in presence of 50% sulphuric acid. If the reaction is carried out in very concentrated solution, a *compound* is produced which has the same empirical formula as methanedisalicylic acid, and does not melt but chars above 260°. When methanedisalicylic acid is heated either above its m. p. or with potassium hydroxide, it is decomposed into hydroxyphenylmethanesalicylic acid, 4 : 4'-dihydroxydiphenylmethane, and carbon dioxide. *Calcium, dicalcium, barium, di-barium, magnesium,* and *zinc* methanedisalicylates are described. The *di-acetyl* derivative, m. p. 142°, forms a white, amorphous powder.

Hydroxyphenylmethanesalicylic acid (*hydroxyphenylhomosalicylic acid*), $OH\cdot C_6H_4\cdot CH_2\cdot C_6H_3(OH)\cdot CO_2H$, m. p. above 60°, is a pale red, amorphous substance.

The following compounds were obtained by the action of bromine and iodine respectively on methanedisalicylic acid in presence of alkali hydroxide.

Tribromoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{10}Br_3$, is a red, amorphous substance, which decomposes above 200°; its *calcium* salt, $C_{30}H_{11}O_{10}Br_3Ca$, and *potassium* salt, $C_{30}H_9O_{10}Br_3K_4$, are described.

Tri-iodoanthratriquinonedihomosalicylic acid, $C_{30}H_{13}O_{10}I_3$, is a red substance which decomposes above 230°; its *calcium* salt, $C_{30}H_{11}O_{10}I_3Ca$, and *potassium* salt, $C_{30}H_9O_{10}I_3K_4$, were prepared. When this acid is heated in a sealed tube with 1% alkali carbonate or 2% mineral acid, it is converted into a *monocarboxylic acid*, which may be regarded as a tri-iodo-derivative of hydroxybenzylideneanthratriquinonehomosalicylic acid (annexed formula).



Heptabromoanthratriquinonedihomosalicylic acid, $C_{30}H_9O_{10}Br_7$, forms a pale yellow powder and decomposes above 200°; its *potassium* salt, $C_{30}H_5O_{10}Br_7K_4$, is described.

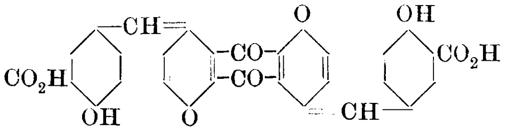
Pentabromohydroxybenzylideneanthratriquinonehomosalicylic acid, $C_{29}H_{11}O_8Br_5$, crystallises in microscopic plates.

Pentaiodohydroxybenzylideneanthratriquinonehomosalicylic acid,

$$C_{29}H_{11}O_8I_5,$$

is a reddish-yellow, amorphous substance; its *potassium* salt, $C_{29}H_{10}O_8I_5K$, forms an olive-green powder.

When tribromoanthratriquinonedihomosalicylic acid is boiled with potassium hydroxide solution and zinc dust, it is converted into *anthratriquinonedihomosalicylic acid* (annexed formula), which forms a brown powder, and decomposes at 185°; the *calcium* salt, $C_{30}H_{14}O_{10}Ca$, and *potassium* salt, $C_{30}H_{12}O_{10}K_4$, are described; the *ethyl* ester forms a colourless, amorphous, resinous mass, and yields a *hexa-acetyl* derivative, m. p. above 70°. E. G.



Derivatives of Amino-acids. IV. Compounds with Glycerol. EMIL ABDERHALDEN and LOUIS BAUMANN (*Zeitsch. physiol. Chem.*, 1911, 72, 50—57. Compare Abderhalden and Guggenheim, Abstr., 1910, i, 226).—Glycerol monotyrosine forms a crystalline *copper* salt, $C_{24}H_{32}O_{10}N_2Cu$, which gives a red coloration with Millon's reagent even in the cold. *Glycerol* m-*tolyl ether*,

$$OH\cdot CH_2\cdot CH(OH)\cdot CH_2\cdot O\cdot C_6H_4Me,$$

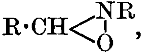
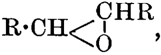
crystallises in long, rectangular plates, m. p. 65—70° (corr.), and *glycerol chloro-*m*-tolyl ether*, $C_{10}H_{13}O_3Cl$, crystallises from benzene in groups of needles, m. p. 90° (corr.).

Glyceroldityrosine, $OH\cdot CH[CH_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(NH_2)\cdot CO_2H]_2$, obtained by the action of glyceryl-α-dichlorohydrin on the sodium derivative of tyrosine, has not been obtained in a crystalline form. It has m. p. 275° (corr.) (decomp.), and yields a *copper* salt, $C_{21}H_{24}O_7N_2Cu$.

*Glycerol di-glycyl-*l*-tyrosine*,

$OH\cdot CH[CH_2\cdot O\cdot C_6H_4\cdot CH_2\cdot CH(CO_2H)\cdot NH\cdot CO\cdot CH_2\cdot NH_2]_2$, prepared by the action of glyceryl-α-dichlorohydrin on the sodium derivative of glycyl-*l*-tyrosine, is precipitated by the addition of alcohol to its aqueous solution, has m. p. 210° and $[\alpha]_D^{20}]$ $+25\cdot3°$ in 5% hydrochloric acid. An isomeride, which is sparingly soluble in water, has m. p. 248° and $[\alpha]_D^{20}$ $+36\cdot6°$ in 5% hydrochloric acid.

Glyceryltrityrosine, $C_9H_{10}O_2N\cdot O\cdot CH[CH_2\cdot O\cdot C_9H_{10}O_2N]_2$, crystallises in minute needles, m. p. 295° (corr.). The *hydrochloride* of the *ethyl* ester, $C_{36}H_{47}O_9N_3Cl_3$, is hygroscopic, and has m. p. 83°. J. J. S.

N-Phenyl Ethers of the Oximes. ANGELO ANGELI, LUIGI ALESSANDRI, and M. AIAZZI-MANCINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 546—555).—The formula  $R\cdot CH<\overset{NR}{\underset{O}{|}}$, which is usually ascribed to the *N*-alkylated aldoximes, does not explain the instability of these compounds towards permanganate, to which the oxides,  $R\cdot CH<\overset{CHR}{\underset{O}{|}}$, are stable. It is, further, not in accord with the observation that, in all the more definite and more gentle transformations which these compounds undergo, the oxygen atom is always obtained united with the nitrogen, never with the carbon atom. The authors therefore suggest the formula $R\cdot CH\colon NR\colon O$, which is supported by the failure of Scheiber (this vol., i, 382) to prepare these compounds in optically active modifications.

It is found that the action of magnesium phenyl bromide or iodide on the *N*-phenyl or *N*-benzyl derivative of benzaldoxime proceeds according to the scheme: $CHPh\colon NPh\colon O \longrightarrow CHPh_2\cdot NPh\cdot OH$, and is hence analogous to the reaction which takes place with benzylideneaniline: $CHPh\colon NPh \longrightarrow CHPh_2\cdot NHPh$ (compare Busch, Abstr., 1904, i, 663).

β-Phenyl-β-diphenylmethylhydroxylamine, $CHPh_2\cdot NPh\cdot OH$, forms colourless prisms, m. p. 127°, and becomes yellow in the light. When oxidised by means of mercuric oxide, benzaldehyde or magnesium phenyl bromide, it is partly converted into the *compound*, $C_{19}H_{15}ON$, which forms pale yellow leaflets, m. p. 214°, and is also obtained in small proportion in the preparation of the triphenylmethylhydroxylamine. When oxidised with chromic acid, either of these compounds yields nitrosobenzene and benzophenone, whilst, on reduction, diphenylanilinomethane (compare Busch, *loc. cit.*) is obtained. Reduction of the *N*-phenyl derivative of benzaldoxime by means of zinc and ammonium chloride, yields benzylideneaniline; under the same conditions the compound, m. p. 214°, gives a substance, m. p. 83°, having the same composition as benzophenoneaniline, but differing from it somewhat in its characters.

Oxidation of β-dibenzylhydroxylamine by means of mercuric oxide yields the *N*-benzyl derivative of benzaldoxime, and the action on this of magnesium phenyl bromide gives *β-benzyl-β-diphenylmethylhydroxylamine*, $CHPh_2\cdot N(CH_2Ph)\cdot OH$, forming white crystals, m. p. 105°; on oxidation with mercuric oxide, the latter gives a *compound*, $C_{20}H_{17}ON$, m. p. 159°, which yields benzaldehyde and benzophenone on treatment with chromic acid. T. H. P.

Action of Acid Chlorides and Anhydrides and of Ketones on the Sodium Derivative of Phenylacetonitrile. FERNAND BODROUX (*Compt. rend.*, 1911, **152**, 1594—1596. Compare Abstr., 1910, i, 257, 482, 557, 622, 623).—The sodium derivative of phenylacetonitrile reacts normally with acetyl chloride or acetic anhydride, giving poor yields of α-cyanobenzyl methyl ketone. Benzoyl chloride gives a 95% yield of the corresponding ketone, but phthalic anhydride is without action.

Double decomposition occurs when aliphatic ketones react with the sodium derivative, and the original substances are regenerated on treating the product with water. In the case of the aromatic ketones, however, a molecule of sodium hydroxide is eliminated; thus benzophenone gives αβ-diphenylcinnamonitrile; phenyl *p*-tolyl ketone forms *α-phenyl-β-p-tolylcinnamonitrile*, $CN\cdot CPh{:}CPh\cdot C_7H_7$, needles, m. p. 123°; α-naphthyl phenyl ketone gives *α-phenyl-β-α-naphthylcinnamonitrile*, small prisms, m. p. 174—175°. W. O. W.

New Method for Obtaining β-Diketones. ÉMILE ANDRÉ (*Compt. rend.*, 1911, **152**, 1488—1490. Compare this vol., i, 268).—The additive compounds formed by the union of amines with acetylenic ketones behave towards acids in the same way as Moureau and Lazennec's β-aminonitriles (Abstr., 1906, i, 956), giving rise to β-diketones and the salt of an amine. A number of diketones, such as acetylacetophenone and dibenzoylmethane, are readily prepared in this way. W. O. W.

Metallic Compounds of Diaryl Ketones. WILHELM SCHLENK and TOBIAS WEICKEL (*Ber.*, 1911, **44**, 1182—1189).—From the observations of Beckmann and Paul (Abstr., 1892, 169) on the sodium derivatives of diaryl ketones, the authors were led to the conclusion that these compounds contained tervalent carbon, and, in order to support this view, have prepared and examined the chemical behaviour of several new representatives.

p-Phenylbenzophenone (phenyl diphenyl ketone) and di-*p*-phenylbenzophenone (di-diphenyl ketone) combine with sodium in benzene or ethereal solution, yielding strongly coloured *sodium* compounds containing one molecule of ketone combined with one atom of sodium; similar *potassium* compounds have also been prepared. The sodium derivative of di-*p*-phenylbenzophenone, when exposed to air in ethereal solution, at once loses its deep green colour with the formation of sodium peroxide and the original ketone. It readily reacts with iodine, yielding di-*p*-phenylbenzophenone and sodium iodide. When treated with methyl iodide it is converted into the original ketone and *di*-p-*phenyldiphenylmethylcarbinol*, $CMe(C_6H_4Ph)_2\cdot OH$; with water, it yields the ketone, together with di-*p*-phenylbenzhydrol.

With respect to the constitution of these metallic derivatives of diaryl ketones, the formula $ONa\cdot CAr_2\cdot CAr_2\cdot ONa$ has been proposed by Acree (Abstr., 1903, i, 724). This formula is in agreement with the observation of the authors that the sodium compound of benzophenone, described by Beckmann and Paul (*loc. cit.*) by the direct combination of benzophenone and sodium, is also obtained by the action of sodium amalgam on benzopinacone in ethereal solution, but affords no explanation of the intense colour of these compounds; nor does it explain why the action of water and of methyl iodide, instead of giving rise to pinacones or their methyl ethers in the normal manner, causes a rupture of the molecule between the two central carbon atoms.

A satisfactory explanation of the behaviour of these metallic derivatives is obtained on the assumption that they contain tervalent carbon, and the authors, therefore, propose the constitution

$$-CR_2\cdot ONa.$$

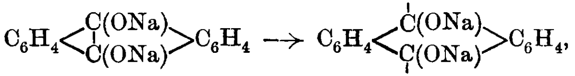
This formula accounts for their intense colour and their activity towards oxygen. From analogy with the triarylmethyls, it is assumed that the action of oxygen first leads to the formation of a peroxide, $ONa\cdot CAr_2\cdot O\cdot O\cdot CAr_2\cdot ONa$, which at once decomposes into sodium peroxide and the ketone $COAr_2$. By the action of water, the metallic derivative gives $-CR_2\cdot OH$ as an intermediate product, which either polymerises with the formation of a pinacone, as in the case of the sodium compound of benzophenone, or gives rise to a mixture of ketone and carbinol, $CHR_2\cdot OH$, as in the case of the sodium derivative of di-*p*-phenylbenzophenone.

The reaction with methyl iodide is represented as follows:

$$\begin{array}{l}ONa\cdot CAr_2-\\ ONa\cdot CAr_2-\end{array} + MeI \longrightarrow \begin{array}{l}ONa\cdot CAr_2I\\ ONa\cdot CAr_2Me\end{array} \longrightarrow \begin{array}{l}COAr_2+NaI\\ HO\cdot CAr_2Me\end{array}.$$

The production of sodium peroxide and anthraquinone by the action of water on the sodium derivative of anthraquinol (Manchot, Abstr., 1901, ii, 93), as well as the formation of anthraquinyl ethyl ether, by the action of ethyl iodide on the same compound (K. Meyer, this vol., i, 193), are explained in a similar manner.

The observation of K. Meyer (*loc. cit*), that the red colour of aqueous solutions of the sodium derivative of anthraquinol increases with rise of temperature, is referred by the authors to a kind of intermolecular dissociation, represented by the scheme:

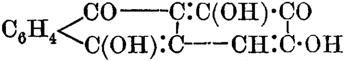


$$C_6H_4<\begin{array}{l}C(ONa)\\ \mid\\ C(ONa)\end{array}>C_6H_4 \longrightarrow C_6H_4<\begin{array}{l}\mid\\ C(ONa)\\ C(ONa)\\ \mid\end{array}>C_6H_4,$$

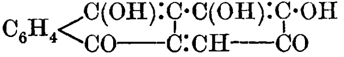
the change here taking place being analogous to that which occurs intramolecularly in the case of triphenylmethyl. F. B.

Anthraquinone Derivatives as Mordant Dyes, and Nature of the Lakes. I. GEORG VON GEORGIEVICS (*Monatsh.*, 1911, 32, 329—345. Compare Abstr., 1905, i, 447).—For eight years the author has conducted experiments with hydroxyanthraquinones to ascertain the relation between the constitution of a dye and its power of forming lakes with mordants. The following deductions are an amplification of those already recorded.

Firstly, the influence of hydroxyl groups on the colour of the lakes of hydroxyanthraquinones. Hydroxyl groups in the α-positions produce red and blue dyes, in the β-positions yellow and brown dyes; however, an α-hydroxyl group may mask the effect of a β-hydroxyl group, and vice versa. Thus the colour of the lakes of the 1 : 2 : 5-, 1 : 2 : 6-, 1 : 2 : 7-, and 1 : 2 : 8-trihydroxyanthraquinones do not differ materially from those of the lakes of alizarin itself. Anthragallol (1 : 2 : 3-trihydroxyanthraquinone), however, forms brown lakes and so also β-oxyanthragallol, whilst 1 : 2 : 3 : 4-tetrahydroxyanthraquinone, under the influence of the new α-hydroxyl group, again forms red lakes. In fact, the distinction is so sharp between alizarin (and the red-dyeing trihydroxyanthraquinones derived therefrom) and anthragallol and other hydroxyanthraquinones which produce yellow or brown colorations, that a difference in the constitutions of members of the two groups must be conceded. The hydroxyanthraquinones, therefore, are divisible into two groups. One group, comprising anthragallol, β-hydroxyanthragallol, xanthopurpurin, anthrachryson, rufigallol, 1 : 6- and 1 : 7-dihydroxyanthraquinone, and other derivatives forming yellow and brown lakes, has a para-quinonoid structure; for example, anthragallol,

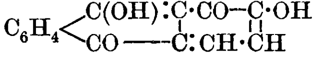


$C_6H_4<\begin{matrix}CO\text{——}C:C(OH)\cdot CO\\ \quad\quad\;\; | \quad\quad\quad\quad |\\ C(OH):C\text{——}CH:C\cdot OH\end{matrix}$ or



$C_6H_4<\begin{matrix}C(OH):C\cdot C(OH):C\cdot OH\\ \quad\quad | \quad\quad\quad\quad |\\ CO\text{——}C:CH\text{——}CO\end{matrix}$,

whilst the other group, which includes alizarin and its derivatives forming red or blue lakes (except hystazarin, which occupies an intermediate position), has an ortho-quinonoid structure; for example, alizarin,



$C_6H_4<\begin{matrix}C(OH):C\cdot CO\text{—}C\cdot OH\\ \quad\quad | \quad\quad\quad \|\\ CO\text{——}C:CH\cdot CH\end{matrix}$. In individual hydroxyanthraquinones the tendency to the production of one or other of the quinonoid forms may be such that one and the same dye may be orthoquinonoid in some of its lakes and para-quinonoid in others; by this means an explanation is found of the fact that, for example, 1 : 6-dihydroxyanthraquinone, which usually yields yellow or brown lakes, produces a strong red tone with a chromium mordant.

With respect to the relation between the positions of the hydroxyl groups and the lake-forming power of the dye, the introduction of another hydroxyl group into a hydroxyanthraquinone may increase or diminish its power of producing lakes. Thus 1 : 2 : 8-trihydroxyanthraquinone forms lakes more readily than alizarin, whilst 1 : 4 : 5 : 8-tetrahydroxyanthraquinone has very little lake-forming power in comparison with 1 : 4 : 5-trihydroxyanthraquinone. Octahydroxyanthraquinone has been prepared (following abstract) and found to exhibit a lake-forming power scarcely more pronounced than that of quinizarin (1 : 4-dihydroxyanthraquinone). This discovery destroys the tenability of Liebermann and Kostanecki's rule; it is true, however, that those members of the hydroxyanthraquinones which contain hydroxyl groups in the ortho-position are the most pronounced mordant dyes.

Mohlau has disputed the author's statement that hystazarin (2:3-dihydroxyanthraquinone) is a more pronounced mordant dye than 1:3- or 1:4-dihydroxyanthraquinone; in reply, the author shows that quinizarin hardly dyes wool mordanted with tin, whilst hystazarin produces a full orange tone which is fast to milling.

C. S.

Octahydroxyanthraquinone. Georg von Georgievics (*Monatsh.*, 1911, **32**, 347—352).—Three parts of rufigallol (1:2:3:5:6:7-hexahydroxyanthraquinone), 100 parts of sulphuric acid (H_2SO_4,H_2O), 4 parts of boric acid, and about 0·05 part of mercuric oxide are heated at 250—260° until a drop of the mixture dissolves in concentrated sulphuric acid with a pure blue colour; the yield of the octahydroxyanthraquinone diminishes rapidly when the heating is too prolonged. The reddish-brown precipitate obtained by pouring the cold mixture into water is washed with boiling water, dried, and crystallised by treating its boiling, saturated solution in pyridine with boiling methyl alcohol and a little water, whereby the dye is obtained in stout, brownish-red needles. *Octahydroxyanthraquinone* can only be crystallised from pyridine or methyl alcohol, yields anthracene by distillation with zinc dust, forms an *octa-acetate*, pale yellow needles, decomp. about 200°, and dissolves in concentrated sulphuric acid, forming a greenish-blue solution (the presence of a red tinge indicates the presence of rufigallol). Its behaviour as a mordant dye has been described (preceding abstract).

C. S.

Preparation of Anthraquinonylglycines. Farbwerke vorm. Meister, Lucius & Brüning (D.R.-P. 232127).—Anthraquinonylglycines may readily be obtained by the action of glyoxylic or thioglyoxylic acid on the corresponding reduced aminoanthraquinones. *β-Anthraquinonylglycine*, orange-yellow crystals, m. p. 236°, is prepared by reducing β-aminoanthraquinone with sodium hyposulphite in aqueous alkaline solution, with the subsequent addition of an alkali glyoxylate and heating during one hour. Unchanged β-aminoanthraquinone is separated by a current of air, and the product precipitated by the addition of mineral acid.

α-Anthraquinonylglycine forms red crystals, m. p. 262° (decomp.).

F. M. G. M.

Desiccation of *cis*-Terpin Hydrate. A. Leulier (*J. Pharm. Chim.*, 1911, [vii], **3**, 440—441).—When terpin hydrate is dried at 100°, part of the terpin formed is volatilised, consequently desiccation should be effected by exposure at atmospheric temperature over sulphuric acid under reduced pressure.

T. A. H.

Sesquiterpene and an Olefinic Camphor Occurring in Southern Cypress. Allan F. Odell (*J. Amer. Chem. Soc.*, 1911, **33**, 755—758).—During the course of some work on the oxidation of cypress (*Taxodium distichum*) sawdust, a fragrant odour was observed, and the present investigation was therefore undertaken.

On extracting cypress sawdust with alcohol, and removing the latter by distillation, a red, viscous product was obtained. By the fractional distillation of this extract under reduced pressure, two new compounds were isolated.

Cypressene, $C_{15}H_{24}$, b. p. 218—220°/35 mm., and 295—300°/778 mm., is a yellowish-green, viscous, nearly odourless liquid, which has D_4^{18} 0·9647, n_D^{22} 1·5240, $[\alpha]_D^{20}$ + 6·53°, reacts violently with moderately strong nitric acid to form a yellow, amorphous oxidation product, and gives a red coloration with concentrated sulphuric acid. The compound contains only one ethylene linking, and is therefore a tricyclic sesquiterpene.

The other new compound, *cypral*, $C_{12}H_{20}O$, is probably an aldehyde. It was obtained as a pale yellow, fragrant, mobile liquid, which has b. p. 182—185°/35 mm., D_4^{20} 0·9469, n_D^{20} 1·5040, is dextrorotatory, and readily reduces ammoniacal solution of silver nitrate. E. G.

Humulene of Oil of Hop Flowers. ERNST DEUSSEN (*J. pr. Chem.*, 1911, [ii], **83**, 483—489).—Humulene, b. p. 118—119°/10 mm., isolated from oil of hop flowers by fractional distillation, has been identified with *i*-α-caryophyllene (Abstr., 1908, i, 353; 1909, i, 171, 813) by a comparison of the nitrosates and nitrosochlorides. C. S.

Essential Oil of the Dwarf Pine. ERICH BÖCKER and ALFRED HAHN (*J. pr. Chem.*, 1911, [ii], **83**, 489—498).—The oil of the dwarf pine (*Pinus pumilo*), freed from terpenes and sesquiterpenes, and having D^{15} 0·8707, $[\alpha]_D$ − 9°45′, and esterification number 13·4, has been examined with respect to its oxygenated constituents. In addition to *l*-bornyl acetate, it contains aldehydic and ketonic substances, and at least 30% of alcohols and esters of the terpene and sesquiterpene series, as yet unexamined.

The oil has been separated into twelve fractions boiling between 85° and 178°/13 mm. The fractions are dissolved separately in 96% alcohol, and shaken for two to three hours with 30% aqueous sodium hydrogen sulphite. The fraction, b. p. 148—160°/13 mm., $[\alpha]_D$ − 14°15′, esterification number 53, gives by this treatment a small yield of a hydrogen sulphite compound, which after hydrolysis yields an *oil*, $C_{15}H_{26}O$, which is unsaturated and restores the colour of Schiff's reagent. The fractions b. p. 138—148°/13 mm. and 127—138°/13 mm. are united and distilled; the portion b. p. 128—135°/15 mm. yields a hydrogen sulphite compound, from which, by hydrolysis, is obtained a *substance*, $C_{15}H_{24}O$, which is lævorotatory, unsaturated, and probably of ketonic nature.

The fractions b. p. 105—109°, 109—113°, 113—118°, and 118—127°, all under 13 mm., do not yield hydrogen sulphite compounds, but contain *l*-bornyl acetate.

The fractions b. p. 85—100°/13 mm. and 100—105°/13 mm. differ from all the others by having an intense, peculiar odour. By combining them and distilling, a portion b. p. 87—95°/14 mm. is obtained, which yields a white, crystalline hydrogen sulphite compound. The *substance*, $C_8H_{14}O$, obtained by the hydrolysis of this compound by 20% sodium carbonate, has ketonic properties, and is called *pumilone*. It has b. p. 216—217°/754 mm., D^{15} 0·9314, D^{20} 0·9288, n_D 1·46459, and $[\alpha]_D$ $-15°$. It has a very intense, not unpleasant odour. The odour of the natural dwarf pine oil is mainly due to pumilone, although it is present only to the extent of 1—2%. Pumilone, which is unsaturated and contains one double linking, does not yield characteristic derivatives, except the hydrogen sulphite compound and the *semicarbazone*, m. p. 116—117°. C. S.

Theory of the Vulcanisation of Caoutchouc. F. WILLY HINRICHSEN (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 245—250. Compare Abstr., 1910, i, 330).—The influence of time on the proportion of free sulphur in a sample of vulcanised para-rubber has been examined. The total and free sulphur were estimated in the original material, of which samples were kept for six months under different conditions. The experimental data show that the proportion of free sulphur diminishes with time, and that the rate of diminution is much greater at 70° than at room temperature. These observations agree with the author's view, that the sulphur present in the vulcanised caoutchouc is partly adsorbed, the remainder being chemically combined. The adsorption equilibrium is attained very quickly, but the chemical action at low temperatures is relatively a very slow process. As the chemical reaction proceeds, the proportion of free sulphur gradually diminishes. H. M. D.

Cold Vulcanisation. F. WILLY HINRICHSEN (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 250—251).—Polemical against Bysoff (compare this vol., i, 390). H. M. D.

Properties of Dammar Resins. CHARLES COFFIGNIER (*Bull. Soc. chim.*, 1911, [iv], **9**, 549—561. Compare Abstr., 1902, i, 633).—The solubilities and analytical constants of some commercial dammar resins are recorded.

Dammar resin from Padang has D^{18} 1·036, m. p. 95°, acid number 31·4, and saponification number 33·7; that from Borneo has D^{18} 1·048, m. p. 120°, acid number 35·1, and saponification number 64·5. Singapore Dammar has D^{18} 1·057, m. p. 95°, acid number 30·1, and saponification number 39·3 Pontianac Dammar has D^{18} 1·025, m. p. 110°, acid number 19·9, and saponification number 30·9. Sumatra Dammar has D^{18} 1·004, m. p. 190°, acid number 59·6, and saponification number 64·5. Batjan Dammar has D^{18} 1·032, m. p. 105°, acid number 18·5, and saponification number 19·6. The solubilities of these dammars in twelve solvents are recorded, and similar data for a number of solvents are given in the cases of Batavian dammar, sandarac, and mastic resins. T. A. H.

Constitution of Bixin. J. F. B. VAN HASSELT (*Rec. trav. chim.*, 1911, **30**, 1—47. Compare Marchlewski and Matejko, Abstr., 1906, i, 760).—The author has obtained bixin from anatto by Zwick's process (Abstr., 1900, i, 513) in large, violet, triclinic crystals, m. p.

187°. The analytical data and the molecular weight by the ebullioscopic method in chloroform point to a formula $C_{29}H_{34}O_5$. Etti and Zwick describe mono- and di-potassium derivatives of bixin, and therefore consider that bixin behaves like a dibasic acid. This is not so, the di-potassium compound being a derivative of a new substance, called norbixin, obtained from bixin by the substitution of its methoxyl methyl group by potassium. When bixin is dissolved in boiling aqueous potassium hydroxide, methyl alcohol is evolved, and is detected as formaldehyde after oxidation; by acidifying the alkaline solution, *norbixin*, $C_{28}H_{32}O_5$, is precipitated. It is a light red, crystalline powder, decomp. 240°, and is insoluble in chloroform.

When a solution of bixin (or of purified anatto) and an equivalent amount of potassium hydroxide, dissolved in boiling methyl alcohol, are treated first with ethyl acetate and then with methyl sulphate and a little potassium hydroxide, *bixin methyl ether*, $C_{30}H_{36}O_5$, m. p. 156°, is obtained. It crystallises in red, pleochroic rhomboids, develops an intense blue coloration with concentrated sulphuric acid, and is hydrolysed by alcoholic potassium hydroxide, yielding norbixin. (*bixin ethyl ether*, $C_{31}H_{38}O_5$, m. p. 138°, prepared in a similar manner, forms violet crystals.) By treatment with methyl sulphate, norbixin yields bixin and bixin methyl ether. Bixin contains one methoxy-group, bixin methyl ether two, and norbixin none.

The preceding transformations show that the relation between norbixin, bixin, and bixin methyl ether is expressed by the formulæ OH·R·OH, OH·R·OMe, and OMe·R·OMe, where R is $C_{28}H_{30}O_3$. When a solution of potassium norbixin, obtained by hydrolysing bixin with alcoholic potassium hydroxide, is treated with ethyl sulphate, the precipitate contains *norbixin diethyl ether*,

$$C_{28}H_{30}O_3(OEt)_2,$$

blue rhomboids, m. p. 121°, whilst *norbixin ethyl ether*,

$$C_{28}H_{30}O_3(OEt)\cdot OH,$$

red needles, m. p. 176°, is obtained by acidifying the mother liquor. The latter is quite analogous to bixin in its behaviour, but is more slowly hydrolysed by potassium hydroxide.

The two hydroxyl groups in norbixin are not symmetrically situated in the molecule, since two isomeric norbixin methyl ethyl ethers have been obtained. The one is bixin ethyl ether, m. p. 138°, described above; the other, iso*bixin ethyl ether*, m. p. 149°, is prepared by methylating norbixin ethyl ether, and crystallises in large, red rhomboids. It follows, therefore, that an isomeride of bixin itself should be capable of existence. This isomeride, iso*bixin*, $OH\cdot C_{28}H_{30}O_3\cdot OMe$, m. p. 178°, is obtained by the partial hydrolysis of bixin methyl ether by alcoholic potassium hydroxide; its points of difference from bixin are recorded in the sequel, the most important being its stability to aqueous potassium hydroxide. When *iso*bixin is treated with ethyl sulphate, norbixin diethyl ether, m. p. 121°, is produced, the methyl group having been ousted by an ethyl group.

The potassium derivative, $OK\cdot C_{28}H_{30}O_3\cdot OH$, of bixin is easily obtained by heating a methyl-alcoholic solution of bixin just to the b. p. with an excess of potassium hydroxide; it crystallises in violet needles, and is quite insoluble in boiling water. The dipotassium derivative of norbixin is formed when bixin is hydrolysed by aqueous or ethyl-alcoholic potassium hydroxide or by treating ethyl-alcoholic norbixin with this alkali; it forms a felted mass of reddish-brown crystals, dissolves easily in water, and oxidises readily in the air. The *disodium* derivative of norbixin and the *potassium* derivatives of norbixin, norbixin ethyl ether, and *iso*bixin are also described.

The unstable orange product, m. p. 200·5°, obtained by Marchlewski and Matejko (*loc. cit.*) by reducing bixin with zinc and acetic acid, is *dihydrobixin*, $C_{29}H_{36}O_5$; it is also formed when the reduction is performed in alkaline solution.

Dihydrobixin methyl ether, $C_{30}H_{38}O_5$, m. p. 174°, *dihydroisobixin*, $C_{29}H_{36}O_5$, m. p. 190°, and *dihydronorbixin*, $C_{28}H_{34}O_5$, decomp. 235°, are obtained by reducing the corresponding bixins with zinc and acetic acid; the last, however, is obtained best by reduction in alkaline solution. All of them are unstable, yellow, crystalline substances, which develop intense blue colorations with concentrated sulphuric acid.

By bromination in cold glacial acetic acid, bixin forms a *decabromide*, $C_{29}H_{34}O_5Br_{10}$, a white, amorphous powder, which does not develop a coloration. Four, six, or eight of the bromine atoms can be eliminated by the more or less prolonged action of zinc and dilute sulphuric acid, the products of reduction being amorphous orange substances, which give a blue coloration with sulphuric acid. Bixin-methyl ether also forms a *decabromide*, $C_{30}H_{36}O_5Br_{10}$, a white powder insoluble in potassium hydroxide. By treatment with iodine chloride in acetic acid, bixin, norbixin, methylbixin, and their dihydro-derivatives, and *iso*bixin all combine with 10 atoms of halogen; consequently hydrogen must attack the molecule of bixin in a different manner from the halogens.

When heated by itself at 190° or in diphenylamine, bixin loses its colour and decomposes into *m*-xylene and a resinous substance, m. p. 145°, which is shown to be a mixture; *iso*bixin, norbixin, the bixin-alkyl ethers, and their dihydro-derivatives also yield *m*-xylene under the same conditions.

The author is unable to confirm Zwick's statements that palmitic acid is produced by the action of steam on bixin at 160° and by the action of light on its sodium derivative. Although the behaviour of bixin with methyl sulphate indicates the presence of a hydroxyl group, attempts to acetylate or benzoylate the substance have been unsuccessful. The failure of bixin methyl ether to react with phenylhydrazine, hydroxylamine, semicarbazide, and magnesium ethyl bromide points to the absence of a carbonyl group. The action of numerous oxidising agents on bixin has been examined; characteristic products, however, have not been isolated. C. S.

The Chlorophyll Group. IV. Phylloporphyrin. LÉON MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1911, 32, 204—221).—The authors describe various modifications of the methods published previously for preparing phylloporphyrin. The most convenient method is from a partly purified phyllotaonin obtained by the method of Kózniewski and Marchlewski. The results of detailed spectroscopic examination of phyllo- and meso-porphyrin are given, and also a comparison is made of the results of Willstätter and Fritsche's porphyrins. The paper is controversial as regards the homogeneity of the products obtained by the different investigators. S. B. S.

The Existence of Two Chlorophyllans. LÉON MARCHLEWSKI (*Biochem. Zeitsch.*, 1911, **32**, 332—333).—Controversial. Reply to Tsvett. S. B. S.

The Solubility of the Chlorophyllins and a New Method for Isolating Them. M. TSVETT (*Ber.*, 1911, **44**, 1124—1127).—The chlorophyllins are insoluble in pure light petroleum, but dissolve readily in this solvent in the presence of a small quantity of alcohol, ether, or benzene. Substances having a similar influence on the solubility must be present in the chloroplasts, since the chlorophyllins may be extracted from the freshly-crushed leaves with pure light petroleum.

These substances may be removed by washing the petroleum solutions first with 80% alcohol and finally with water; the mixture of α- and β-chlorophyllins then becomes insoluble, and separates out. In this manner a waxy mixture has been obtained from *Cytisus* leaves, probably identical with a substance mentioned by Willstätter and Stoll (this vol., i, 141), and having similar properties. F. B.

Natural Dyes and Colouring Matters of the Philippines. BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1910, **5**, 439—452).—Annatto, old fustic or morin, indigo, and Brazil wood are four of the principal natural dyes occurring in the Philippines which have not as yet entirely been displaced by the synthetic articles.

An alcoholic extract of narra wood, *Pterocarpus* spp., was found to contain a resin, a tannin, an amorphous, red colouring matter, two colourless, crystalline substances, and a yellow, fluorescent substance.

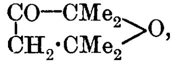
The red colouring matter, which is named *narrin*, swells and chars at about 180°, yields phloroglucinol and resorcinol by fusion with potassium hydroxide and vanillin by oxidation with alkaline potassium permanganate, produces a small amount of resorcinol dimethyl ether by distillation with zinc dust, and forms a brown, amorphous benzoyl derivative. A comparison of narrin with santalin, isolated from *P. santalinus*, shows that the two substances are closely related. Both are decolorised by zinc and potassium hydroxide or by sodium amalgam in dilute alcohol, yielding solutions in which the colour is restored by atmospheric oxidation; both yield potassium salts by precipitation of their alcoholic solutions by alcoholic potassium acetate. The *copper* salt of santalin has the formula $Cu(C_{15}H_{13}O_5)_2$, whilst that of narrin contains only 6·24% of copper. The dyeing properties of the two substances are very similar. Narrin is insoluble in water, but dissolves in alkaline solutions. Metallic mordants, such as chromium and copper hydroxides, are the most suitable, but the shades are not very fast to soap.

The two colourless, crystalline substances are shown to be pterocarpin and homopterocarpin. Pterocarpin has the formula $C_{14}H_{12}O_4$

and m. p. 163°. Cazeneuve and Hugonenq (Abstr., 1887, 971; 1889, 160) state that it has the composition $C_{20}H_{16}O_6$, and m. p. 152°. Homopterocarpin, $C_{17}H_{16}O_4$, m. p. 86° (Cazeneuve and Hugonenq, *loc. cit.*, give $C_{24}H_{24}O_6$, and m. p. 82—86°), is insoluble in concentrated potassium hydroxide, but yields a little resorcinol at 200—210°. It produces resorcinol dimethyl ether by distillation with zinc dust, but does not react with phenylhydrazine or phosphorus pentachloride. Probably it is closely related to narrin. C. S.

Reduction of Biliary Pigments by the Hydrogen Evolved from Palladium, Hydrogenised in Presence of Sodium Hypophosphite: Formation of Urobilinogen. Jules Ville (*Bull. Soc. chim.*, 1911, [iv], 9, 480—483).—To a solution of pigments obtained from biliary calculi from a cow, sodium hydroxide and palladium, precipitated from the chloride by means of sodium hypophosphite, were added, and the whole warmed to 100°. Into this sodium hypophosphite solution was gradually introduced. In a short time urobilinogen was formed, and could be detected by Erhlich's reagent, or by its conversion into urobilin and observation of the characteristic absorption spectrum of the latter. The reaction also takes place in the cold, but more slowly. T. A. H.

Catalytic Isomerisation of Acetylenic Pinacone [βε-Dimethyl-Δ^{γ}-hexinene-βε-diol]. Synthesis of 3-Keto-2:2:5:5-tetramethyltetrahydrofuran. Georges Dupont (*Compt. rend.*, 1911, 152, 1486—1488. Compare this vol., i, 173).—When dimethyl-Δ^{γ}-hexinene-βε-diol is heated with an aqueous solution of mercuric sulphate and the mixture distilled in steam, a mobile liquid is obtained, having a camphoraceous odour, m. p. −20·5°, b. p. 149°, D^{18} 0·9251, n_D^{18} 1·4198. This is not the expected dihydroxy-ketone, but an internal anhydride, 3-*keto*-2 : 2 : 5 : 5-*tetramethyltetrahydrofuran*,



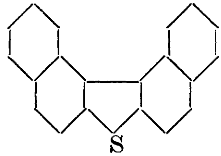
$$\begin{array}{l}CO\text{—}CMe_2\\ |\\ CH_2\cdot CMe_2\end{array}\!\!>O,$$

a very stable substance, yielding a *semicarbazone*, needles, m. p. 190°, an *oxime*, leaflets, m. p. 128°, and a *phenylhydrazone*, m. p. 134°. When treated with magnesium methyl bromide it forms a tertiary alcohol, m. p. 77°, identical with that obtained from βγε-trimethylhexane-βγε-triol (Bouveault and Locquin, this vol., i, 2). The ketone is converted by the magnesium derivative of acetylene dibromide into a *substance*, $C_8H_{15}O_2\cdot C{:}C\cdot C_8H_{15}O_2$, m. p. 97—98°. It also behaves as an enol, giving a normal *sulphate*, $(C_8H_{13}O)_2SO_4$, m. p. 67—70°, a *sodium*, and a *potassium* salt. When the latter is treated with ethyl iodide, 3-*ethoxy*-2 : 2 : 5 : 5-*tetramethyl*-2 : 5-*dihydrofuran*, $C_8H_{13}O\cdot OEt$, is formed as a liquid, b. p. 157—159°, D^{18} 0·8878, n_D 1·4237. W. O W.

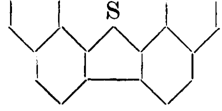
Constitution of Thiophenoquinones and Mechanism of Quinone Reactions. Theodor Posner (*J. pr. Chem.*, 1911, [ii], 83, 471—483).—Final reply to Michael (Abstr., 1910, i, 748) and to Michael and Cobb (*ibid.*, i, 748). C. S.

Phenothioxin. Enos Ferrario (*Bull. Soc. chim.*, 1911, [iv], 9 536—537).—There is very little interaction when sulphur and diphenyl ether are heated together, unless a catalyst, such as aluminium or magnesium chloride, is present, in which case phenothioxin (Mauthner, Abstr., 1906, i, 447) is formed. Phenothioxin combines with two atoms of hydrogen when reduced, and when heated with copper at 250° forms diphenylene oxide. T. A. H.

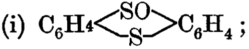
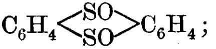
Dinaphthathiophen. M. Lanfry (*Compt. rend.*, 1911, **152**, 1254—1256. Compare this vol., i, 151).—From the products of the action of sulphur on naphthalene at a red heat a substance, *dinaphthathiophen*, has been isolated in the form of pearly, yellow scales, m. p. 250·5° (corr.), b. p. above 440°, without appreciable decomposition. Its constitution is represented by the annexed formula. When the substance is oxidised with chromic acid, it yields phthalic acid. The *hexabromo*-derivative, $C_{20}H_6Br_6S$, m. p. 260°, furnishes 3 : 6-dibromophthalic acid on oxidation.

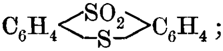


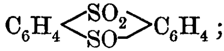
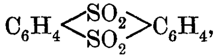
or



Boiling nitric acid converts dinaphthathiophen into a yellow *tetranitro*-derivative, $C_{20}H_8(NO_2)_4S$, m. p. about 210°. W. O. W.

Thianthren. Karl Fries and Wilhelm Vogt (*Annalen*, 1911, **381**, 312—337).—Of the five possible oxidation products of thianthren, namely : (i)  $C_6H_4{<}\begin{matrix}SO\\S\end{matrix}{>}C_6H_4$; (ii)  $C_6H_4{<}\begin{matrix}SO\\SO\end{matrix}{>}C_6H_4$;

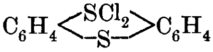
(iii)  $C_6H_4{<}\begin{matrix}SO_2\\S\end{matrix}{>}C_6H_4$;

(iv)  $C_6H_4{<}\begin{matrix}SO_2\\SO\end{matrix}{>}C_6H_4$; (v)  $C_6H_4{<}\begin{matrix}SO_2\\SO_2\end{matrix}{>}C_6H_4$, the disulphoxide (ii) has been recently shown (this vol., i, 395) to exist in two isomeric forms. Thianthrenmonosulphoxide (i) can be obtained by oxidising a glacial acetic acid solution of thianthren with dilute nitric acid (D 1·2) (compare Fries and Volk, Abstr., 1909, i, 406). The monosulphone (iii) is formed by the action of chlorine on a boiling dilute acetic acid solution of thianthren, and when oxidised with concentrated nitric acid yields the trioxide (iv), which is also formed by the action of chlorine and water on the monosulphoxide or the isomeric disulphoxides.

Thianthren is most readily prepared by a modification of Genvresse's method (Abstr., 1897, i, 240), and yields a *compound*, $C_{12}H_8S_2,FeCl_3$, in the form of glistening, bronzy needles, readily decomposed by water.

Thianthrenmonosulphoxide, $C_{12}H_8OS_2$, crystallises from methyl alcohol or benzene in long needles, m. p. 143°. Its solution in concentrated sulphuric acid has a brownish-red colour, which changes to a deep blue on the addition of a little water. The addition of much water precipitates the original sulphoxide, but when the solutions are kept for some time or warmed, thianthren is formed. When the solution in concentrated hydrochloric acid is kept for some time, chlorothianthren is deposited, but hydrogen bromide reacts with a glacial acetic acid solution of the sulphoxide, yielding thianthren. *Thianthrenmonosulphone*, $C_{12}H_8O_2S_2$, is best prepared by leading chlorine into a glacial acetic acid solution of thianthren and boiling, each operation being repeated several times. It crystallises from acetic acid in colourless, glistening plates, m. p. 159°, and is quite stable towards hydrogen bromide or zinc dust and acetic acid. Its solution in concentrated sulphuric acid has a rose colour, and does not decompose when kept.

Thianthrensulphonesulphoxide (*thianthrentrioxide*), $C_{12}H_8O_3S_2$, crystallises from alcohol in small, compact prisms, m. p. 216°; its solution in concentrated sulphuric acid is colourless, and with hydrobromic acid it yields the monosulphone.

Thianthren dichloride,  $C_6H_4<\begin{matrix}SCl_2\\S\end{matrix}>C_6H_4$ or $C_6H_4\ll\begin{matrix}SCl\\SCl\end{matrix}>C_6H_4$, obtained by the action of dry chlorine on a benzene solution of thianthren, forms brilliant red prisms, which are readily affected by moisture, yielding hydrogen chloride and the sulphoxide. When heated alone the crystals decompose into chlorine and thianthren. 4-*Chlorothianthren*, $C_{12}H_7ClS_2$, crystallises from glacial acetic acid in prisms, m. p. 84°, and gives a pale violet-red coloration with concentrated sulphuric acid, but this gradually changes to a deep violet-blue. It can be prepared by the action of chlorine on a chloroform solution of thianthren and exposing the product to the action of atmospheric moisture, or from thianthren sulphoxide and an acetic acid solution of hydrogen chloride. 4 : 4′-*Dichlorothianthren*, $C_{12}H_6Cl_2S_2$, obtained by the action of chlorine on thianthren or its monochloro-derivative, or by the condensation of chlorobenzene and chloride of sulphur in the presence of carbon disulphide and aluminium chloride, crystallises from benzene or glacial acetic acid in long, slender needles, m. p. 171°. It dissolves slowly in concentrated sulphuric acid, and the solution has a brilliant blue colour.

2′-*Ethoxydiphenylsulphone*-2-*sulphinic acid*,

$$SO_2H\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot OEt,$$

obtained by boiling thianthrendisulphone (Graebe, *Annalen*, 1875, **179**, 178) with alcohol and 50% potassium hydroxide solution, forms slender needles, m. p. 151° (decomp.), and yields a sparingly soluble *sodium* salt. When reduced with zinc dust and alcoholic hydrochloric acid, the sulphinic acid yields 2′-*ethoxy*-2-*thioldiphenylsulphone*,

$$SH\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot OEt,$$

which crystallises from alcohol in small needles, m. p. 131°. Its solutions in alkalis are oxidised rapidly on exposure to the air. The *methyl ether*, $C_{15}H_{16}O_3S_2$, crystallises from benzene in compact needles, m. p. 178°. 2′-*Ethoxydiphenylsulphone disulphide*,

$$(OEt\cdot C_6H_4\cdot SO_2\cdot C_6H_4)_2S_2,$$

obtained by oxidising the thiol with bromine water, crystallises from glacial acetic acid in compact prisms, m. p. 270° (decomp.). 2′-*Ethoxydiphenylsulphone*-2-*sulphonyl chloride*,

$$OEt\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot SO_2Cl,$$

prepared by the action of chlorine on a glacial acetic acid solution of the sulphinic acid, crystallises from benzene in brilliant, compact rhombs, m. p. 159°. The corresponding *bromide*, $C_{14}H_{13}O_5BrS_2$, has m. p. 177°, and with excess of bromine yields a substituted *bromide*,

$$C_{14}H_{12}O_5Br_2S_2,$$

which crystallises in needles, m. p. 179°, and yields a *perbromide*, $C_{14}H_{12}O_5S_2Br_4$, in the form of orange-coloured needles. *2′-Ethoxydiphenylsulphone-2-sulphonic acid*, $OEt\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot SO_3H$, crystallises from glacial acetic acid in compact needles, m. p. 178°. The corresponding *anilide*, $C_{20}H_{19}O_5NS_2$, crystallises in prisms, m. p. 204°.

2′-Methoxydiphenylsulphone-2-sulphinic acid,

$$OMe\cdot C_6H_4\cdot SO_2\cdot C_6H_4\cdot SO_2H,$$

obtained by hydrolysing the disulphone with methyl-alcoholic potash, has m. p. 161° (decomp.). *2′-Methoxy-2-thioldiphenylsulphone*,

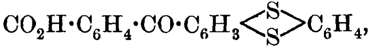
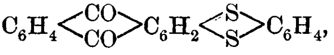
$$C_{13}H_{12}O_3S_2,$$

has m. p. 157°, and its *methyl ether*, $C_{14}H_{14}O_3S_2$, m. p. 197°. *2′-Methoxydiphenylsulphone-2-sulphonyl chloride*, $C_{13}H_{11}O_5ClS_2$, forms compact prisms, m. p. 210°, and *2′-methoxydiphenylsulphone-2-sulphonic acid*, $C_{13}H_{12}O_6S_2$, compact needles, m. p. 202°. The *anilide* forms rhombic crystals, m. p. 193°. J. J. S.

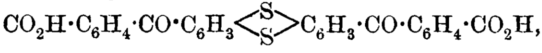
Introduction of Several Phthalic Acid Groups into Aromatic Compounds. III. Experiments with Thianthren, Dimethylthianthren, Thiodiphenylamine, and *N*-Methylthiodiphenylamine.

ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1911, 44, 1233—1249. Compare this vol., i, 452, 453).—By the action of phthalic anhydride and aluminium chloride on thianthren in the presence of carbon disulphide, thianthren-2-phthaloylic acid and the 2:6-diphthaloylic acid are formed.

The yield of the dibasic acid is increased by using more anhydride and less carbon disulphide, and heating for twenty-four hours. The mixture of the two acids can be separated by means of their ammonium salts, as the salt of the monobasic acid is sparingly, and that derived from the dibasic acid readily, soluble in water.

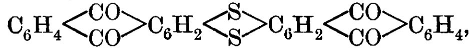
Thianthren-2-phthaloylic acid,  $CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3\genfrac{<}{>}{0pt}{}{S}{S}C_6H_4$, crystallises from boiling xylene, has m. p. 219—221°, and dissolves in concentrated sulphuric acid, yielding a violet-coloured solution. When heated with anhydrous zinc chloride for one hour at 230—235°, it yields 2 : 3-*phthaloylthianthren*,  $C_6H_4\genfrac{<}{>}{0pt}{}{CO}{CO}C_6H_2\genfrac{<}{>}{0pt}{}{S}{S}C_6H_4$, which crystallises from nitrobenzene in brilliant dark red needles, m. p. 253°. With alkaline hyposulphite it gives a dark reddish-brown solution, which does not dye unmordanted cotton.

Thianthren-2 : 6-diphthaloylic acid,



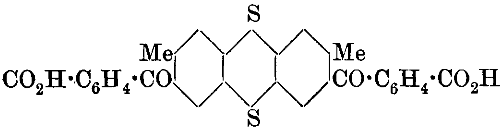
$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_3\genfrac{<}{>}{0pt}{}{S}{S}C_6H_3\cdot CO\cdot C_6H_4\cdot CO_2H,$$

does not crystallise well, has m. p. 143—160°, and gives a dark brown coloration with concentrated sulphuric acid. When heated with the concentrated acid for forty minutes at 120—124°, it yields 2 : 3 : 6 : 7-*diphthaloylthianthren*,



$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2{<}\begin{matrix}S\\S\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4,$$

This separates from nitrobenzene in minute, brownish-red crystals, which are not molten at 325°. Its solution in concentrated sulphuric acid is grass-green, and its reduction product is dark red, but does not dye unmordanted cotton.



2 : 6-*Dimethylthianthren*-3 : 7-*diphthaloylic acid* (annexed formula), prepared by heating 2 : 6 - dimethylthianthren (Jacobson and Ney, Abstr., 1894, i, 125), phthalic anhydride, and aluminium chloride, first at 60—100°, and then for seven hours at 100—104°, forms a light red powder, and with concentrated sulphuric acid at 120—124° yields 2 : 6-*dimethyl*-3 : 4 : 7 : 8-*diphthaloylthianthren*, $C_{30}H_{16}O_4S_2$, which crystallises from nitrobenzene in reddish-brown needles, m. p. 380—385° (decomp.). The vat dye obtained by the action of alkaline hyposulphite colours unmordanted cotton yellow.

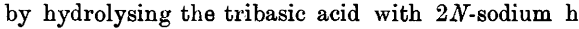
Phenylsulphidephthaloylic [*phenylthiolbenzoylbenzoic*] *acid*,

$$SPh{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

crystallises from light petroleum, and has m. p. 121—122°. The *ammonium* salt is sparingly soluble, and crystallises in glistening needles, m. p. 171°. When warmed at 60° with concentrated sulphuric acid it is largely sulphonated, but with zinc chloride yields *phthaloylphenyl sulphide*, $C_6H_4{:}C_2O_2{:}C_6H_3{\cdot}SPh$.

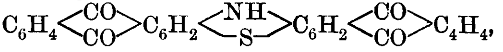
Thiodiphenylamine reacts with phthalic anhydride and aluminium chloride in the presence of carbon disulphide, yielding a tribasic acid; two $\cdot CO{\cdot}C_6H_4{\cdot}CO_2H$ groups are introduced into the para-positions with respect to the imino-group and meta with respect to the sulphur atom, and the third group becomes attached to nitrogen. When *N*-methylthiodiphenylamine is used, only two phthalic acid groups are introduced.

Thiodiphenylamine-2 : 7-*diphthaloylic acid*,



$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_3{<}\begin{matrix}NH\\S\end{matrix}{>}C_6H_3{\cdot}CO{\cdot}C_6H_4{\cdot}CO_2H,$$

prepared by hydrolysing the tribasic acid with 2*N*-sodium hydroxide solution, crystallises from nitrobenzene in brick-red, glistening plates, and turns dark-coloured and decomposes at 250°. 2 : 3 : 6 : 7-*Diphthaloylthiodiphenylamine thiodianthraquinonylamine*,

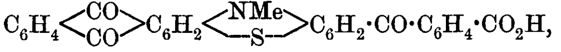


$$C_6H_4{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_2{<}\begin{matrix}NH\\S\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\\CO\end{matrix}{>}C_4H_4,$$

obtained by heating the dibasic acid with concentrated sulphuric acid at 100—106°, crystallises from nitrobenzene, aniline or quinoline, and has m. p. 380°. It is bluish-black when dry, greenish-blue when moist, and yields a dark red vat-dye. Its *sulphonic acid* dyes wool a grey-green.

[With WALTER TRITSCH.]—N-*Methylthiodiphenylamine*-2 : 7-*diphthaloylic acid*, $C_{29}H_{19}O_6NS$, crystallises from cumene, decomposes at

170°, and its solution in concentrated sulphuric acid has an olive-green or in thin layers a reddish-brown colour. With concentrated sulphuric acid at 100—105°, it yields 6 : 7-*phthaloyl*-N-*methylthiodiphenylamine-2-phthaloylic acid*,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{NMe}{S}{>}C_6H_2\cdot CO\cdot C_6H_4\cdot CO_2H,$$

which crystallises from nitrobenzene as a violet-black powder. 2 : 3 : 6 : 7-*Diphthaloyl*-N-*methylthiodiphenylamine*, $C_{29}H_{15}O_4NS$, crystallises from aniline in black needles, m. p. 370°, and gives a dark red vat dye.

Thio-β-dinaphthylamine also condenses with phthalic anhydride and aluminium chloride in the absence of a diluent, yielding a mixture of phthaloylic acids and *thiodinaphthanthraquinoylamine*, from which the amine can be obtained by treatment with concentrated sulphuric acid. It is best purified by reduction and subsequent oxidation, and has a black colour.

mp-*Ditolylamine*, $C_{14}H_{15}N$, obtained by heating *m*-iodotoluene and *p*-toluidine with soda-lime at 335—340° for five hours, and finally for an hour at 370°, yields a *hydrochloride*, $C_{14}H_{16}NCl$, in the absence of water, and has m. p. 202—203°. The base forms a thick oil with b. p. above 300°.

mmp-*Tritolylamine*, $C_{21}H_{21}N$, obtained by heating a mixture of *m*-iodotoluene, *p*-toluidine, and soda-lime for fifteen hours at 320—330°, crystallises from alcohol in colourless needles, m. p. 89—90°, and does not combine with hydrogen chloride.

J. J. S.

Preparation of Acid Esters of Quinine Halogen Additive Products. VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 231961).—*Ethyl hydrochloroquininecarboxylate*, $C_{20}H_{24}O_2N_2Cl\cdot CO_2Et$, colourless, tasteless needles, m. p. 124°, soluble in dilute acids and re-precipitated by alkalis, is prepared by boiling a benzene solution of hydrochloroquinine with ethyl chloroformate, dissolving out the product with dilute hydrochloric acid, and re-precipitating with ammonia.

*Ethyl hydrochloro*iso*quininecarboxylate* is prepared similarly, but in the presence of pyridine; it forms large, colourless, tasteless prisms, m. p. 191—192°; its solution in dilute sulphuric acid exhibits a green fluorescence.

Ethyl hydrobromoquininecarboxylate, columnar-shaped crystals, has m. p. 168—169°.

Salicylhydrobromoquinine, $C_{20}H_{24}O_2N_2Br\cdot CO\cdot C_6H_4\cdot OH$, colourless, tasteless powder, m. p. 106—107°, is obtained by allowing quinine ethyl salicylate (1 part) dissolved in five parts of hydrobromic acid (D 1·78) to remain during a week at a temperature of 0° and then extracting the product with ether.

Benzoylhydrobromoquinine salicylate,

$$C_{20}H_{24}O_2N_2Br\cdot COPh,C_6H_4(OH)\cdot CO_2H,$$

red leaflets, m. p. 110—115°, is prepared by leaving a solution of benzoyl quinine (1 part) in three parts of hydrobromic acid (D 1·78) during a fortnight at 0°, extracting with ether, and washing with ammonium hydroxide; the ethereal solution of *benzoyl hydrobromoquinine* so obtained, is dried and treated with salicylic acid in the same solvent, when the product slowly separates.

Ethyl hydriodoquininecarboxylate, $C_{20}H_{24}O_2N_2I \cdot CO_2Et$, a pale yellow powder, m. p. 74—78°, is obtained by boiling together molecular proportions of hydriodoquinine and ethyl chloroformate in ethereal solution.
F. M. G. M.

Intramolecular Change of Quinidine (Conchinine) by Sulphuric Acid. MICHAEL PFANNL (*Monatsh.*, 1911, **32**, 241—255).—The intramolecular changes of quinidine and of cinchonidine caused by various means have received far less attention than those of cinchonine. The present paper deals with a change of quinidine. This cannot be accomplished by the usual process of adding on a halogen acid and then eliminating it again by suitable means, because quinidine only dissolves in hydriodic acid at a temperature at which partial demethylation occurs. Pure quinidine sulphate,

$$2C_{20}H_{24}O_2N_2,H_2SO_4,2H_2O,$$

$[\alpha]_j$ 177·5°, therefore, is dissolved in 66·5% sulphuric acid. After two hours at 100°, the specific rotation becomes constant at 22°. The solution is neutralised by ammonia, the liberated bases are extracted with ether, the ethereal solution is washed with water to remove the sulphonated bases (about 17% of which is formed), the ether is distilled off, and an alcoholic solution of the residue is treated with water and neutralised by hydriodic acid. By fractional crystallisation the very sparingly soluble quinidine hydriodide is easily separated from the hydriodide of the new isomeric base, which is called *iso*quinidine. A careful examination of the mother liquor shows that *iso*quinidine is the only isomeride produced.

*iso*Quinidine, $C_{20}H_{24}O_2N_2$, m. p. 142° (corr.), $[\alpha]_j$ $-9°$, crystallises with difficulty, forming long, white needles. It forms a *sulphate*, $2C_{20}H_{24}O_2N_2,H_2SO_4,7H_2O$, $[\alpha]_j$ $-35·5°$, *hydrogen sulphate*,

$$C_{20}H_{24}O_2N_2,H_2SO_4,2H_2O,$$

$[\alpha]_j$ 10·2°, *hydrogen tartrate*, $C_{20}H_{24}O_2N_2,C_4H_6O_6,2H_2O$, and *hydriodide*, $C_{20}H_{24}O_2N_2,HI$, which is five times as soluble as quinidine hydriodide in water at 30°.

In the experiments, 16·5% of the quinidine is lost by sulphonation, 66% is recovered as quinidine and *iso*quinidine, and a further 13·4% in the form of the hydrogen tartrates, leaving only 4% unaccounted for.
C. S.

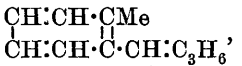
Intramolecular Change of Quinidine (Conchinine) and of Cinchonidine by Sulphuric Acid. FRITZ PANETH (*Monatsh.*, 1911, **32**, 257—274. Compare preceding abstract).—The results obtained by Pfannl with quinidine are unchanged when the action of the sulphuric acid is prolonged to nine hours. With 96% sulphuric acid, however, the striking observation is made that quinidine, in the form of its hydrogen sulphate, is not converted into the isomeric *iso*quinidine, but is almost entirely sulphonated. Thus, after forty-six hours at the ordinary temperature, 15% of the quinidine is recovered unchanged, whilst 80% has been sulphonated. At 75° the results are almost the same; 86% of the base is sulphonated, and 10% is recovered unchanged.

At the ordinary temperature, 66·5% sulphuric acid has scarcely any action on cinchonidine (in the form of the tetrasulphate), but after two hours at 100° it converts the base entirely into sulphonated products (up to 11·5%) and a new isomeride, iso*cinchonidine*, m. p. 252°. (From the agreement of their other properties this base and Hesse's *iso*cinchonidine, m. p. 235°, may be identical substances.) *iso*Cinchonidine has $[\alpha]_D$ $-128°$ in a mixture of two volumes of chloroform and one volume of 97% alcohol, and forms a *hydriodide*, $C_{19}H_{22}ON_2HI$, m. p. 225° (decomp.), $[\alpha]_D$ $-58°$ in chloroform–alcohol. Its *sulphate* in neutral solution differs from that of cinchonidine by not yielding a precipitate with potassium sodium tartrate. C. S.

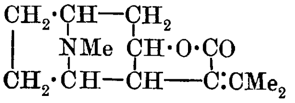
Preparation of Cotarnine Salts of Organic Acids. MARTIN FREUND (D.R.-P. 232003).—Crystalline, well characterised derivatives of cotarnine with hydrogen sulphide, hydrogen peroxide, and hydrogen cyanide have been described (Abstr., 1900, i, 248), but the salts with organic acid have not previously been prepared.

Cotarnine cholate, a yellow powder, m. p. 116—120° (decomp.), is obtained by digesting cotarnine (1 mol.) with cholic acid (2 mols.) in aqueous solution, filtering, and evaporating the solution to dryness in a vacuum.

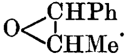
Cotarnine phthalate, m. p. 102°, is prepared in a similar manner with one molecular proportion of phthalic acid. F. M. G. M.

Constitution of Dioscorine. K. GORTER (*Rec. trav. chim.*, 1911, 30, 161—176. Compare this vol., i, 222).—Its behaviour with hydriodic acid, acetic anhydride, and potassium hydroxide proves that dioscorine does not contain methoxy- or hydroxyl groups, and that it is a γ-lactone. When examined by Hofmann's process of exhaustive methylation, it yields a series of products which indicate that it is a derivative of *cyclo*heptane, not of *cyclo*hexane as suggested previously. Thus by treatment with silver oxide, dioscorine methiodide yields a strongly alkaline hydroxide, which is converted by distillation in a vacuum into carbon dioxide, water, and a new base, *demethyldioscoridine*, $C_{13}H_{21}N$, b. p. 116—120°/8 mm., D_4^{26} 0·8987, n_D^{26} 1·50525. The exaltation of the molecular refraction over that calculated for the formula $C_{13}H_{21}N|^{=}_{3}$ indicates that demethyldioscoridine contains a conjugated double linking. With methyl iodide, demethyldioscoridine yields a methiodide convertible by silver oxide into a hydroxide which is decomposed into trimethylamine and a *hydrocarbon*, $C_{11}H_{14}$, by distillation in a vacuum. Were dioscorine a derivative of *cyclo*hexane this hydrocarbon would certainly be an unsaturated aromatic hydrocarbon; however, it does not yield an aromatic acid by oxidation with potassium permanganate. When a solution of the hydrocarbon in cold acetic acid is saturated with hydrogen bromide, and the yellow liquid additive compound formed is distilled with quinoline in a vacuum, a hydrocarbon is obtained which yields *o*-toluic acid by oxidation with potassium permanganate. This hydrocarbon, then, should have the constitution  $\begin{array}{l}\mathrm{CH{:}CH{\cdot}CMe}\\ \mathrm{CH{:}CH{\cdot}C{\cdot}CH{:}C_3H_6}\end{array}$, and the original hydrocarbon would be a butenyl*cyclo*heptatriene.

Assuming this to be correct, the author advances reasons for ascribing to dioscorine the annexed constitution. This formula harmonises well with the behaviour of dioscorine and its derivatives recorded above. The presence of the group $\cdot CO\cdot C{:}C<$ suggests that dioscorine should be reduced by sodium amalgam. This is so, an aqueous solution of its hydrobromide yielding *bisdihydrodioscorine*, a saturated *substance*, $(C_{13}H_{20}O_2N)_2$, m. p. 266—267°, the *aurichloride* of which has m. p. 243° (decomp.).



The physiological action of dioscorine is similar to that of picrotoxin, and is connected with the presence of the group $\cdot CO\cdot C{:}C<$. When the double linking is suppressed or when the lactone ring is ruptured, the resulting substances (bisdihydrodioscorine and dioscoric acid respectively) no longer have the property of causing cramp. C. S.

Ephedrine and ψ-Ephedrine. ERNST SCHMIDT (*Arch. Pharm.*, 1911, **249**, 305—310. Compare Abstr., 1909, i, 322; Rabe, this vol., i, 396).—Dimethylephedrineammonium hydroxide, when heated in a current of steam, furnishes as nitrogen-free product an oil with an odour recalling those of dill and estragon. On treatment with trimethylamine in alcohol at 100°, this oil is, in part, converted into a substance which furnishes an *aurichloride*, $C_9H_{10}ONMe_3,HAuCl_4$, m. p. 190—191°, which crystallises in glancing leaflets, and is sparingly soluble in water. *Dimethylephedrine aurichloride*, m. p. 185—186°, crystallises in yellow needles, and is very soluble in water. The *platinichlorides* prepared from both these substances had m. p. 249—251°, crystallised in long needles, and were sparingly soluble in water. This reaction indicates the presence in the original oil of an alkylene oxide of the formula  $O<\begin{array}{l}\mathrm{CHPh}\\ \mathrm{CHMe}\end{array}$. The residue of the oil unattacked by trimethylamine contained propiophenone and a third *substance*, possibly the glycol, $C_9H_{10}(OH)_2$, which furnishes a *dibenzoate*, m. p. 83—85°, crystallising in colourless needles (compare Schmidt and Gaze, *Apoth. Zeit.*, 1911, p. 368). T. A. H.

Sparteine. XXIII. Decomposition of *iso*Sparteine α′-Methylhydroxide. XXIV. Methyl*iso*sparteine. CHARLES MOUREU and AMAND VALEUR (*Bull. Soc. chim.*, 1911, [iv], **9**, 476—478, 478—479).—These two papers give experimental details of work already published (this vol., i, 319), and add some new data.

Measurements of the optical rotation of solutions of *iso*sparteine α′-methyl hydroxide, to which 2 mols. of hydrogen iodide have been added, show that it does not undergo isomerisation to the α-methyl hydroxide, in its formation from the α′-methiodide by the action of silver hydroxide.

Methyl*iso*sparteine, the formation of which has been described already (*loc. cit.*), has m. p. 24°, b. p. 169—170°/13 mm., D_4^{19} 0·9651, n_D 1·5131, $[\alpha]_D$ +23·58° in alcohol. Methyl*i*sparteine dimethiodide (*loc. cit.*), m. p. 281—282°, $[\alpha]_D$ +21·35°, is readily soluble in water or boiling methyl alcohol. T. A. H.

The Relative Stability of the Pyrrolidine Ring. JULIUS VON BRAUN (*Ber.*, 1911, **44**, 1252—1260. Compare Abstr., 1909, i, 507, 604).—The reaction of cyanogen bromide with 1-ethylpiperidine and 1-ethylpyrrolidine proves that the pyrrolidine is less stable than the piperidine ring for example, 34% of the ethylpiperidine compound is decomposed in such a manner that the ring is ruptured, and from 66% the ethyl group is simply removed, whereas under similar conditions practically the whole of the ethylpyrrolidine undergoes rupture. Somewhat similar results are obtained when the corresponding propyl derivatives are used. The pyrrolidine ring is thus more readily formed and also more readily ruptured than the piperidine ring, and according to Harries (*Annalen*, 1910, **374**, 288), *cyclo*pentene is more readily ruptured than *cyclo*hexene.

1-*Propylpyrrolidine*, C_4NH_8Pr, obtained by the action of *n*-propylamine on αδ-di-iodobutane, is a mobile liquid with b. p. 130°. It is readily soluble in water, and has an intense basic odour. The *picrate*, $C_{13}H_{13}O_7N_4$, crystallises in yellow plates, m. p. 105°, and the *platinichloride*, $C_{14}H_{32}N_2Cl_6Pt$, forms red crystals, which begin to turn black at 184°, and are completely decomposed at 190°. The product obtained by the action of cyanogen bromide cannot be distilled, but after treatment with piperidine, it yields *pentamethylenecyanopropylputrescine*, $C_5NH_{10}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NPr^{\alpha}\cdot CN$, as a viscid, colourless liquid, b. p. 191—192°/16 mm. Its salts are oily, and the base is comparatively stable, but when heated for twelve hours at 155° with fuming hydrochloric acid yields *α-piperidino-δ-*n*-propylaminobutane* (*pentamethylenepropylputrescine*),

$$C_5NH_{10}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot NHPr,$$

as a mobile liquid, b. p. 130°/10 mm. The *picrate*,

$$C_{12}H_{26}N_2,2C_6H_3O_7N_3,$$

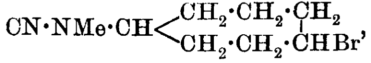
has m. p. 139—140°, and the *platinichloride*, $C_{12}H_{28}N_2Cl_6Pt$, crystallises in yellow plates, m. p. 217° (decomp.).

1-*Ethylpyrrolidine*, $C_6H_{13}N$, has b. p. 106°; the *picrate*, $C_{12}H_{16}O_7N_4$, crystallises in glistening plates, m. p. 185°, and the *platinichloride* does not crystallise well. *Pentamethylenecyanoethylputrescine*,

$$C_5NH_{10}\cdot[CH_2]_4\cdot NEt\cdot CN,$$

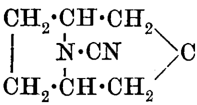
has b. p. 182°/16 mm., and *pentamethylene-ethylputrescine* (*α-piperidino-δ-ethylaminobutane*), $C_5NH_{10}\cdot[CH_2]_4\cdot NHEt$, b. p. 125—126°/13 mm. The *picrate*, $C_{11}H_{24}N_2,2C_6H_3O_7N_3$, forms a fine yellow powder, m. p. 113°, and the *platinichloride*, $C_{11}H_{26}N_2Cl_6Pt$, has m. p. 216—217° (decomp.).

When tropan is treated with cyanogen bromide in ethereal solution, a small amount of methyl bromide is eliminated, but the chief product is a quaternary ammonium salt insoluble in ether. It is highly probable that this salt is formed by the rupture of the ring and the formation of a brominated cyanamide,

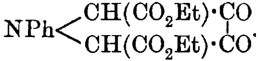


$$CN\cdot NMe\cdot CH\genfrac{}{}{0pt}{}{\diagup CH_2\cdot CH_2\cdot CH_2}{\diagdown CH_2\cdot CH_2\cdot CHBr},$$

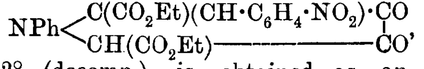
which combines with the excess of tropan, yielding the quaternary salt. The other product, *cyanonortropan*, has b. p. 148—150°/17 mm. and m. p. 108° (annexed formula), and on hydrolysis yields nortropan (Ladenburg, Abstr., 1887, 740). Cyanotropan, when heated at 150° with an excess of aniline hydrochloride and then distilled in steam, yields *s-nortropylphenylguanidine*, $C_7H_{12}N\cdot C(:NH)\cdot NHPh$, which crystallises from aqueous alcohol in glistening needles, m. p. 145°. The *picrate* has m. p. 157—158°, and the *platinichloride* decomposes at 208°. J. J. S.



Syntheses of Pyrrole Compounds from Imino-acids. *N*-Phenyl-*αα′*-dicarbethoxy-*ββ′*-diketopyrrolidine [Ethyl 3 : 4-Diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate]. TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1911, **33**, 745—755).—It has been shown by Johnson and Johns (Abstr., 1906, i, 874) that ethyl oxalate condenses with ethyl diglycollate with formation of ethyl 3 : 4-diketotetrahydrofuran-2 : 5-dicarboxylate. In continuation of this work, a study has now been made of the condensation of ethyl oxalate with ethyl phenylglycinoacetate.

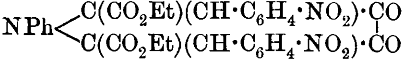
Mouilpied (Trans., 1905, **87**, 435) has found that ethyl oxalate condenses with ethyl phenylglycinoacetate in presence of sodium ethoxide to form a compound, $C_{16}H_{17}O_6N$, m. p. 137°, to which he was unable to assign a satisfactory constitutional formula, but regarded it as having a quinonoid structure, as it yields a yellow sodium salt. A re-investigation of this substance has shown that it is ethyl 3 : 4-diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate,  $\mathrm{NPh}\!<\!\begin{matrix}\mathrm{CH(CO_2Et)\cdot CO}\\ \mathrm{CH(CO_2Et)\cdot CO}\end{matrix}$. This compound gives a yellow di-sodium salt and a colourless *mono-sodium* salt; the *barium* salt crystallises with $1H_2O$.

When the yellow sodium salt is heated with *p*-nitrobenzyl chloride in presence of alcohol, a small quantity of *ethyl* 3 : 4-*diketo*-1-*phenyl*-2-p-*nitrobenzylpyrrolidine*-2 : 5-*dicarboxylate*,

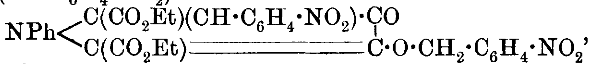


$$\mathrm{NPh}\!<\!\begin{matrix}\mathrm{C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO}\\ \mathrm{CH(CO_2Et)\text{———————}CO}\end{matrix},$$

m. p. 180—182° (decomp.), is obtained as an orange-coloured powder. The main product of the reaction, however, is *ethyl* 3 : 4-*diketo*-1-*phenyl*-2 : 5-*di*-p-*nitrobenzylpyrrolidine*-2 : 5-*dicarboxylate*,



$$\mathrm{NPh}\!<\!\begin{matrix}\mathrm{C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO}\\ \mathrm{C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO}\end{matrix}\ \text{or}$$



$$\mathrm{NPh}\!<\!\begin{matrix}\mathrm{C(CO_2Et)(CH\cdot C_6H_4\cdot NO_2)\cdot CO}\\ \mathrm{C(CO_2Et)\text{=========}C\cdot O\cdot CH_2\cdot C_6H_4\cdot NO_2}\end{matrix},$$

m. p. 132°, which forms yellow prisms.

Attempts to reduce ethyl 3 : 4-diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate with hydriodic acid and also with aluminium amalgam were not successful.

Mouilpied (*loc. cit.*) observed that if the condensation of ethyl oxalate with ethyl phenylglycinoacetate is effected in presence of sodium methoxide instead of the ethoxide, the ethyl ester, m. p. 137°, is not produced, but the corresponding methyl ester, m. p. 188°, is formed. He therefore carried out the several condensations of methyl and ethyl oxalates with methyl and ethyl phenylglycinoacetates in presence of sodium methoxide and of sodium ethoxide. From these eight condensations, he obtained six different compounds. These experiments have now been repeated, and it has been found that only two compounds are actually produced. The compound, m. p. 137°, is formed by the condensation of ethyl or methyl oxalate with ethyl or methyl phenylglycinoacetate in presence of sodium ethoxide, whilst by the condensation of these esters in presence of sodium methoxide, the compound, m. p. 188—189°, is obtained. It is evident, therefore, that the product of the reaction is determined by the particular alkyloxide used. The compound, m. p. 188—189°, is methyl 3 : 4-diketo-1-phenylpyrrolidine-2 : 5-dicarboxylate. E. G.

Pyridinoiridopentachlorides. MARCEL DELÉPINE (*Compt. rend.*, 1911, **152**, 1390—1393. Compare Abstr., 1908, ii, 702; 1910, ii, 44).—The metallic pyridinoiridopentachlorides are formed by introducing a molecule of pyridine into an aquoiridopentachloride in place of $1H_2O$, or into an alkali iridohexachloride in place of a molecule of alkali chloride.

Potassium, sodium, and *ammonium pyridinoiridopentachlorides* conform to the type $IrCl_5(C_5H_5N)M_2$, and are best prepared by treating a hot solution of the iridochloride with excess of pyridine and removing the excess as rapidly as possible. The products vary in colour from orange to red according to the size of the crystals. The *thallium, silver, mercurous,* and *mercuric* salts are amorphous and insoluble in water. Orange crystals having the composition $IrCl_5(C_5H_5N)(NH_3Ag)_2,H_2O$ are obtained when the silver salt is dissolved in ammonia. The alkali salts are very stable, and the pyridine is not removed by concentrated sulphuric acid at 100°. Chromic acid and hydrogen peroxide are without action, but chlorine and nitric acid convert them into a new series of salts of the type $IrCl_5(C_5H_5N)M$. W. O. W.

Pyridinoiridipentachlorides. MARCEL DELÉPINE (*Compt. rend.*, 1911, **152**, 1589—1591. Compare preceding abstract).—The pyridinoiridipentachlorides of the type $IrCl_5(C_5H_5N)M$ are related to the pyridinoiridopentachlorides previously described, in the same way as the iridihexachlorides are to the iridohexachlorides. They are best obtained by the action of nitric acid on the corresponding pyridinoiridopentachlorides. The *potassium, ammonium, rubidium, caesium,* and *sodium* salts form very deep red crystals, and are anhydrous except in the last case. Like the pyridinoiridopentachlorides they give precipitates with aqueous solutions of thallium, silver, mercurous, and mercuric salts, but differ from them in giving no precipitate with lead salts. The *silver* salt crystallises in slender, violet needles.

These salts are remarkably stable towards acids, but lose pyridine when heated with hydrochloric acid in sealed tubes at 150—160°, giving the corresponding hexachlorides. W. O. W.

Pyridylacetylcatechol and Related Bases. CARL MANNICH and O. HÜBNER (*Ber. Deut. pharm. Ges.*, 1911, 21, 294—297. Compare Abstr., 1910, i, 411).—A number of bases somewhat similar in structure to adrenaline have been prepared by condensing pyridine, piperidine, or quinoline with chloroacetylcatechol or the bromoacetyl derivative of catechol dimethyl ether.

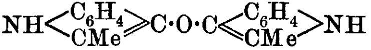
Chloroacetylcatechol, $C_6H_3(OH)_2\cdot CO\cdot CH_2Cl$, condenses with pyridine when gently warmed with it in alcohol to form *pyridylacetylcatechol hydrochloride*, $C_6H_3(HO)_2\cdot CO\cdot CH_2\cdot C_5NH_5Cl$, m. p. 272° (decomp.). which crystallises from hot water, and on addition of ammonia yields the free *base* (or pseudo-base), m. p. 199° (decomp.), in the form of yellow crystals. *Pyridylacetylveratrole hydrobromide*,

$$C_6H_3(OMe)_2\cdot CO\cdot CH_2\cdot C_5NH_5Br,$$

m. p. 258° (decomp.), similarly obtained, also crystallises from hot water, but the free base could not be isolated by the action of alkalis. When heated with hydrochloric acid, the methoxyl groups were eliminated and pyridylacetylcatechol hydrochloride was formed. *Piperidylacetylcatechol hydrochloride*, m. p. 257° (decomp.), forms colourless needles from water; the free *base*, m. p. 199—205° (decomp.), is liberated from the hydrochloride by ammonia. *Quinolylacetylveratrole hydrobromide*, $C_6H_3(OMe)_2\cdot CO\cdot CH_2\cdot C_9NH_7Br$, m. p. 222° (decomp.), crystallises from hot water. With ammonia it furnishes a reddish-brown, amorphous *product*, and when heated with hydrochloric acid yields a *product*, $C_{17}H_{14}O_3NCl$, m. p. 248° (decomp.), which separates from water in yellowish-brown crystals and gives catechol reactions. The free base could not be obtained. Quinoline does not condense directly with chloroacetylcatechol. T. A. H.

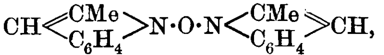
New Oxidation of 2-Methylindole. GIUSEPPE PLANCHER and U. COLACICCHI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 453—457).—With the exception of fusion with potassium hydroxide, all methods previously used for the oxidation of 2-methylindole result in the rupture of the nucleus and the formation of anthranilic acid and its substitution products.

Oxidation of 2-methylindole by means of 15% ethereal hydrogen peroxide solution yields, however, the *compound*,



$$NH<\substack{C_6H_4\\CMe}>C\cdot O\cdot C<\substack{C_6H_4\\CMe}>NH$$

or



$$CH<\substack{CMe\\C_6H_4}>N\cdot O\cdot N<\substack{CMe\\C_6H_4}>CH,$$

which forms greenish-yellow crystals, m. p. 209—210°, and has the normal molecular weight in freezing naphthalene. It gives a red coloration with boiling acetic acid, whilst with concentrated sulphuric acid it yields a blue solution, which becomes green and deposits green flocks on dilution with water. On reduction with tin and hydrochloric acid, it gives dihydro-2-methylindole.

The same product is formed from 2-methylindole by oxidation with aqueous hydrogen peroxide or Caro's acid, and together with other compounds, not yet studied, with ozone in presence of water or chloroform.

Attempts to oxidise 2-phenylindole and 2 : 3-dimethylindole by means of hydrogen peroxide have as yet led to no definite results.

T. H. P.

8-Hydroxyquinoline. Georg Cohn (*J. pr. Chem.*, 1911, [ii], 83, 498—506).—8-Hydroxyquinoline and formaldehyde, which yield hydroxymethyl-8-hydroxyquinoline under Manasse's conditions (Abstr. 1903, i, 28), produce another substance, called "*new hydroxyquinolinecarbinol*," when a mixture of 5 grams of 8-hydroxyquinoline, 15 c.c. of formalin, and 10 c.c. of 20% sodium hydroxide are heated on the water-bath; by dilution with water and neutralising with hydrochloric or acetic acid, the new compound, $C_{12}H_9O_2N$, is obtained as a yellow, amorphous powder. It does not melt at 250°, evolves formaldehyde at higher temperatures, forms a solution in dilute hydrochloric acid which is coloured dark green by ferric chloride, yields a yellow sodium salt, couples with diazobenzenesulphonic acid, and is oxidised by alkaline potassium ferricyanide to a dark green substance.

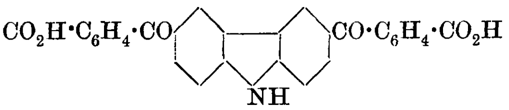
8-Hydroxyquinoline-5-sulphonic acid is formed when loretin (7-iodo-8-hydroxyquinoline-5-sulphonic acid) is boiled with water and aniline or phenetidine, with piperidine, or with guaiacol and sodium hydroxide.

5-Nitroso-8-hydroxyquinoline is reduced by phenylhydrazine on the water-bath, yielding *5-azo-8-hydroxyquinoline*,

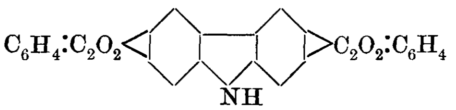
$$OH{\cdot}C_9NH_5{\cdot}N{:}N{\cdot}C_9NH_5{\cdot}OH,$$

m. p. 220° (decomp.), brownish-red needles with a blue reflex. By reduction with potassium sulphite the nitroso-compound yields a substance, not yet fully examined, which is probably an aminohydroxyquinolinesulphonic acid. C. S.

Introduction of Several Phthalic Acid Groups into Aromatic Compounds. IV. Experiments with Carbazole. Roland Scholl and Werner Neovius (*Ber.*, 1911, 44, 1249—1252. Compare this vol., i, 452, 453, 557).—Carbazole reacts with phthalic anhydride and aluminium chloride, either with or without a diluent, yielding *carbazole-3:6-diphthaloylic acid* (I.), and this reacts with concentrated sulphuric acid at 90° and then at 100°, yielding 2:3:6:7-*diphthaloylcarbazole* (II.). In the preparation of the dibasic acid a certain amount of the *N*-phthaloylic acid (carbazole-*N*-carbonyl-*o*-benzoic acid: Stummer, Abstr., 1907, i, 723) is formed, and can be removed by hydrolysis with sodium hydroxide, and also a certain amount of the 3-phthaloylic acid, which is removed by adding a small amount of magnesium sulphate to the solution of the ammonium salts. The dibasic acid, $C_{28}H_{17}O_6N$, forms a colourless, amorphous powder, m. p. 300—301°.



(I.)

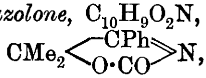


(II.)

2:3:6:7-*Diphthaloylcarbazole*, $C_{28}H_{13}O_4N$ (II.), crystallises from quinoline in golden-yellow needles, which are not molten at 450°. With alkaline hyposulphite solutions, it yields a dark brown vat-dye. J. J. S.

Oximes and Phenylalkyl*iso*oxazolones Obtained from Ethyl Benzoylpropionate, Benzoyl-*n*-butyrate, and Benzoyl*iso*butyrate. ALBIN HALLER and EDMOND BAUER (*Compt. rend.*,1911, 152, 1446—1450. Compare this vol., i, 299).—The substance, m. p. 91°, obtained by Hantzsch and Miolati (Abstr., 1893, 583) by acting on ethyl benzoyl-*n*-butyrate with hydroxylamine hydrochloride and potassium hydroxide gives analytical results indicating it to be *phenylethyl*iso*oxazolone*, and not an oxime, as these authors supposed. The corresponding *oxime*, however, is formed when the ester is treated with hydroxylamine zincochloride in alcoholic solution, and occurs in prisms, m. p. 80—81°. Similar results were obtained with alkyl derivatives of ethyl benzoylacetate, Crismer's reagent always leading to the production of an oxime, and hydroxylamine to that of a phenyl*iso*oxazolone. The latter is also formed by withdrawing $1H_2O$ from the oxime.

*Phenylmethyl*iso*oxazolone*, $C_{10}H_9O_2N$, has m. p. 123—124°; *phenyldimethyl*iso*oxazolone*,



$CMe_2<\begin{matrix}CPh\\O\cdot CO\end{matrix}>N$, has m. p. 70—71°.

W. O. W.

The Simplest Quinonoid Dyes. JEAN PICCARD (*Annalen*, 1911, 381, 351—366).—The *meri*quinonedi-imonium salts,

$NH_2Br{:}C_6H_4{:}NH_2Br{:}{:}NH_2{\cdot}C_6H_4{\cdot}NH_2$,

and their methyl derivatives exist in α- and β-modifications (compare Abstr., 1910, i, 66). The α-compounds exhibit characteristic absorption spectra, all of much the same type, although the colour of the solutions passes from yellow through orange, red, and violet to blue with an increase in the number of methyl groups present. The more strongly coloured salts, the β-modifications, are most readily obtained at low temperatures, especially in the presence of water, whereas alcohol favours the formation of the α-compounds. The solutions, as a rule, consist of equilibrated mixtures, but the equilibrium can be appreciably altered by changing the conditions. The imonium salt itself and its mono- and di-methyl derivatives exist in the solid state as the β-forms only, whereas the tri- and tetra-methyl derivatives exist as the solid α-forms. The absorption spectra of the β-modifications are essentially different from those of the α, and do not consist of a number of characteristic bands. By the use of the colorimetric dilution law (this vol., ii,561,) it is shown that the α- and β-modifications are not isomeric, but polymeric, and the conversion of the β- into the α-form consists in depolymerisation or dissociation.

The rate of transformation is extremely rapid, so that a given salt does not exist in both forms under given specific conditions. The α-form of the *meri*quinonedi-imonium bromide exists only in dilute solution at 0°; under all other conditions the β-form is the stable form, but with the tetramethyl derivative the α-form is the only one which has been observed either in the solid state or in solution.

As a rule, the β- are more stable than the α-compounds. *meri*-Quinonedi-imonium bromide (compare Jackson and Calhane, Abstr., 1902, i, 645; Pringsheim, *ibid.*, 1905, i, 934; Kehrmann, *ibid.*, 1906, i, 46) crystallises as a heavy, brown powder with a golden-yellow lustre when it is deposited gradually from a mixture of alcohol and glacial acetic acid. The corresponding *nitrate*, $C_{12}H_{16}O_6N_6$, has a brassy lustre. The meri*methylquinonedi-imonium bromide*,

$C_{14}H_{20}N_4Br_2$,

is amorphous. meri*Trimethylquinonedi-imonium ferricyanide*,

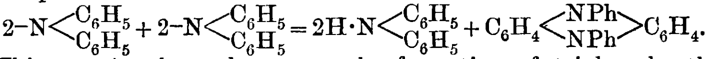
$NHMe\cdot C_6H_4\cdot NMe_2,HFeC_6N_6,2NHMe\cdot C_6H_4\cdot NMe_2$,

crystallises in brilliant black needles. J. J. S.

Aromatic Hydrazines. IX. Tetraphenylhydrazine and Hexaphenylethane. Heinrich Wieland (*Annalen*, 1911, **381**, 200—216).—Tetra-arylated hydrazines are readily hydrolysed to diarylated amines and diarylated hydroxylamines, but as the latter are unstable they cannot be directly isolated, but are transformed into decomposition or condensation products (compare Abstr., 1906, i, 830; 1907, i, 1076; 1908, i, 1014, 1026; this vol., i, 83).

It is now shown that tetraphenylhydrazine is partly depolmerised (dissociated) when boiled with toluene, and thus resembles hexaphenylethane, which is partly dissociated into triphenylmethyl in benzene solution. It has not been found possible to isolate the primary dissociation product, $-NPh_2$, as this is extremely unstable and undergoes further transformation.

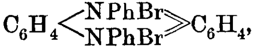
[With Hans Lecher.]—When the toluene solution of tetraphenylhydrazine is boiled, a green colour is developed, but this changes rapidly to brown, and on cooling the colour does not disappear. After boiling for thirty minutes, removing the toluene under reduced pressure, and then adding ether, crystals of diphenyldihydrophenazine are obtained, and diphenylamine and *o*-anilinotriphenylamine remain in solution. Details for the separation of the three compounds are given. The diphenylamine and diphenyldihydrophenazine are regarded as being formed by the reduction of one portion of the dissociation product at the expense of the other:



$$2\text{-}N<\begin{matrix}C_6H_5\\C_6H_5\end{matrix} + 2\text{-}N<\begin{matrix}C_6H_5\\C_6H_5\end{matrix} = 2H\cdot N<\begin{matrix}C_6H_5\\C_6H_5\end{matrix} + C_6H_4<\begin{matrix}NPh\\NPh\end{matrix}>C_6H_4.$$

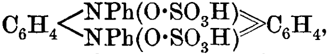
This reaction is analogous to the formation of triphenylmethane and a complex bimolecular hydrocarbon from triphenylmethyl. The formation of *o*-anilinotriphenylamine [triphenyl-*o*-phenylenediamine], $NHPh\cdot C_6H_4\cdot NPh_2$, from tetraphenylhydrazine is due to a semidine transformation, and is analogous to the formation of benzhydryltetraphenylmethane from hexaphenylethane, except that in the latter case the substituents occupy the para-position.

Diphenyldihydrophenazine, $C_{24}H_{18}N_2$, crystallises from a mixture of benzene and alcohol in colourless needles, m. p. 172—175°. On exposure to the air it turns green, as it is readily oxidised to a *o*-quinonoid salt. Its benzene solutions have more or less colloidal properties, and with bromine it yields a *bromide*,

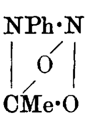


$$C_6H_4<\begin{matrix}NPhBr\\NPhBr\end{matrix}\gg C_6H_4,$$

the chloroform solutions of which have a brilliant green colour.

Triphenyl-o-*phenylenediamine*, $C_{24}H_{20}N_2$, is amorphous, has m. p. 85°, and yields a crystalline *hydrochloride*. The base reacts with bromine, evolving hydrogen bromide and yielding diphenyldihydrophenazine dibromide. The blue compound obtained by treating diphenylamine with concentrated sulphuric acid and an oxidising agent is shown to be identical with the *o*-quinonoid sulphate of diphenyldihydrophenazine,  $C_6H_4<\begin{matrix}NPh(O\cdot SO_3H)\\NPh(O\cdot SO_3H)\end{matrix}>C_6H_4$, and its formation is due to the following series of reactions. Oxidation of diphenylamine to tetraphenylhydrazine, hydrolysis of the latter to diphenylamine and diphenylhydroxylamine, and condensation of the hydroxylamine to diphenyldihydrophenazine (phenoperazine), and, finally, oxidation of this to the *o*-quinonoid salt.

The dissociation of tetraphenylhydrazine can also be shown by passing nitric oxide into a toluene solution of the hydrazine, heated at 90—95° and protected from atmospheric oxygen. After some twenty to thirty minutes the hydrazine is transformed quantitatively into diphenylnitrosoamine. The nitrosoamine when heated at 130° gives a theoretical yield of nitric oxide, showing that the reaction is reversible. The other products are diphenylamine and diphenyldihydrophenazine, although the amount of the latter is very small. Di-*p*-tolylnitrosoamine and di-*p*-anisylnitrosoamine behave in a similar manner. Nitrosoarylamides behave in quite a different manner (Bamberger, Abstr., 1894, i, 412; 1910, i, 908); when heated in an indifferent solvent, for example, light petroleum, they explode or evolve nitrogen, but not nitric oxide. The annexed structural formula is suggested for these compounds.

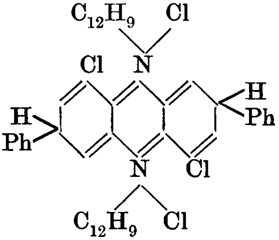


When triphenylmethyl is heated on the water-bath with a toluene solution of tetraphenylhydrazine in the absence of air, crystals of *triphenylmethyldiphenylamine*, $CPh_3\cdot NPh_2$, are obtained. The formation of this compound is due to the union of the two unsaturated groups, CPh_3- and $-NPh_2$. It forms large, colourless, transparent needles, m. p. 172°, and with concentrated sulphuric acid yields triphenylcarbinol and diphenylamine. In boiling xylene the compound is partly dissociated the solution has a red colour, and gives all the characteristic reactions of triphenylmethyl. *Triphenylmethyldi*-p-*tolylamine*, $C_{33}H_{29}N$, has m. p. 164°, and, like the diphenylamine derivative, gives a red melt.

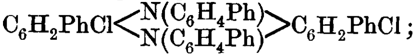
Tetraphenyl-, di-*p*-tolyl-, and di-*p*-anisyl- hydrazines give a blue phosphorescence when subjected to the action of cathode rays, and themselves turn green in the course of a few seconds. Tetratolylhydrazine and *p*-tetradiphenylhydrazine are coloured dark yellow, but these colours disappear rapidly when the substances are removed from the influence of the cathode rays. J. J. S.

Aromatic Hydrazines. X. Tetradiphenylhydrazine. HEINRICH WIELAND and ARTHUR SÜSSER (*Annalen*, 1910, **381**, 217—229. Compare preceding abstract).—Tetradiphenylhydrazine is not dissociated so readily as tetraphenylhydrazine, and its properties resemble tetra-*p*-tolyl- rather than tetraphenyl-hydrazine. It is prepared by oxidising an acetone solution of *p*-didiphenylamine with finely-powdered permanganate at 10°. p-*Didiphenylamine*, $NH(C_{12}H_9)_2$, can be obtained as its acetyl derivative by boiling *p*-iododiphenyl and *p*-acetylaminodiphenyl, potassium carbonate, copper bronze, a little iodine, and potassium iodide with nitrobenzene for twenty-four hours. The base, obtained by hydrolysing the acetyl derivative with alcoholic potassium hydroxide, crystallises from benzene or xylene in glistening, nacreous plates, m. p. 209°. The *hydrochloride* forms long prisms; the *nitrosoamine*, $C_{24}H_{18}ON_2$, crystallises from benzene in yellow needles, m. p. 172°.

Tetradiphenylhydrazine, $N_2(C_6H_4Ph)_4$, crystallises slowly from a mixture of benzene and alcohol, has m. p. 165°, and, when warmed with glacial acetic acid, gives a characteristic intense violet coloration. When boiled for some time in xylene solution, dissociation can be recognised by the separation of the sparingly soluble didiphenylamine. *Didiphenyldihydrophenazine*, $C_{48}H_{34}N_2$, does not appear to be formed, but was met with in the mother liquors from the hydrazine after they had been kept for several months. It crystallises from xylene in yellow needles, m. p. 325—330°, and yields a *hydrochloride* in the form of broad, violet needles, with a quinonoid constitution.


(I.)

The hydrazine combines with hydrogen chloride in the presence of benzene, light petroleum, and ether, yielding a flocculent, green *hydrochloride*, $C_{48}H_{36}N_2,2HCl$, which is gradually transformed into didiphenylamine hydrochloride, the violet *chloride* of *dichlorodiphenoperazine*, together with an isomeride of the tetra-arylated hydrazine and *o*-chlorodiphenylamine. The violet chloride (I), when treated with a little ammonia or alcoholic potassium hydroxide, yields *dichlorodiphenoperazine*,



$$C_6H_2PhCl{<}\begin{matrix}N(C_6H_4Ph)\\N(C_6H_4Ph)\end{matrix}{>}C_6H_2PhCl\,;$$

this crystallises from xylene in yellow needles, which are not molten at 380°. When reduced with sodium and amyl alcohol in the presence of xylene the dichloro-derivative yields didiphenyldihydrophenazine (diphenoperazine). The isomeride of the hydrazine is probably *o-diphenylaminotridiphenylamine*, $C_6H_4Ph{\cdot}NH{\cdot}C_6H_3Ph{\cdot}N(C_6H_4Ph)_2$; it crystallises from hot xylene in felted needles, m. p. 275°, and gives a green coloration with ferric chloride or with bromine.

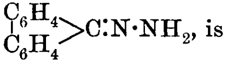
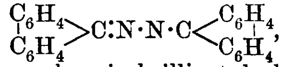
o-Chlorodidiphenylamine, $C_{24}H_{18}NCl$, crystallises from alcohol, melts to a turbid liquid at 119°, and becomes clear at 130°.

Tetradiphenylhydrazine and bromine yield an unstable, dark green bromide, which is rapidly decomposed, yielding didiphenylamine and *dibromodidiphenylamine*, $C_{24}H_{17}NBr_2$, in the form of long, glistening needles, m. p. 151°. J. J. S.

The Stability of the Nitrogen Linking in Ketazines.

HEINRICH WIELAND and A. ROSEEU (*Annalen*, 1911, **381**, 229—233).—According to Curtius and his pupils, the ketazines which contain a grouping similar to nitric oxide (bimolecular form), $O{:}N{\cdot}N{:}O$ and $R_2C{:}N{\cdot}N{:}CR_2$, are extremely stable and do not dissociate. The ketazines derived from the following ketones have been prepared and examined: benzophenone, fluorenone, and tetramethyldiaminobenzophenone. All the compounds are stable, they dissolve in concentrated sulphuric acid without decomposition, can be distilled to a certain extent without decomposition, and when hydrolysed by hot mineral acids yield hydrazine and ketone.

Benzophenoneketazine (Curtius and Rauterberg, *J. pr. Chem.*, 1901, **63**, 94) is quite colourless, but its solutions have a yellow colour, and the intensity of the colour in different solvents increases in the order: Ethyl alcohol, ether, acetone, benzene, chloroform. It yields an unstable lemon-yellow hydrochloride and a reddish-orange bromide.

Fluorenonehydrazone,  $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C{:}N\cdot NH_2$, is formed when the ketone and hydrazine hydrate are warmed with a little alcohol on the water-bath, and crystallises from alcohol in pale yellow plates, m. p. 149°. When oxidised with the theoretical amount of iodine in alcoholic solution, it yields *fluorenoneketazine*,  $\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\!\!>C{:}N\cdot N{:}C\!\!<\!\!\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}$, and nitrogen. The ketazine crystallises from xylene in brilliant dark red needles, m. p. 259°, and its solution in concentrated sulphuric acid has a purple-red colour. When reduced with zinc dust and glacial acetic acid it yields 9-aminofluorene.

Tetramethyl-p-*diaminodiphenylketone hydrazone*,

$$C(C_6H_4\cdot NMe_2)_2{:}N\cdot NH_2,$$

obtained by heating the components with a little alcohol at 180°, crystallises from alcohol in pale yellow needles, m. p. 150°. The *benzylidene* derivative, $C_{24}H_{26}N_4$, crystallises from alcohol in pale orange-yellow needles, m. p. 141°, and the *ketazine*,

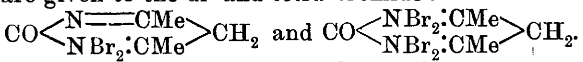
$$C(C_6H_4\cdot NMe_2)_2{:}N\cdot N{:}C(C_6H_4\cdot NMe_2)_2,$$

obtained by oxidising the hydrazone with mercuric oxide and a little iodine, crystallises from xylene in large, brownish-red prisms, m. p. 253°. Its solution in concentrated sulphuric acid is practically colourless.

J. J. S.

Preparation of 5:5-dialkyliminobarbituric Acid (2-Imino-4:6-diketo-5:5-dialkylpyrimidine). EMANUEL MERCK (D.R.-P. 231887).—When 5:5-dialkylmalonic acid diaryl esters are heated with guanidine (or a guanidine salt), they yield imino-5:5-dialkylbarbituric acids. 2-Iminodiethylbarbituric acid, prepared by heating diphenyl diethylmalonate with guanidine carbonate at 160°, may subsequently be converted into diethylbarbituric acid. F. M. G. M.

Relationships between Perbromides and Bromo-substitution Products Observed with Acetylacetonecarbamide [4:6-Dimethyl-2-pyrimidone] and its Tautomeride. OTTO STARK (*Annalen*, 1911, **381**, 143—199).—Evans's acetylacetonecarbamide [4:6-dimethyl-2-pyrimidone] (Abstr., 1893, i, 129; 1894, i, 111; Stark, 1909, i, 259) combines with two or with four atoms of bromine, yielding products which are regarded as perbromides and not as compounds formed by the addition of bromine to unsaturated linkings, since the bromine is not firmly attached to the molecule. As pyridine and quinoline also yield perbromides, it is suggested that the bromine combines with the nitrogen atoms of the molecule, and the following formulæ are given to the di- and tetra-bromide:

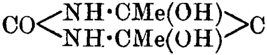


$$CO<\begin{array}{l}N{=\!=\!=}CMe\\NBr_2{:}CMe\end{array}>CH_2 \text{ and } CO<\begin{array}{l}NBr_2{:}CMe\\NBr_2{:}CMe\end{array}>CH_2.$$

To distinguish the two tautomeric forms, the name acetylacetonecarbamide will be used in this abstract for the original compound and 4 : 6-dimethyl-2-pyrimidone for its isomeride. The latter also yields perbromides, and these with water or alcohol yield the same products as are obtained from the perbromide of the carbamide. The two sets of perbromides are not regarded as being identical, since the one from the pyrimidone loses its colour more rapidly than that derived from the carbamide.

The perbromide of acetylacetonecarbamide, $C_6H_8ON_2Br_2$, can be obtained by the addition of bromine to a chloroform solution of the carbamide (Abstr., 1909, i, 259), or to a solution of the carbamide in hydrobromic acid (b. p. 121°). In the latter case orange-yellow needles are obtained, which darken in colour when heated, but have no definite m. p. When triturated with water, it yields a pentabromide, $C_6H_7ON_2Br_5$, Evans's dibromodihydroxy-derivative (5-dibromo-4 : 6-dihydroxy-4 : 6-dimethyl-2-tetrahydropyrimidone), and 5-bromo-4 : 6-dimethyl-2-pyrimidone.

The last compound is contained in the aqueous liquid, and can be isolated as its sodium derivative. The first two compounds are present in the colourless solid, and after this has been dried the pentabromo-derivative can be extracted by chloroform.

5-Dibromo-4 : 6-dihydroxy-4 : 6-dimethyl-2-tetrahydropyrimidone,  $CO<\begin{array}{l}NH{\cdot}CMe(OH)\\NH{\cdot}CMe(OH)\end{array}>CBr_2$, is sparingly soluble in most solvents; its solubility in ethyl alcohol is 1 in 100, but at the same time it undergoes partial decomposition, yielding a dye, which crystallises in deep violet prisms.

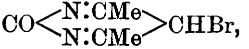
The same decomposition occurs when the compound is boiled or kept some time in contact with water, and also when the solid is heated for some time at 100°. With carbon disulphide, the dihydroxy-derivative forms a gelatinous mass, which crystallises on the addition of a solvent miscible with carbon disulphide. It dissolves in cold sodium hydroxide solution (4 mols.), and when acidified after two to three hours yields carbon dioxide, acetic and lactic acids, ammonia, and hydrobromic acid. It is claimed that the formation of these products is more in harmony with the author's view of the constitution of the dihydroxy-derivative than with Evans's view.

Colourless anhydrous 4 : 6-dimethyl-2-pyrimidone is obtained when anhydrous acetylacetonecarbamide is dissolved in absolute alcohol, mixed with the theoretical amount of sodium ethoxide, the precipitated sodium derivative removed, dried, suspended in absolute alcohol, and dry carbon dioxide passed in. The filtered solution is evaporated to dryness at the ordinary temperature over potassium hydroxide and concentrated sulphuric acid, and the residue crystallised from acetone, when the pyrimidone is obtained as colourless, glistening needles, m. p. 200°.

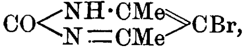
Acetylacetonecarbamide perbromide, $C_6H_8ON_2Br_4$, obtained from either chloroform or distilled hydrobromic acid solution, forms red, microscopic needles; it has no definite m. p., it changes colour at 150° to 160°, and is completely decomposed at 220°. With water it yields 5-dibromo-4 : 6-dihydroxy-4 : 6-dimethyl-2-tetrahydropyrimidone and 5-bromo-4 : 6-dimethyl-2-pyrimidone.

By the action of a solution of bromine in dilute acetic acid on a glacial acetic acid solution of acetylacetonecarbamide at 30—40° it has not been found possible to obtain the bromohydroxy-derivative previously described (*loc. cit.*); the only product obtained was the *hydrobromide* of the carbamide, $C_6H_8ON_2,HBr$. The same product was also obtained by the action of alcohol on the perbromide of the carbamide, and by dissolving the carbamide in a mixture of glacial acetic acid and concentrated hydrobromic acid. It crystallises from alcohol in colourless needles, which decompose at 345° after changing colour at 240—250°.

An aqueous solution of sodium hypobromite reacts with acetylacetonecarbamide, yielding the *sodium* salt of 5-bromo-4 : 6-dimethyl-2-pyrimidone, in the form of slender, colourless needles, decomposing rapidly at 336—338°. The corresponding hydrogen compound exists in two forms. *Bromoacetylacetonecarbamide*,

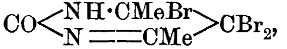


$$\mathrm{CO}<{\mathrm{N{:}CMe}\atop \mathrm{N{:}CMe}}>\mathrm{CHBr},$$

obtained by the action of acetic acid on the sodium salt, crystallises in pale yellow needles or prisms, and decomposes at 228—231°. 5-*Bromo*-4 : 6-*dimethyl*-2-*pyrimidone*,  $\mathrm{CO}<{\mathrm{NH{\cdot}CMe}\atop \mathrm{N{=\!=}CMe}}>\mathrm{CBr}$, obtained by boiling the sodium salt and the theoretical amount of acetic acid, crystallises in colourless needles or in colourless, glistening prisms. The yellow compound can be transformed into the colourless by boiling with water and adding a few drops of concentrated ammonium hydroxide solution, and can be transferred back into the yellow modification by boiling with dilute acetic acid. The monobromo-derivative yields a colourless *nitrate*, $C_6H_7ON_2Br,HNO_3$, in the form of glistening needles, which decompose between 160° and 200°; it also yields a reddish-yellow *dinitrate*, $C_6H_7ON_2Br,2HNO_3,3H_2O$, which explodes at about 196—197°.

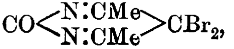
The *perbromide* of bromoacetylacetonecarbamide, $C_6H_7ON_2Br,Br_2$, forms chrome-yellow needles, decomposes at 160—200°, and with water yields 5-dibromo-4 : 6-dihydroxy-4 : 6-dimethyltetrahydro-2-pyrimidone. The bromopyrimidone also yields a perbromide with Br_2, but this rapidly becomes colourless when kept.

5 : 5 : 6-*Tribromo*-4 : 6-*dimethyldihydro*-2-*pyrimidone*,



$$\mathrm{CO}<{\mathrm{NH{\cdot}CMeBr}\atop \mathrm{N{=\!=\!=}CMe}}>\mathrm{CBr_2},$$

obtained by mixing a chloroform solution of 5-bromo-4 : 6-dimethyl-2-pyrimidone with a chloroform solution of bromine at 30—40°, and shaking at the given temperature until hydrogen bromide is evolved, forms colourless crystals, which begin to decompose at 220—240°. It cannot be recrystallised, and when heated with chloroform or treated with water yields *dibromoacetylacetonecarbamide*,



$$\mathrm{CO}<{\mathrm{N{:}CMe}\atop \mathrm{N{:}CMe}}>\mathrm{CBr_2},$$

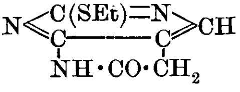
as colourless needles, decomposing at 160—170°. When water is used, *bromoacetylacetonecarbamide hydrobromide*, $C_6H_8ON_2Br_2$, is also formed. This crystallises from methyl alcohol. The *perbromide* of the monobromo-derivative, $C_6H_7ON_2Br,Br_4$, forms red needles, decomposing between 160° and 200°.

[With P. HORRMANN.]—When acetylacetonecarbamide or its monobromo-derivative is brominated in the presence of boiling chloroform, hydrogen bromide is evolved during ten to twelve hours, and the following products are formed: (1) The pentabromide (see above), which remains dissolved in the chloroform; (2) a heptabromide which is insoluble in chloroform, but soluble in benzene; (3) perbromides, insoluble in chloroform and benzene; these on treatment with water yield the dibromodihydroxydimethyldihydropyrimidone and the hydrobromide of bromoacetylacetonecarbamide. The *pentabromide*, probably $\mathrm{CO}<\begin{matrix}\mathrm{NH\cdot CBr(CH_2Br)}\\ \mathrm{NH\cdot CBr(CH_2Br)}\end{matrix}>\mathrm{CHBr}$, is stable, and crystallises from chloroform or benzene in well-developed, pale yellow prisms, m. p. 183—184° (decomp.). It is not appreciably decomposed when boiled with water for two to three hours, is distinctly acidic, and yields a *sodium* salt, $C_6H_6ON_2Br_5Na$, in the form of slender, colourless needles, which are not decomposed by carbonic acid. It also yields a *hydrobromide* in the form of a yellow, crystalline precipitate, which decomposes when removed from the mother liquor. The *heptabromide*, $C_6H_7ON_2Br_5,Br_2$, crystallises from benzene with partial decomposition in yellow, felted needles, and also tends to give up bromine when kept in a desiccator. It is most readily prepared by the addition of bromine to the pentabromide, and yields the pentabromide by the action of hydroxylic compounds

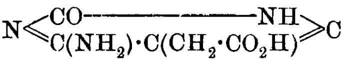
A table showing the genetic relationships of the different bromo-derivatives is given. J. J. S.

Pyrimidines. LI. Synthesis of Cytosine-5-acetic Acid.

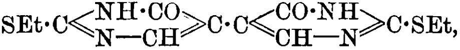
TREAT B. JOHNSON [with HARLEY T. PECK and JOSEPH A. AMBLER] (*J. Amer. Chem. Soc.*, 1911, **33**, 758—766).—It has been shown by Johnson and Speh (Abstr., 1907, i, 1083) that ψ-ethylthiocarbamide condenses with the sodium derivative of ethyl formylsuccinate to form ethyl 2-ethylthiol-6-pyrimidone-5-acetate. When this compound is heated with phosphoryl chloride, *ethyl 6-chloro-2-ethylthiolpyrimidine-5-acetate*, $\mathrm{N}<\begin{matrix}\mathrm{C(SEt)}\text{=====}\mathrm{N}\\ \mathrm{CCl\cdot C(CH_2\cdot CO_2Et)}\end{matrix}>\mathrm{CH}$, b. p. 203—203·5°/16 mm., 215°/28 mm., and 220°/31 mm., is obtained as an oil. If this chloropyrimidine is heated with alcoholic ammonia in a sealed tube at 120—130°, the corresponding amino-compound is not produced, but the γ-*lactam* of *6-amino-2-ethylthiolpyrimidine-5-acetic acid* (*2-ethylthiol-5:6-α-pyrrolidone-pyrimidine*) (annexed formula), m. p. 208°, is formed as a red, granular powder, which, on hydrolysis with concentrated hydrochloric acid, is converted into the *hydrochloride* of cytosine-5-acetic acid, which crystallises in minute needles containing $1H_2O$ and decomposes at 135—140°.



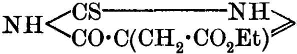
$$\mathrm{N}<\begin{matrix}\mathrm{C(SEt)=N}\\ \mathrm{C}\text{———}\mathrm{C}\\ |\qquad\quad |\\ \mathrm{NH\cdot CO\cdot CH_2}\end{matrix}>\mathrm{CH}$$

Cytosine-5-acetic acid,  $\mathrm{N}{<}\begin{matrix}\mathrm{CO}\text{——————}\mathrm{NH}\\ \mathrm{C(NH_2)\cdot C(CH_2\cdot CO_2H)}\end{matrix}{>}\mathrm{CH}$, forms colourless crystals, and blackens at 240—250°, but does not melt below 290°; it is not precipitated by phosphotungstic acid, mercuric chloride, or copper sulphate, but yields an amorphous precipitate with potassiobismuth iodide; the *picrate,* m. p. 217—218°, crystallises in needles.

Thiocarbamide condenses with ethyl formylsuccinate in presence of sodium ethoxide with formation of ethyl 2-thio-6-pyrimidone-5-acetate, together with a small quantity of another crystalline substance, probably 6 : 6′-*diketo*-2 : 2′-*ethylthiol*-5 : 5′-*dipyrimidine,*

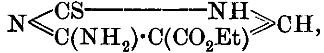
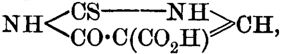
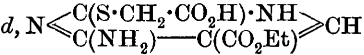


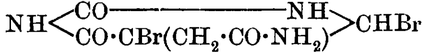
$$\mathrm{SEt\cdot C}{<}\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{N—CH}\end{matrix}{>}\mathrm{C\cdot C}{<}\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CH—N}\end{matrix}{>}\mathrm{C\cdot SEt},$$

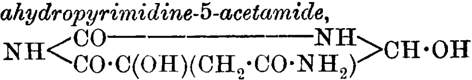
which decomposes on heating, but has no definite m. p. *Ethyl 2-thio-6-pyrimidone-5-acetate,*  $\mathrm{NH}{<}\begin{matrix}\mathrm{CS}\text{————}\mathrm{NH}\\ \mathrm{CO\cdot C(CH_2\cdot CO_2Et)}\end{matrix}{>}\mathrm{CH}$, m. p. 178—180°, and the corresponding *acid,* m. p. about 260° (decomp.), form prismatic crystals.

E. G.

Pyrimidines. LII. Thiocytosine-5-carboxylic Acid. Treat B. Johnson and Joseph A. Ambler (*J. Amer. Chem. Soc.*, 1911, **33**, 978—985).—It has been shown by Johnson (Abstr., 1910, i, 69) that ethyl α-cyano-β-ethoxyacrylate reacts with ethyl-ψ-thiocarbamide in two ways, yielding a mixture of 5-cyano-2-ethylthiol-6-pyrimidone and ethyl 6-amino-2-ethylthiolpyrimidine-5-carboxylate.

A study has now been made of the behaviour of ethyl cyanoethoxyacrylate towards thiocarbamide, and it has been found that condensation takes place with formation of only one compound, namely, *ethyl 6-amino-2-thiopyrimidine-5-carboxylate,*  $\mathrm{N}{<}\begin{matrix}\mathrm{CS}\text{————}\mathrm{NH}\\ \mathrm{C(NH_2)\cdot C(CO_2Et)}\end{matrix}{>}\mathrm{CH}$, which crystallises in needles and decomposes at 260—265°; the *hydrochloride* decomposes at 209—211°. On hydrolysing this ester with potassium hydroxide, the corresponding *acid* (2-*thiocytosine*-5-*carboxylic acid*) is produced, which forms colourless prisms containing $1H_2O$, and decomposes at 253—263°. If this acid is boiled for twenty hours with 20% sulphuric acid, it is converted into 2-*thio*-6-*pyrimidone*-5-*carboxylic acid,*  $\mathrm{NH}{<}\begin{matrix}\mathrm{CS}\text{———}\mathrm{NH}\\ \mathrm{CO\cdot C(CO_2H)}\end{matrix}{>}\mathrm{CH}$, m. p. 246—247° (decomp.), which forms granular crystals. An attempt which was made to desulphurise ethyl 6-amino-2-thiopyrimidine-5-carboxylate by means of chloroacetic acid resulted in the formation of 6-*amino*-5-*carbethoxypyrimidine*-2-*thioglycollic acid,*  $\mathrm{N}{<}\begin{matrix}\mathrm{C(S\cdot CH_2\cdot CO_2H)\cdot NH}\\ \mathrm{C(NH_2)—C(CO_2Et)}\end{matrix}{>}\mathrm{CH}$, m. p. 174—177° (decomp.), which forms a light brown powder.

When 2 : 6-dioxypyrimidine-5-acetamide, obtained by heating ethyl 2 : 6-dioxypyrimidine-5-acetate with ammonia, is treated with bromine in presence of potassium hydroxide, 4 : 5-*dibromo*-2 : 6-*dioxyhexahydropyrimidine*-5-*acetamide,*  $\mathrm{NH}{<}\begin{matrix}\mathrm{CO}\text{——————}\mathrm{NH}\\ \mathrm{CO\cdot CBr(CH_2\cdot CO\cdot NH_2)}\end{matrix}{>}\mathrm{CHBr}$, is produced as a light yellow powder; its *picrate* crystallises in yellow needles, and decomposes above 280°. When this compound is warmed gently with alkali hydroxide, it is transformed into 4 : 5-*dihydroxy-2 : 6-diketohexahydropyrimidine-5-acetamide*,



$$\mathrm{NH}\!<\!\begin{matrix}\mathrm{CO}\text{——————————}\mathrm{NH}\\ \mathrm{CO\cdot C(OH)(CH_2\cdot CO\cdot NH_2)}\end{matrix}\!>\!\mathrm{CH\cdot OH},$$

which forms minute, lemon-yellow prisms, and decomposes at about 270—280°; on reduction with hydriodic acid, it yields 2 : 6-dioxypyrimidine-5-acetic acid and ammonium iodide. 2 : 6-Dioxypyrimidine is not reduced at the double bond by hydriodic acid, but can be recovered unchanged after three hours' digestion. E. G.

Hydroxyindazoles. PAUL FREUNDLER (*Compt. rend.*, 1911, **152**, 1256—1259; *Bull. Soc. chim.*, 1911, [iv], **9**, 601—605. Compare Abstr., 1903, i, 371; 1904, i, 121, 667, 699; 1906, i, 544).—The position of the chlorine atoms in the 2 : 5-dichloro-3-hydroxy-2-phenylindazole, previously described (Abstr., 1907, i, 158), has been established by oxidising it with chromic acid, when it yields *benzeneazo*-3 : 5-*dichlorobenzoic acid*, red prisms, m. p. 142—143°; sodium hyposulphite converts this into the corresponding diamine. A mixture of phosphorus oxychloride and pentachloride converts the indazole into 2 : 5 : 7-*trichloro-3-hydroxy-2-phenylindazole*, $C_{13}H_7N_2Cl_3$, needles, m. p. 172·5°.

In their general behaviour, hydroxyindazoles resemble phenols, but have feebly basic properties. The foregoing dichloro-compound forms a *potassium* salt, a *methyl ether*, m. p. 144·5°, a *benzoyl* derivative, m. p. 204°, and an *acetyl* derivative occurring in large prisms, m. p. 133°. The *hydrochloride* is hydrolysed by water. Phosphoryl chloride forms a *compound*, $C_{13}H_8ON_2Cl,POCl_3$. Sodium hypochlorite in alkaline solution oxidises it to the corresponding azo-acid, but with the formation of an intermediate compound crystallising in green leaflets. W. O. W.

A Negative Case of Indigotin Condensation. ELIE E. PISOVSCHI (*Bull. Soc. chim.*, 1911, [iv], **9**, 548—549).—It was to be expected that 6-nitroveratraldehyde (Pschorr and Sumuleanu, Abstr., 1900, i, 178) would give Baeyer and Drewsen's reaction, condensing with acetone in presence of an alkali to form 5 : 6 : 5′ : 6′-tetramethoxyindigotin, but whilst 2-nitroveratraldehyde in this reaction furnishes the corresponding tetramethoxyindigotin, already described by Hayduck (Abstr., 1903, i, 826), the 6-nitroveratraldehyde is recovered unchanged. T. A. H.

Constitution of Indirubin. ANDRÉ WAHL and P. BAGARD (*Bull. Soc. chim.*, 1911, [iv], **9**, 546—548).—A reply to Maillard (this vol., i, 326). T. A. H.

Constitution of Auramine. LEOPOLD SEMPER (*Annalen*, 1911, **381**, 234—264).—An attempt is made to decide between the two formulæ $C(C_6H_4\cdot NMe_2)_2\!:\!NH_2Cl$ and

$$NMe_2\cdot C_6H_4\cdot C(NH_2)\!:\!C_6H_4\!:\!NMe_2Cl$$

for auramine (compare Graebe, Abstr., 1899, i, 702).

Auramine differs from other dyes with a quinonoid structure in its yellow colour and its general absorption in the blue and violet end of the spectrum, whereas most quinonoid dyes give characteristic absorption bands. A number of acylated auramine bases have been examined, more especially the acetyl derivative, and it is shown that although the bases themselves are pale yellow in colour, they yield deep bluish-violet or bluish-green compounds with acids, metallic haloids, and alkyl haloids. These compounds resemble the quinonoid diphenylmethane dyes in the following properties: (1) deep colour, (2) selective absorption, (3) instability, and (4) ability to form pale orange-yellow acid salts. The conversion of the bases by acids in either the presence or absence of water into the quinonoid salts is so marked and rapid that they can be used as indicators. These deeply coloured salts derived from acylauramines are so essentially different from the salts of auramine, of methyl- or phenyl-auramine, and of mono-, di- and tri-nitroauramines, that the conclusion is drawn that the latter group of salts cannot have a quinonoid structure, and hence Graebe's imino-structure is accepted.

The gradual change in electrical conductivity observed by Hantzsch and Osswald (Abstr., 1900, i, 256) when an equivalent quantity of alkali is added to a solution of an auramine salt is attributed to the formation of supersaturated solutions and the gradual separation of the excess of solute, and not to the slow conversion of an ammonium base into a carbonium pseudo-base. This conclusion is supported by the fact that the initial conductivity at 25° is greater than at 0°, whereas if the change in conductivity is due to molecular rearrangement, the velocity of the latter should be diminished by fall of temperature, and hence the initial conductivity increased. It is suggested that there is an equilibrium between the imonium base or its ions and the imine:

$$:C:NH_2{\cdot}OH \rightleftarrows :C:NH_2^{\cdot} + OH' \rightleftarrows :C:NH + H_2O,$$

and as the sparingly soluble imine separates, the equilibrium is shifted towards the right. This is supported by the fact that after the crystallisation of the imine is complete, the solution is still yellow, owing to the presence of a small amount of the $:C:NH_2^{\cdot}$ ion and the colour remains, but can be destroyed by the addition of an appreciable excess of alkali (excess of OH' ions) and restored again by the addition of much water. It is shown that the auramine base is more soluble in dilute sodium chloride solution than in water; when a colourless benzene solution of the imine is shaken with water, the aqueous solution assumes a pale colour, but when sodium chloride solution is used the aqueous layer becomes golden-yellow in colour (compare also Baeyer and Villiger, *Ber.*, 1904, **37**, 2852).

Auramine is a strong base, as shown by the fact that it reacts readily with carbon dioxide; the aqueous solution of its carbonate is strongly alkaline, and its trinitro-derivative can form stable salts. This is probably due to the influence of the ${\cdot}NMe_2$-group on the imino-radicle.

The halochromism of amines (Kauffmann) is more pronounced when the molecule contains a number of unsaturated groups. This can be effected by introduction of olefine linkings, phenyl groups, or auxochromes. The more strongly unsaturated the molecule the deeper is the colour tone produced by salt formation. The formation of dyes from auramine and Homolka's base by salt formation are examples of halochromism. Further examples are met with in the salts of Michler's ketone, although the salts themselves are too unstable for isolation (compare Staudinger, Abstr., 1909, i, 907; Straus and Bormann, 1910, i, 281). The additive *compound*,

$$CO(C_6H_4{\cdot}NMe_2)_2,SnCl_4,$$

forms a blood-red precipitate, which turns orange in contact with atmospheric moisture.

A perfectly colourless auramine base, free from carbonate and decomposition products, can be obtained by treating the pure hydrochloride with excess of dilute sodium hydroxide solution and benzene in the cold. The solution is filtered in an atmosphere of hydrogen or nitrogen, and evaporated under reduced pressure, when the base is obtained as a colourless, glistening, crystalline mass. It is not affected by light, and its benzene turns yellow on the addition of a little alcohol. An aqueous-alcoholic solution colours phenolphthalein orange-red. The *perchlorate* forms yellow crystals sparingly soluble in water. Ethereal solutions of mercuric chloride or stannic chloride yield yellow precipitates with a benzene solution of the base. The aqueous solution of the hydrochloride does not give an immediate precipitate with silver nitrate, but a precipitate is formed on warming, or on the addition of nitric acid.

Aqueous and alcoholic solutions of auramine salts have a much deeper colour when warm than when cold; magenta and acidified solutions of Michler's ketone behave similarly. An orange-coloured acid hydrochloride has been isolated by the action of excess of hydrogen chloride on the base and drying under reduced pressure. The salt is readily decomposed by the addition of most solvents.

Acetylauramine, $NAc{:}C(C_6H_4{\cdot}NMe_2)_2$, prepared by the action of acetic anhydride on a benzene solution of the base, crystallises from alcohol in slender, pale yellow needles, m. p. 221°, and turns blue in contact with acids, even with atmospheric carbon dioxide. Its solution in phenol has a moss-green colour, which is removed by the addition of ether.

The quinonoid *hydrochloride*, $NMe_2{\cdot}C_6H_4{\cdot}C(NHAc){:}C_6H_4{:}NMe_2Cl$, crystallises in glistening, green needles, containing 1EtOH. Its aqueous solution has a violet-blue colour or in deep layers, a red colour. The salt reacts readily with warm water or acids, yielding Michler's ketone and acetamide, but the primary product in the case of acids is a diacid salt, which has an orange colour and is stable in the presence of excess of acid. With mercuric chloride, acetylauramine yields an additive *compound* in the form of deep coloured crystals. The *methiodide*, $NMe_2{\cdot}C_6H_4{\cdot}C(NMeAc){:}C_6H_4{:}NMe_2I$, forms a hygroscopic solid, which readily loses methyl iodide; its aqueous and alcoholic solutions have a greenish-blue colour, and its absorption spectrum resembles that of the hydrochloride. With picryl chloride, acetylauramine forms a reddish-violet additive *compound*, which is readily dissociated. As an indicator, it approaches phenolphthalein, and gives a reaction with a hydrion concentration of 10^{-8}. It has the drawback that it is fairly readily decomposed by water or acids, and should, therefore, be added just before the end of the titration.

Benzoylauramine (Finkh and Schwimmer, Abstr., 1895, i, 184) yields a quinonoid *chloride*, $NMe_2 \cdot C_6H_4 \cdot C(NHBz):C_6H_4:NMe_2Cl$, in the form of a dark violet, hygroscopic powder.

Benzenesulphonylauramine, $SO_2Ph \cdot N:C(C_6H_4 \cdot NMe_2)_2$, crystallises from ethyl acetate in glistening, yellow prisms, m. p. 182°. Its solutions in phenol or glacial acetic acid have a reddish-brown colour, the hydrochloride and oxalate are unstable, and it yields a green *compound* with stannic chloride.

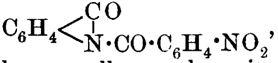
4-*Nitrophenylauramine*, $NO_2 \cdot C_6H_4 \cdot N:C(C_6H_4 \cdot NMe_2)_2$, obtained by heating auramine base with *p*-nitroaniline at 160°, separates from ethyl acetate in dark yellow crystals, m. p. 226°. Its solutions in phenol and glacial acetic acid have a blood-red colour similar to the hydrochloride. 2 : 4-*Dinitrophenylauramine*, $C_{23}H_{23}O_4N_5$, obtained by condensing auramine with chloro-2 : 4-dinitrobenzene in benzene solution, crystallises from amyl alcohol as a brick-red powder. The *hydrochloride* forms a dark red, hygroscopic mass.

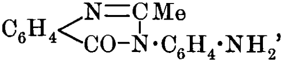
2 : 4 : 6-*Trinitrophenylauramine*, $C_{23}H_{22}O_6N_6 \cdot \frac{1}{2}C_6H_6$, forms large, glistening, black prisms, and loses its benzene at 150°. It crystallises from alcohol in glistening, red needles, m. p. 211°, and is only slowly decomposed by acids. The *hydrochloride*, $C_{23}H_{23}O_6N_6Cl$, forms glistening, bronzy needles. J. J. S.

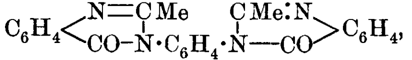
Quinazolines. XXVII. Synthesis of 3-Aminoaryl-4-quinazolones from Acylanthranils and Aromatic Diamines.

MARSTON T. BOGERT, ROSS A. GORTNER, and CARL G. AMEND (*J. Amer. Chem. Soc.*, 1911, **33**, 949—962).—The work on the synthesis of quinazolines from acylanthranils and primary amines (this vol., i, 162, and previous abstracts) has been extended to the aromatic diamines. The condensation in this case is remarkably smooth, and can be best effected by gently fusing a mixture of the reagents. The diamine must possess one primary amino-group, whilst the other may be primary, secondary, or tertiary. The aminoarylquinazolones thus produced, which contain a primary amino-group, are crystalline or pulverulent solids, and when diazotised in the usual way yield diazo- or tetra-azo-compounds, which unite with suitable couplers to form valuable azo-dyes. The following diamines were used: *o*-, *m*-, and *p*-phenylenediamines, 2 : 4′- and 2 : 5′-tolylenediamines, benzidine, *o*-tolidine, 3-ethoxybenzidine, and di-*o*-anisidine. All these condensed smoothly to form aminoarylquinazolones, except *o*-phenylenediamine. Condensations have also been carried out with di- and poly-amines containing only one primary amino-group. The acylanthranils employed were acetylanthranil, 5-bromoacetylanthranil, 5-nitroacetylanthranil, 4- and 5-acetylaminoacetylanthranils, benzoylanthranil, and *m*- and *p*-nitrobenzoylanthranils. The benzoylanthranils do not yield aminoarylquinazolones, but diquinazolonyl compounds. In this paper, corrected m. p.'s are recorded in all cases, except where otherwise stated.

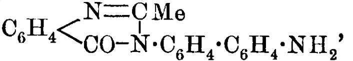
m-*Nitrobenzoylanthranilic acid*, $CO_2H \cdot C_6H_4 \cdot NH \cdot CO \cdot C_6H_4 \cdot NO_2$, m. p. 233·5°, obtained by the action of *m*-nitrobenzoyl chloride on sodium anthranilate, forms colourless prisms. p-*Nitrobenzoylanthranilic acid*, m. p. 235·5°, prepared in a similar manner,

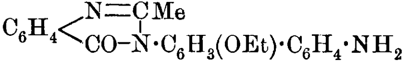
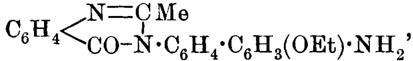
crystallises in nearly colourless needles. m-*Nitrobenzoylanthranil*,

$C_6H_4<\begin{array}{l}CO\\ N\cdot CO\cdot C_6H_4\cdot NO_2\end{array}$, m. p. 167—168°, forms small, almost colourless needles, and p-*nitrobenzoylanthranil*, m. p. 207°, light yellow needles.

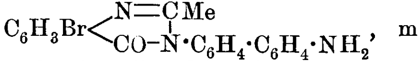
The following compounds were obtained by the condensation of aromatic diamines with acetylanthranil. 3-m-*Aminophenyl*-2-*methyl*-4-*quinazolone*,

$C_6H_4<\begin{array}{l}N{=}CMe\\ CO{-}N\cdot C_6H_4\cdot NH_2\end{array}$, m. p. 210°, from *m*-phenylenediamine. In one experiment, an aqueous solution of *m*-phenylenediamine was treated with acetylanthranil, and the product recrystallised from alcohol. On diluting the mother liquor, another *substance*, m. p. 158°, separated, which contained 10·22% of nitrogen. 3-p-*Aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 220°, from *p*-phenylenediamine. In one case, this substance was found to be accompanied by a small quantity of 3 : 3′-*phenylenebis*-2-*methyl*-4-*quinazolone*,

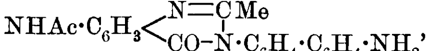

$$C_6H_4<\begin{array}{l}N{=}CMe\\ CO{-}N\cdot C_6H_4\cdot N{-}{-}CO\end{array}\begin{array}{r}CMe{:}N\\ \end{array}>C_6H_4,$$

m. p. above 300°. 3-m-*Aminotolyl*-2-*methyl*-4-*quinazolone*, m. p. 131·4°, from 2 : 4-tolylenediamine. *Acetylanthranyl*-m-*aminotoluidide*, m. p. 137—138°, forms stellate groups of colourless needles. 3-p-*Aminotolyl*-2-*methyl*-4-*quinazolone*, m. p. 169°, from 2 : 5-tolylenediamine. 3-(4′-*Aminodiphenyl*)-2-*methyl*-4-*quinazolone*,

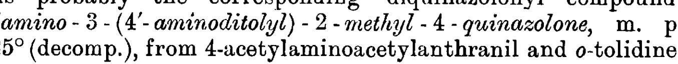

$$C_6H_4<\begin{array}{l}N{=}CMe\\ CO{-}N\cdot C_6H_4\cdot C_6H_4\cdot NH_2\end{array},$$

m. p. 282—283°, from benzidine. 3-(4′-*Aminoditolyl*)-2-*methyl*-4-*quinazolone*, m. p. 80—81°, from *o*-tolidine. 3-(4′-*Aminoethoxydiphenyl*)-2-*methyl*-4-*quinazolone*,

$C_6H_4<\begin{array}{l}N{=}CMe\\ CO{-}N\cdot C_6H_3(OEt)\cdot C_6H_4\cdot NH_2\end{array}$ or

$C_6H_4<\begin{array}{l}N{=}CMe\\ CO{-}N\cdot C_6H_4\cdot C_6H_3(OEt)\cdot NH_2\end{array}$, m. p. 86—87°, from ethoxybenzidine. 3-(4′-*Aminodianisyl*)-2-*methyl*-4-*quinazolone*, m. p. 72—73°, from *o*-dianisidine.

The following compounds were prepared by condensation with derivatives of acetylanthranil. 6-*Bromo*-3-p-*aminodiphenyl*-2-*methyl*-4-*quinazolone*,

$C_6H_3Br<\begin{array}{l}N{=}CMe\\ CO{-}N\cdot C_6H_4\cdot C_6H_4\cdot NH_2\end{array}$, m. p. 198—199°, from 5-bromoacetylanthranil and benzidine. 6-*Nitro*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 259—260° (decomp.), from 5-nitroacetylanthranil and *p*-phenylenediamine. 6-*Acetylamino*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 280° (uncorr.), from 3-acetylaminoacetylanthranil and *p*-phenylenediamine. 7-*Acetylamino*-3-m-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. above 310°, from 4-acetylaminoacetylanthranil and *m*-phenylenediamine. 7-*Acetylamino*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. above 360°; when this substance is boiled with 20% hydrochloric acid, a purple solution is obtained, which, on treatment with sodium hydroxide, yields 7-*amino*-3-p-*aminophenyl*-2-*methyl*-4-*quinazolone*, m. p. 287°. 7-*Acetylamino*-3-*aminotolyl*-2-*methyl*-4-*quinazolone*, m. p. 290°, from 4-acetylaminoacetylanthranil and

2-4-tolylenediamine, yields an *acetyl* derivative, m. p. 268·5°, and when boiled with 10% hydrochloric acid gives *7-amino-3-aminotolyl-2-methyl-4-quinazolone*, m. p. 262°. *7-Acetylamino-3-(4′-aminodiphenyl)-2-methyl-4-quinazolone*,  $NHAc\cdot C_6H_3<\begin{matrix}N{=}CMe\\ \vert\\ CO{-}N\cdot C_6H_4\cdot C_6H_4\cdot NH_2\end{matrix}$, m. p. 296—297°, from 4-acetylaminoacetylanthranil and benzidine; this compound is accompanied by another *substance*, m. p. 256° (decomp.), which is probably the corresponding diquinazolonyl compound. *7-Acetylamino-3-(4′-aminoditolyl)-2-methyl-4-quinazolone*, m. p. 120—125° (decomp.), from 4-acetylaminoacetylanthranil and *o*-tolidine. *7-Acetylamino-3-(4′-amino-?-ethoxydiphenyl)-2-methyl-4-quinazolone*, m. p. about 105—110°, from 4-acetylaminoacetylanthranil and ethoxybenzidine. *7-Acetylamino-3-(4′-aminodianisyl)-2-methyl-4-quinazolone*, m. p. about 144°, from 4-acetylaminoacetylanthranil and di-*o*-anisidine, yields a *tetra-acetyl* derivative, m. p. 239°.

Anschütz, Schmidt, and Greiffenberg (Abstr., 1903, i, 58) have shown that when ammonia is passed into a boiling alcoholic solution of benzoylanthranil, *o*-benzoylaminobenzamide is produced. It is now found that if benzoylanthranil is boiled with excess of a strong aqueous solution of ammonia, a compound, probably *di-o-benzoylaminodibenzamide*, $(NHBz\cdot C_6H_4\cdot CO)_2NH$, m. p. 118°, is formed, which, when boiled with potassium hydroxide solution, is converted into 2-phenyl-4-quinazolone. When benzoylanthranil is heated with *p*-phenetidine, a *compound*, m. p. 213°, is produced. *3 : 3′-m-Phenylenebis-2-m-nitrophenyl-4-quinazolone*,



$$C_6H_4<\begin{matrix}N{=}C\cdot C_6H_4\cdot NO_2 & & NO_2\cdot C_6H_4\cdot C{=}N\\ \vert\quad\ \vert & & \vert\quad\ \vert\\ CO\cdot N & {-}{-}{-}C_6H_4{-}{-}{-} & N\cdot CO\end{matrix}>C_6H_4,$$

m. p. 226°, is obtained by the action of *m*-nitrobenzoylanthranil on *m*-phenylenediamine. The corresponding *p*-nitrophenyl derivative, m. p. 207°, is produced when *p*-nitrobenzoylanthranil is used.

E. G.

Hydrazones of Phenacylamines. MAX BUSCH and GEORG HEFELE (*J. pr. Chem.*, 1911, [ii], **83**, 425—453).—With the hope of obtaining a direct proof of the stereoisomerism of hydrazones, the evidence for which at present is based chiefly on analogy with the stereoisomerism of the oximes, the authors have prepared hydrazones of amino-ketones of the type $Ar\cdot CO\cdot CH_2\cdot NHR$, the *syn*-forms of which, by intramolecular reaction of the hydrazino- and the amino- (or substituted amino-) groups, might be expected to undergo ring closure. Many amino-ketones of the preceding type have been prepared, but only in the case of the ψ-cumidine derivative,

$$COPh\cdot CH_2\cdot NH\cdot C_9H_{11},$$

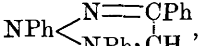
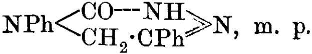
have two forms of the phenylhydrazone been isolated; unfortunately, one form has been obtained in amount so small that the special purpose of the research has not been fulfilled. The phenylhydrazones condense with aldehydes to form tetrahydrotriazines, and are readily oxidised by an excess of the hydrazine or by chromic acid to dihydro-1 : 2 : 3-triazoles, which are reduced by sodium and alcohol to tetrahydrotriazoles.

The authors' goal has not been reached by an examination of the semicarbazones and thiosemicarbazones of the preceding amino-ketones; the semicarbazones show a tendency to yield ketotetrahydrotriazines. Only with amino-ketones of the type $COPh\cdot CH_2\cdot NR_2$ have two forms of the phenylhydrazone been obtained; in these cases, unfortunately, the configurations cannot be determined by the authors' method, because ring closure cannot occur. Phenacylamines, $COPh\cdot CH_2\cdot NHR$, are readily obtained by the interaction of ω-bromoacetophenone and an amine (2 mols.) in alcoholic solution. The hydrazones are obtained in about 80% yield by adding a small excess of the hydrazine to a suspension of the amino-ketone in cold alcohol containing a little acetic acid and also hydrogen sulphide to prevent the oxidation of the hydrazone to the dihydrotriazole.

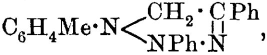
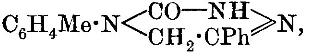
The following new compounds have been prepared by the preceding methods.

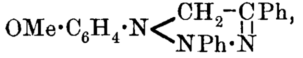
ω-Benzylaminoacetophenone forms a *phenylhydrazone*,

$$NHPh\cdot N{:}CPh\cdot CH_2\cdot NH\cdot CH_2Ph,$$

m. p. 76°, an alcoholic solution of which is converted by boiling glacial acetic acid into a *substance*, m. p. 176°, which is probably the dihydrotriazole. With phenylhydrazine, ω-anilinoacetophenone yields 1 : 2 : 4-*triphenyl*-2 : 5-*dihydro*-1 : 2 : 3-*triazole*,  $NPh<\begin{matrix}N{=\!=}CPh\\ NPh\cdot CH_2\end{matrix}$, m. p. 136·5°, whilst with semicarbazide and thiosemicarbazide it yields the *semicarbazone*, m. p. 171° (decomp.), and *thiosemicarbazone*, m. p. 167° (decomp.), respectively; the former forms a *hydrochloride*, m. p. 230° (decomp.), and at 200° loses ammonia, yielding 2-*keto*-1 : 5-*diphenyl*-1 : 2 : 3 : 6-*tetrahydro*-1 : 3 : 4-*triazine*,  $NPh<\begin{matrix}CO{-}{-}NH\\ CH_2\cdot CPh\end{matrix}>N$, m. p. 181° (decomp.). ω-p-Toluidinoacetophenone forms a *phenylhydrazone*, $C_{21}H_{21}N_3$, m. p. 147°, which reacts with phenylcarbimide on the water-bath to form a *carbamide*,

$$NHPh\cdot CO\cdot NPh\cdot N{:}CPh\cdot CH_2\cdot NH\cdot C_6H_4Me,$$

m. p. 184°, and with benzoyl chloride in pyridine, yielding a *benzoyl* derivative, $NPhBz\cdot N{:}CPh\cdot CH_2\cdot NH\cdot C_6H_4Me$, m. p. 110°. The preceding phenylhydrazone reacts with benzaldehyde at 120° and with salicylaldehyde at 150° to form *substances* (which are probably tetrahydrotriazines), which have various m. p.'s (decomp.) on account of their property of retaining variable quantities of different solvents. The phenylhydrazone is also readily converted into 2 : 4-*diphenyl*-1-p-*tolyl*-2 : 5-*dihydro*-1 : 2 : 3-*triazole*,  $C_6H_4Me\cdot N<\begin{matrix}CH_2\cdot CPh\\ NPh\cdot N\end{matrix}$, m. p. 152°, which does not react with phenylcarbimide, aldehydes, nitrous acid, or benzoyl chloride, and is reduced by sodium and alcohol to the *tetrahydrotriazole*, $C_{21}H_{21}N_3$, m. p. 122°. ω-p-Toluidinoacetophenone forms a *semicarbazone*, $C_{16}H_{18}ON_4$, m. p. 182° (decomp.), which evolves ammonia at 205°, and yields the 2-*keto*-5-*phenyl*-1-p-*tolyldihydro*-1 : 3 : 4-*triazine*,  $C_6H_4Me\cdot N<\begin{matrix}CO{-}NH\\ CH_2\cdot CPh\end{matrix}>N$, m. p. 208°. ω-o-*Anisidinoacetophenone*, $OMe\cdot C_6H_4\cdot NH\cdot CH_2\cdot COPh$, yellow needles, m. p. 89°, forms a *semicarbazone*, $C_{16}H_{18}O_2N_4$, m. p. 176° (decomp.), and a *phenylhydrazone*, $C_{21}H_{21}ON_3$, m. p. 105°; from the latter is obtained the 2 : 4-*diphenyl*-1-o-*anisyldihydro*-1 : 2 : 3-*triazole*,



$$OMe\cdot C_6H_4\cdot N{<}\begin{matrix}CH_2-CPh,\\ \| \\ NPh\cdot N\end{matrix}$$

m. p. 151·5°. The reaction between ω-bromoacetophenone and *p*-anisidine yields three products: ω-p-*anisidinoacetophenone*, m. p. 93°, yellow leaflets (which differs from all the other phenacylamines by giving a violet coloration with alcoholic ferric chloride), a *substance*, m. p. 181°, crystallising in orange-yellow plates, and *diphenacyl*-p-*anisidine*, $OMe\cdot C_6H_4\cdot N(CH_2\cdot COPh)_2$, m. p. 180°, yellow needles. ω-*p*-Anisidinoacetophenone forms a *semicarbazone*, m. p. 145° (decomp.), and an oily phenylhydrazone, from which the corresponding *dihydrotriazole*, $C_{21}H_{19}ON_3$, m. p. 156°, is obtained; ω-*p*-chloroanilinoacetophenone forms a *semicarbazone*, $C_{15}H_{17}ON_4Cl$, m. p. 167° (decomp.), and a *phenylhydrazone*, m. p. 147°, from which 2 : 4-*diphenyl*-1-p-*chlorophenyldihydro*-1 : 2 : 3-*triazole*, $C_{20}H_{16}N_3Cl$, m. p. 153°, is obtained.

ω-ψ-*Cumidinoacetophenone*, $C_6H_2Me_3\cdot NH\cdot CH_2\cdot COPh$, yellow needles, m. p. 122°, forms a *semicarbazone*, m. p. 179° (decomp.), and a *phenylhydrazone*, m. p. 155°; from the mother liquor in the latter preparation a very small amount of a yellow *substance*, m. p. 118°, is sometimes obtained, which crystallises in rhombohedra, and shows the reactions of a hydrazone. From the phenylhydrazone, m. p. 155°, is obtained 2 : 4-*diphenyl*-1-ψ-*cumyldihydro*-1 : 2 : 3-*triazole*, $C_{23}H_{23}N_3$, m. p. 139°.

ω-Dibenzylaminoacetophenone yields two isomeric *phenylhydrazones*, which are separated by alcohol; the less soluble form crystallises in colourless leaflets, m. p. 107°, the more soluble in needles, m. p. 75°. The latter change to the former at 105°, or by treating an alcoholic solution of the needles with hydrogen chloride and basifying the resulting *hydrochloride*, m. p. 255° (decomp.), with ammonia.

ω-Phenylmethylaminoacetophenone forms a *phenylhydrazone*, $C_{21}H_{21}N_3$, m. p. 98°, and a *semicarbazone*, $C_{16}H_{18}ON_4$, m. p. 202° (decomp.). ω-Phenylethylaminoacetophenone forms, in the absence of air, two isomeric *semicarbazones*, $C_{17}H_{20}ON_4$, one, m. p. 153°, crystallising in leaflets, the other, m. p. 145°, in needles. C. S.

[Preparation of a Carbamide Derivative.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 231448).—2 : 2'-*Diamino*-4 : 4'-*dihydroxy*-s-*diphenylcarbamide*-6-6'-*disulphonic acid*,

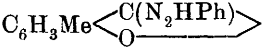
$$CO[NH\cdot C_6H_2(NH_2)(OH)\cdot SO_3H]_2,$$

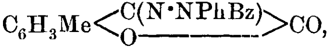
prepared by the action of carbonyl chloride on 2-nitro-4 : 1-aminophenol-6-sulphonic acid with subsequent reduction is of value in the preparation of azo-dyes. F. M. G. M.

Xanthine Substances from Uric Acid. ERNST EDW. SUNDWIK (*Skand. Arch. Physiol.*, 1911, **25**, 256—258. Compare Abstr., 1899, i, 174).—The author finds that calcium urate when heated yields xanthine. A mixture of equal weights of uric acid, calcium formate, and calcium hydroxide is moistened with water until it sets (formation of calcium urate), and the roughly powdered mass is then gradually heated in a tube in a combustion furnace until evolution of gas begins. The xanthine is precipitated by acidifying the solution of the product, the uric acid removed as acid ammonium urate, and the xanthine finally obtained in the form of its silver nitrate compound.

R. V. S.

Hydroxyazo-compounds and Ketohydrazones. IV—VI. KARL AUWERS (*Annalen*, 1911, **381**, 265—312. Compare Abstr., 1908, i, 477; this vol., i, 168).—The three diketones, 4-methylcoumarandione, thionaphthenquinone, and isatin, yield α- and β-monophenylhydrazones, and an investigation of these derivatives by the methods already described shows that they possess the hydrazone and not the azo-structure.

IV. Phenylhydrazone Derivatives of 4-Methylcoumarandione. [With R. APITZ.]—The 2-*phenylhydrazone* of 4-methylcoumarandione (Fries, Abstr., 1909, i, 175),  $C_6H_3Me{<}\begin{matrix}C(N_2HPh)\\O\end{matrix}{>}CO$, crystallises from dilute acetic acid in light yellow needles, m. p. 148°, and dissolves in concentrated sulphuric acid to a brownish-red solution. When left in contact with aqueous-alcoholic sodium hydroxide solution for fifteen to thirty minutes and then acidified, it yields the *phenylhydrazone* of 4-hydroxy-*m*-tolylglyoxylic acid (Fries and Finck, Abstr., 1909, i, 43), which crystallises from dilute alcohol in greenish-yellow needles, m. p. 160° (decomp.). The same product can be obtained by the action of phenylhydrazine on the ketonic acid, and when heated for five minutes with glacial acetic acid the lactone is re-formed. 4-*Methylcoumarandione*-2-*benzoylphenylhydrazone*,



$$C_6H_3Me{<}\begin{matrix}C(N{\cdot}NPhBz)\\O\end{matrix}{>}CO,$$

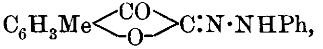
prepared by the action of an aqueous solution of benzoylphenylhydrazine hydrochloride on a methyl-alcoholic solution of the ketone, forms colourless needles, m. p. 168—169°, and yields an orange-yellow solution in concentrated sulphuric acid, and when its solution in ethyl acetate is reduced with zinc dust and glacial acetic acid in the cold, benzanilide is formed, but not aniline. Aqueous alcoholic sodium hydroxide converts the benzoylphenylhydrazone into the *benzoylphenylhydrazone* of 4-hydroxy-*m*-tolylglyoxylic acid,

$$C_{22}H_{18}O_4N_2,$$

which forms small, colourless crystals, m. p. 112° (decomp.).

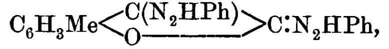
The *phenylhydrazone* of 4-*hydroxy*-m-*tolylglyoxylic acid phenylhydrazide*, $OH{\cdot}C_6H_3Me{\cdot}C(N_2HPh){\cdot}CO{\cdot}NH{\cdot}NHPh$, obtained by boiling an alcoholic solution of the 4-methylcoumarandione with an excess of free phenylhydrazine, crystallises in colourless needles, m. p. 183°, and reduces Fehling's solution.

4-*Methylcoumarandione*-1-*phenylhydrazone*,



$$C_6H_3Me{<}\begin{matrix}CO\\O\end{matrix}{>}C{:}N{\cdot}NHPh,$$

can be prepared by condensing the diketone with benzenediazonium chloride in alkaline or in acetic acid solution, and crystallises from boiling alcohol in golden-yellow plates, m. p. 224°. Its solution in concentrated sulphuric acid has a cherry-red colour. So far acetyl derivatives have not been prepared. The *osazone*,



$$C_6H_3Me<^{C(N_2HPh)}_{O}>C{:}N_2HPh,$$

obtained by warming the 1-phenylhydrazone with excess of phenylhydrazine on the water-bath, crystallises from glacial acetic acid in golden-yellow plates, m. p. 223°, and does not reduce Fehling's solution.

V. Phenylhydrazone Derivatives of Thionaphthenquinone. [With KARL MÜLLER.]—Thionaphthenquinone-2-phenylhydrazone (Bezdrik, Friedländer, and Koeniger, Abstr., 1908, i, 201) has m. p. 165—166°, and does not yield an osazone. With warm dilute alkalis, it yields the *phenylhydrazone* of thiolphenylglyoxylic acid,

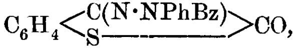
$$SH{\cdot}C_6H_4{\cdot}C(CO_2H){:}N{\cdot}NHPh,$$

m. p. 80—86°, but this is rapidly transformed into the original phenylhydrazone when warmed with various solvents. The 2-phenylhydrazone of the diketone reacts with methyl iodide and sodium methoxide in the cold, yielding the *dimethyl* derivative of the phenylhydrazone of 2-thiolphenylglyoxylic acid,

$$SMe{\cdot}C_6H_4{\cdot}C(CO_2Me){:}N{\cdot}NHPh,$$

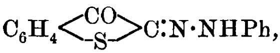
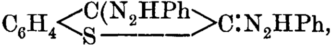
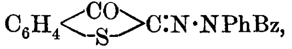
which crystallises from alcohol in pale yellow, flat needles, m. p. 107·5°. When boiled with sodium hydroxide solution it yields the *monomethyl ether*, $SMe{\cdot}C_6H_4{\cdot}C(CO_2H){:}N{\cdot}NHPh$, in the form of sulphur-yellow needles, m. p. 180° (decomp.).

Thionaphthenquinone-2-benzoylphenylhydrazone,

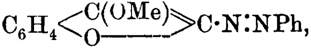


$$C_6H_4<^{C(N{\cdot}NPhBz)}_{S}>CO,$$

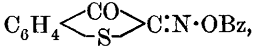
prepared by condensing the ketone with benzoylphenylhydrazine hydrochloride in hot alcoholic solution, crystallises in brilliant, deep red, flat needles, m. p. 199°. It is readily hydrolysed to the corresponding phenylhydrazone, and when its solution in ethyl acetate is reduced with zinc dust and glacial acetic acid in the cold, no trace of aniline is obtained. *Thionaphthenquinone-2-phenylmethylhydrazone*, $C_{15}H_{12}ON_2S$, crystallises from alcohol in dark red, glistening needles, m. p. 98—99°. When heated with excess of phenylmethylhydrazine for four hours at 130°, an *isomeride* is obtained, which crystallises in sulphur-yellow prisms, m. p. 122—123°.

Thionaphthenquinone-1-phenylhydrazone,  $C_6H_4<^{CO}_{S}>C{:}N{\cdot}NHPh$, crystallises in flat, glistening, reddish-brown prisms, has m. p. 194°, and is identical with Friedländer's 1-benzeneazo-2-hydroxythionaphthen (Abstr., 1909, i, 504). It is also formed by condensing phenylhydrazine with the ketodibromide, and with excess of phenylhydrazine at 100° yields the *osazone*,  $C_6H_4<^{C(N_2HPh)}_{S}>C{:}N_2HPh$, which crystallises from benzene in slender, orange-yellow needles, m. p. 199—200°. The 1-phenylhydrazone reacts with benzoyl chloride in the presence of 9% sodium hydroxide solution, yielding the *1-benzoylphenylhydrazone*,  $C_6H_4<^{CO}_{S}>C{:}N{\cdot}NPhBz$, which exists in two modifications, the one crystallises from glacial acetic acid and a little water in yellow needles or orange-yellow prisms, and has m. p. 156°

the other crystallises from alcohol in ruby-red rhombs or carmin-red, pointed prisms with a blue shimmer. Both compounds when reduced with zinc dust and glacial acetic acid yield benzanilide, but no trace of aniline.

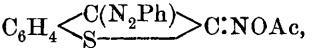
When the 1-phenylhydrazone is methylated by means of methyl sulphate in the presence of sodium hydroxide or of methyl iodide and sodium methoxide, a mixture of *O*- and *N*-methyl derivatives is obtained. *Thionaphthenquinone*-1-*phenylmethylhydrazone*, $C_{15}H_{12}ON_2S$, is sparingly soluble in ether, crystallises from alcohol in long, lustrous, red needles, m. p. 133—134°, and on reduction yields methylaniline. It is also formed when 2-dibromo-3-ketodihydrothionaphthen is condensed with phenylmethylhydrazine. 1-*Benzeneazo*-2-*methoxythionaphthen*,  $C_6H_4{<}\begin{array}{c}C(OMe)\\O\end{array}{>}C\cdot N{:}NPh$, is readily soluble in ether, and crystallises in orange-yellow plates, or from glacial acetic acid in carmine-red, pointed needles. Its solutions are mostly golden-yellow coloured, whereas those of the isomeric *N*-methyl derivative have an orange-red colour. When reduced the *O*-ether yields aniline.

The *benzoyl* derivative of 1-thionaphthenquinoneoxime,



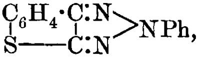
$$C_6H_4{<}\begin{array}{c}CO\\S\end{array}{>}C{:}N\cdot OBz,$$

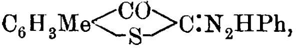
obtained by benzoylating the oxime in the presence of pyridine, crystallises from benzene in glistening, sulphur-yellow prisms, m. p. 170°, and on hydrolysis yields *o*-thiolbenzoic acid. When warmed with phenylhydrazine and glacial acetic acid the benzoyl derivative yields thionaphthenquinone-1-phenylhydrazone. The 2-phenylhydrazone of thionaphthenquinone-1-oxime (D.R.-P. 213458) crystallises from alcohol in glistening, golden-yellow, felted needles, m. p. 172° (not 154°, compare D.R.-P. 213458), and when boiled for five minutes with excess of phenylhydrazine yields the osazone. The *O*-*acetate*,

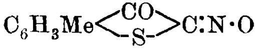
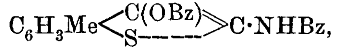


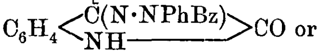
$$C_6H_4{<}\begin{array}{c}C(N_2Ph)\\S\end{array}{>}C{:}NOAc,$$

crystallises from benzene in compact, golden-yellow prisms, m. p. 156—157°. The corresponding *O*-*benzoyl* derivative forms golden-yellow, felted needles, m. p. 141—142°.

Thionaphthenphenylosotriazole,  $\begin{array}{l}C_6H_4\cdot C{:}N\\ \vert \qquad\quad \vert\\ S\text{——}C{:}N\end{array}{>}NPh$, obtained by the action of sodium hydroxide solution on an alcoholic solution of the *O*-acetyl or *O*-benzoyl derivative, forms colourless, glistening needles, m. p. 152°, and is extremely stable.

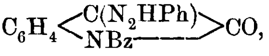
[With F. ARNDT.]—4-*Methylthionaphthenquinone*-1-*phenylhydrazone*,  $C_6H_3Me{<}\begin{array}{c}CO\\S\end{array}{>}C{:}N_2HPh$, prepared from hydroxy-4-methylthionaphthen (Auwers and Arndt, Abstr., 1909, i, 175) and benzenediazonium chloride in the presence of alkali, crystallises in dark brick-red needles with a strong greenish-yellow shimmer and has m. p. 186·5°.

The *benzoyl* derivative, $C_{22}H_{16}O_2N_2S$, exists in two forms, the one crystallises from alcohol in glistening, orange-yellow needles, m. p. 145°, and the other from benzene and light petroleum in sulphur-yellow prisms, m. p. 157°. By benzoylating in the presence of pyridine the more readily fusible compound is the chief product. The corresponding 1-*oxime*,  $C_6H_3Me<{\substack{CO\\S}}>C:N\cdot OH$, crystallises in glistening, yellow plates and flat needles, m. p. 188° (decomp., when fairly quickly heated). The *dibenzoyl* derivative of 4-methyl-2-hydroxy-1-aminothionaphthen,  $C_6H_3Me<{\substack{C(OBz)\\S}}>C\cdot NHBz$, obtained by reducing the oxime and benzoylating the product, crystallises from benzene in colourless plates, m. p. 233·5°.

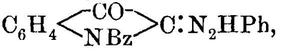
VI. Isatinphenylhydrazones.—[With A. BOENNECKE.]—*Isatin 3-benzoylphenylhydrazone*,  $C_6H_4<{\substack{C(N\cdot NPhBz)\\NH}}>CO$ or

$$C_6H_4<{\substack{C(N\cdot NPhBz)\\N}}>C\cdot OH,$$

obtained by condensing an alkaline solution of isatin with benzoylphenylhydrazine hydrochloride, crystallises from benzene in slender orange-coloured needles, m. p. 195—196°, and with alcoholic sodium hydroxide solution yields the phenylhydrazone and benzoic acid; when reduced with zinc dust and glacial acetic acid, no trace of aniline is obtained.

1-*Benzoylisatin-3-phenylhydrazone*,  $C_6H_4<{\substack{C(N_2HPh)\\NBz}}>CO$, obtained by benzoylating isatin-3-phenylhydrazone by the Schotten-Baumann method or in the presence of pyridine, crystallises in golden-yellow, felted needles, m. p. 203°, and on reduction with zinc dust and glacial acetic acid yields large quantities of aniline, but no benzanilide. The same benzoyl derivative is formed when *N*-benzoylisatin is condensed with phenylhydrazine.

Isatin-β-acetylphenylhydrazone, $C_{16}H_{13}O_2N_3$, prepared from isatin and acetylphenylhydrazine, forms small, pale yellow, octahedral crystals, m. p. 199°, and is readily hydrolysed to the 3-phenylhydrazone of isatin (Fischer, Abstr., 1884, 1151). The 1-acetyl-3-phenylhydrazone (Schunck and Marchlewski, Abstr., 1895, i, 288) has m. p. 132—134°, and on reduction yields aniline, but no acetanilide, and is therefore the *N*- and not the *O*-acetyl derivative.

Isatin-2-phenylhydrazone (Heller, Abstr., 1907, i, 442) yields an N-*benzoyl* derivative,  $C_6H_4<{\substack{CO\\NBz}}>C:N_2HPh$, which crystallises in slender, yellow, felted needles, m. p. 188—189°. It is not hydrolysed by cold alcoholic potassium hydroxide, but when warmed yields the 2-phenylhydrazone, and when reduced yields aniline. J. J. S.

The Diacetyl Reaction for Proteins. ARTHUR HARDEN and DOROTHY NORRIS (*J. Physiol.*, 1911, **42**, 332—336).—Acetylmethylcarbinol, a product of growth of certain bacteria on sugars, is readily oxidised to diacetyl (dimethyl diketone), which then combines in the presence of alkali with some part of the protein molecule, imparting to the solution a pink colour and green fluorescence. It is now shown that the group in protein on which the reaction depends is $NH:C(NH_2)\cdot NH\cdot R$, but the exact significance of R has not yet been worked out. Only complex protein substances give any fluorescence, and this is lost if time is allowed for hydrolysis to occur before the dimethyl diketone is added. W. D. H.

Cleavage Products Obtained by the Partial Hydrolysis of Proteins. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, **72**, 1—14).—The fibroin of Canton and Bengal silks was subjected to hydrolysis with 70% sulphuric acid at 25° for four days. It was found that *d*-alanyl-glycine which was obtained in previous experiments on fibroin had been split into its components, but the tripeptide *d*-alanyl-glycyl-*l*-tyrosine, identical with Fischer's synthetic product, was separated out. This is the first instance of a tripeptide actually obtained by protein hydrolysis. From the horny material of the cow's hoof, a polypeptide was similarly obtained, which yielded on further hydrolysis tyrosine, cystine, tryptophan, glutamic acid, and other amino-acids. Another polypeptide, not fully identified, was obtained by the action of trypsin on casein. W. D. H.

The Refractive Indices of Solutions of Certain Proteins. V. Gliadin. T. BRAILSFORD ROBERTSON and J. E. GREAVES (*J. Biol. Chem.*, 1911, **9**, 181—184).—The value of a in the equation $n - n_1 = ac$, where n is the refractive index of the solution of the protein, n_1 that of the solvent, and c the percentage concentration of the protein, was determined for gliadin in various solvents. In the less highly refractive solvents, the introduction of gliadin increases the refractive index, but in the most highly refractive solvent employed, namely, 75% phenol, the addition of gliadin reduces the refractive index. W. D. H.

Hydrolysis of Casein. THOMAS B. OSBORNE and H. H. GUEST (*J. Biol. Chem.*, 1911, **9**, 333—353).—The methods of preparing the casein and estimating its hydrolytic products are given with full details. A table is finally drawn up from the results of the authors and of others of the cleavage products; 36·4% of the nitrogen is still left unaccounted for. The calculations give no evidence that casein differs in constitution to any marked degree from other proteins that do not contain phosphorus. W. D. H.

The Composition of Certain Substances Produced by the Action of Pepsin on the Products of the Complete Peptic Hydrolysis of Casein. T. BRAILSFORD ROBERTSON and H. C. BIDDLE (*J. Biol. Chem.*, 1911, **9**, 295—302).—The term para-nuclein is adopted for the precipitate obtained when pepsin acts on neutral or faintly acid solutions of caseinates. When this is subjected to partial digestion by weak alkalis, the product obtained is poorer in phosphorus, and is called paranuclein-A. The two contain the same amount of carbon, hydrogen, and nitrogen, and differ from most other proteins by their low content of carbon. The synthetic product obtained at 60—70° by the action of concentrated pepsin on unconcentrated products of complete peptic hydrolysis of casein is identical so far as carbon, hydrogen, and nitrogen are concerned with para-nuclein. If the products of hydrolysis are concentrated, the synthetic product contains more carbon, but this is attributed to contamination. W. D. H.

Substances Accompanying Oxyhæmoglobin in its Crystallisation. Pierre Thomas (*Compt. rend.*, 1911, **152**, 1424—1426).—Solvents such as ether, light petroleum, and chloroform extract small quantities of pale coloured substances from crystallised oxyhæmoglobin, but the amount hitherto obtained is insufficient to determine their nature. Light petroleum extracts 0·03—0·04% of a crystalline material, possibly a mixture of cholesterol esters. W. O. W.

Reduction of Oxyhæmoglobin. Jules Wolff (*Compt. rend.*, 1911, **152**, 1332—1334).—Ewald (Abstr., 1907, ii, 184) has stated that the reduction of oxyhæmoglobin by ammonium sulphide is facilitated by the catalase of blood. If this is destroyed, however, by boiling, the liquid still retains the power of accelerating reduction. When the reduced hæmoglobin is shaken with air, re-oxidation occurs, and the process can be repeated a certain number of times until the pigment is destroyed. It has been found, however, that the alternate reduction and oxidation can be repeated indefinitely if, instead of ammonium sulphide, a maceration of Roquefort cheese is used after it has been allowed to grow a bacterial flora by exposure to air. A species of *Coccus* has been isolated from this culture, and found to have a strong reducing action on oxyhæmoglobin. W. O. W.

Changes in Physical Condition of Colloids. XI. Imbibition by Gelatin in Acids and Bases. Richard Chiari (*Biochem. Zeitsch.*, 1911, **33**, 167—181).—The experiments were carried out with gelatin, which had been freed from electrolytes by prolonged washing with conductivity water. The plates of gelatin thus treated were exposed to the action of acids and bases, and the amount of water imbibed or lost was determined by weighing the plates. In this way the imbibition grade was determined. If gelatin is purified in the above-mentioned manner, it is extremely sensitive, as regards its imbibition qualities, to acids and bases. A concentration can be determined, in the presence of acids, at which, instead of imbibition, there is a loss of water. The maximum for this loss lies at the isoelectric point of gelatin at $2 \cdot 10^{-5}n$. Acids of different strength, in isohydric concentrations, cause a greater imbibition the smaller their dissociation constant is; thus acetic acid $>$lactic acid$>$hydrochloric acid. The deviation of trichloroacetic and sulphuric acids from this rule may be ascribed to the small ionisation of their protein salts, as deduced from viscosity determinations with other proteins. Analogous results were obtained with bases, the weaker bases causing greater imbibition than the stronger bases in isohydroxylic solutions. Amphoteric electrolytes cause smaller imbibition than acids with the same dissociation constants. Theoretical explanations of the results are given, based on Pauli's conception that neutral proteins have a smaller capacity of forming hydrated aggregates than protein salts. S. B. S.

Diastases. I. Ivar Bang (*Biochem. Zeitsch.*, 1911, **32**, 417—442).—Ptyalin, after prolonged dialysis, still retains its diastatic power, although very much weakened. This fact can be demonstrated when the reducing sugar is estimated by the author's method. After adsorption by starch, and washing by centrifugalisation the adsorption-product, the ptyalin is still diastatically active. The addition of sodium chloride to the dialysed ptyalin increases its diastatic action. The optimum action of this salt takes place when the quantities added are of about the same order as those found in saliva. The addition of relatively very much larger quantities of sodium chloride does not, however, reduce to any very large extent the diastatic action. Nitrate and sulphate exert a very much less marked action. Disodium hydrogen phosphate also inhibits the action, which can be entirely destroyed if the saliva is dialysed after treatment with the phosphate. The action can, however, be restored again by addition of chloride. This action is explained by assuming that dialysis of saliva does not entirely remove the chloride; if phosphate is added, however, the pytalin-chloride compound is converted into the corresponding phosphate, and subsequent dialysis then removes all the chloride. Monosodium phosphate in small quantities inhibits only slightly the action of undialysed saliva, but in large quantities it acts strongly; it reactivates dialysed saliva when in small quantities, but to a smaller extent than the chloride; in larger quantities its action again is inhibitory, and this is probably due to the larger hydrogen ion concentration which inhibits ptyalin. This action can be antagonised by addition of the disodium phosphate. Sodium chloride does not act as an activator in presence of lecithin, whereas disodium phosphate does. The monosodium salt acts in the same way as in absence of lecithin. Experiments on the action of saliva under similar conditions to the above (on soluble starch) were carried out on glycogen. In this case the monosodium phosphate was found to exert a strong activating action.

S. B. S.

Influence of the Viscosity of the Medium on Diastatic Activity. Pierre Achalme and M. Bresson (*Compt. rend.*, 1911, **152**, 1328—1330).—A close parallelism has been found to exist between the curves showing for aqueous glycerol solutions, (*a*) variations in the viscosity of the liquid with concentration, and (*b*) the variations in the rate of hydrolysis of sucrose by invertase at different concentrations of glycerol. The rate of hydrolysis diminishes as the viscosity of the medium increases. Similar results were obtained with emulsin, amylase, trypsin, and organic and inorganic oxydases. That the parallelism is not dependent on the chemical nature of the substance causing viscosity is shown by the fact that mannitol acts in the same way.

W. O. W.

Rôle of Viscosity in Variations of the Action of Invertase According to the Concentration of Sucrose. Pierre Achalme and M. Bresson (*Compt. rend.*, 1911, **152**, 1420—1422. Compare preceding abstract).—A curve showing the variation in viscosity of a sucrose solution with concentration is almost parallel to the curve showing the time necessary for invertase to hydrolyse a definite percentage of the sugar.

W. O. W.

Viscosity and Diastatic Actions. Hypothesis on the Nature of Diastases. Pierre Achalme (*Compt. rend.*, 1911, **152**, 1621—1624. Compare preceding abstracts).—A theoretical paper. The author is led to regard an enzyme in colloidal solution as composed of granules undergoing Brownian movements, and in consequence losing energy as electrons or vibrations in the ether. When the speed of the electrons or the period of the vibrations corresponds with the intramolecular vibration of a substance capable of being acted on by the enzyme, phenomena of resonance occur, bringing about disruption in a similar way to that produced by ultra-violet light. The specific nature of an enzyme depends on accordance of the radiations with the nature of the passive substance. W. O. W.

Action of Heat on Emulsin. Gabriel Bertrand and Arthur Compton (*Compt. rend.*, 1911, **152**, 1518—1521).—Amygdalin was heated for fifteen hours at different temperatures with emulsin. The curve representing the amount of hydrogen cyanide liberated at each temperature is found to be superposable on the curve showing the amount of dextrose, the optimum temperature in each case being about 40°. The curves are no longer superposable, however, if the heating is limited to two hours; the two optimum temperatures under these conditions are 58° and 56° respectively. These observations are held to confirm the view that two distinct diastases are concerned in the hydrolysis of the glucoside, one changing it into a diose and a nitrile, whilst the other effects only fission of the diose. The curves differ from those given by cellase, and hence this also is a specific enzyme, different from the two foregoing (compare Abstr., 1900, i, 290, 800). W. O. W.

Is the So-called Peroxydase Actually a Ferment? Hesse and W. D. Kooper (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 385—393).—The results of the authors' experiments lead them to the conclusion that the coloration obtained when milk is treated with Rothenfusser's reagent (guaiacum, *p*-phenylenediamine hydrochloride, and alcohol) is not due to peroxydase, but solely to the presence of alkaline substances in the milk. As soon as the alkaline reaction of these substances is affected by the addition of acids, or mercuric chloride, or by boiling the milk, the latter does not give a coloration with the reagent. When the added acid is neutralised, a coloration is again obtained. The authors have not ascertained definitely whether the alkaline substances consist of calcium-casein compounds or phosphates; probably several substances are present which produce the effect. W. P. S.

The Inhibitory Action of Inorganic Salts on Catalase. W. Favre (*Biochem. Zeitsch.*, 1911, **33**, 32—48).—The influence of the following salts on the action of the catalase of the blood was investigated: sodium chloride and sulphate, potassium chloride and sulphate, magnesium chloride and sulphate, copper chloride and sulphate, ferrous chloride and sulphate, manganese chloride and sulphate; the action of colloidal silver was also investigated. From the amount of hydrogen peroxide decomposed by the salts, etc., alone and in the presence of catalase, the action of the salts on the catalase itself was determined. S. B. S.

Derivatives of *p*-Aminophenylarsine Oxide. ALFRED BERTHEIM (*Ber.*, 1911, 44, 1070—1075. Compare Ehrlich and Bertheim, Abstr., 1910, i, 451).—p-*Aminophenylarsine dichloride hydrochloride*, $NH_2\cdot C_6H_4\cdot AsCl_2,HCl$, m. p. 139—140°, is obtained by adding a solution of *p*-aminophenylarsine oxide in cold 2*N*-hydrochloric acid to strongly cooled hydrochloric acid, D 1·19. The corresponding *dibromide*, $NH_2\cdot C_6H_4\cdot AsBr_2,HBr$, m. p. 134°, and *di-iodide*, $NH_2\cdot C_6H_4\cdot AsI_2,HI$, are prepared in a similar manner; the latter, a yellow, crystalline powder, forming a colourless solution in water, is also obtained by reducing arsanilic acid with hydriodic acid. All three substances volatilise almost without residue, yielding crystalline sublimates (probably compounds of aniline and the arsenic trihalogenide) which are decomposed by water into aniline, arsenious acid, and the halogen acid.

p-*Acetylaminophenylarsine oxide*, $NHAc\cdot C_6H_4\cdot AsO$, exists in two forms. The one, indistinctly crystalline, anhydrous, and sparingly soluble, is obtained by reducing acetylarsanilic acid by hydriodic and sulphurous acids, and has m. p. 288—289° (decomp.). The other, obtained by the action of acetic anhydride on an aqueous suspension of *p*-aminophenylarsine oxide, is crystalline and soluble, contains H_2O, and melts partly at 100° (decomp.), completely at 271°. The anhydrous form is converted into the hydrated form by solution in 2*N*-sodium hydroxide, acidifying with 2*N*-acetic acid, and inoculating the solution with a crystal of the hydrated form. p-*Acetylaminophenylarsine dichloride hydrochloride*, $2NHAc\cdot C_6H_4\cdot AsCl_2,HCl$, m. p. 137° (decomp.), is obtained by the action of phosphorus trichloride on a suspension of acetylarsanilic acid in ethyl acetate; from its solution in sodium hydroxide, acetic acid precipitates the hydrated form, and ammonium chloride the anhydrous form of *p*-acetaminophenylarsine oxide. C. S.

Reduction Products of Arsanilic Acid and its Derivatives. II. *pp'*-Diaminoarsenobenzene. PAUL EHRLICH and ALFRED BERTHEIM [and, in part, E. SCHMITZ] (*Ber.*, 1911, 44, 1260—1269. Compare Abstr., 1910, i, 451).—Arsanilic acid can be reduced directly to the corresponding arseno-derivative, *pp'*-diaminoarsenobenzene,

$$NH_2\cdot C_6H_4\cdot As\colon As\cdot C_6H_4\cdot NH_2,$$

by means of the following reducing agents: (1) Sodium hyposulphite; (2) stannous chloride, alone or in the presence of hydriodic acid as catalyst. An alternative method is to reduce the arsanilic acid to *p*-aminophenylarsine oxide (*loc. cit.*), and then to reduce this to the arseno-derivative by means of sodium amalgam, stannous chloride, and hydrochloric acid or sodium hyposulphite. As a rule, the indirect method of reduction yields a purer product. Derivatives of quinquevalent arsenic are more difficult to reduce than those of tervalent arsenic; thus arsenic acids react slowly with a warm solution of sodium hyposulphite or of stannous chloride, whereas the corresponding arsine oxide even in the cold gives an immediate precipitate of the arseno-derivative. This reaction can be made use of for distinguishing between organic arsinic acids and arsine oxides. The arseno-compounds cannot be distilled; many possess colloidal properties. They are extremely reactive, and many undergo rapid oxidation on exposure to the air.

pp′-*Diaminoarsenobenzene*, $C_{12}H_{12}N_2As_2$, has m. p. 260°, and is insoluble in most solvents, with the exception of acetic acid and pyridine. It possesses basic properties and yields a *hydrochloride*, $C_{12}H_{12}N_2As_2,2HCl$, which decomposes at 151°, and a sparingly soluble *sulphate*. It reduces ammoniacal solutions of silver nitrate in the cold, and is readily oxidised by alkaline hydrogen peroxide or by an acetic acid suspension of iodine to aminophenylarsinic acid. The arseno-compound can be diazotised, and the resulting diazo-salt coupled with phenols to azo-dyes. It also yields condensation products with aldehydes and β-naphthaquinonesulphonic acid. When warmed with acids, the arseno-compounds yield strongly coloured products.

The *sulphite*, $2C_{12}H_{12}N_2As_2,H_2SO_3$, forms a yellow precipitate, very sparingly soluble in the usual solvents.

p-Aminophenylarsine oxide and *pp′*-diaminoarsenobenzene have pronounced toxic properties. In the case of rabbits the former is the more active. J. J. S.

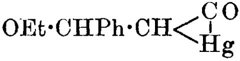
Preparation of a Nitro-1-aminophenyl-4-arsinic Acid.

FARBWERKE VORM. MEISTER, LUCIUS, and BRÜNING (D. R.-P. 231969).—*Oxanil*-4-*arsinic acid*, $CO_2H\cdot CO\cdot NH\cdot C_6H_4\cdot AsO(OH)_2$, a crystalline powder, is prepared by heating sodium *p*-aminophenylarsinite (347 parts) with crystalline oxalic acid (378 parts) at 120—130° and subsequently at 160°. When dissolved in concentrated sulphuric acid and treated with nitric acid (D 1·4) in the same solvent (at a temperature not exceeding 20°), it yields a crystalline paste of *nitro-oxanil*-4-*arsinic acid*; this is converted by boiling water into *nitro*-1-*aminophenyl*-4-*arsinic acid*, yellow needles, which separate as the solution cools. F. M. G. M.

Preparation of Soluble Compounds from Hydroxymercuri-carboxylic Acids.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 229574, 229575, 229781. Compare Abstr., 1910, i, 347, 459).—When sodium diethylbarbiturate is treated with hydroxymercuribenzoic anhydride in aqueous solution and the mixture evaporated, it yields a crystalline neutral *compound*. The *product* from hydroxymercuri-*o*-chlorobenzoic anhydride and glutarimide is also crystalline, and the reaction is stated to be applicable to other metals, such as lithium and sodium.

The second and third patents record the preparation of soluble crystalline, double *compounds* from hydroxymercuri-*m*-hydroxybenzoic anhydride with acetamide, and with alanine; and from hydroxymercuribenzoic anhydride with caffeine, and with asparagine. These products are decomposed by concentrated hydrochloric acid with separation of mercurous chloride. F. M. G. M.

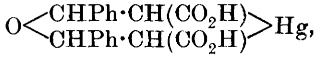
Complex Mercury Compounds of Cinnamic Acid and its Esters. WALTHER SCHRAUTH, WALTER SCHOELLER, and RICHARD STRUENSEE (*Ber.*, 1911, **44**, 1048—1057).—By the use of various alcohols and esters of cinnamic acid, the following complex mercury compounds, and the internal anhydrides obtained therefrom by hydrolysis, have been prepared by the methods already described (Abstr., 1910, i, 347) in order to show that the reaction follows the course previously suggested. *Methyl α-acetoxymercuri-β-ethoxy-β-phenylpropionate*, $OEt{\cdot}CHPh{\cdot}CH(CO_2Me){\cdot}Hg{\cdot}OAc$, m. p. 123° (corr.), long needles, forms a *mercurichloride*, $C_{12}H_{15}O_3HgCl$, m. p. 114°, *mercuribromide*, m. p. 85°, and *mercuri-iodide*, m. p. 71°, and yields by hydrolysis the internal *anhydride*,  $OEt{\cdot}CHPh{\cdot}CH{<}\begin{matrix}CO_2\\|\\Hg\end{matrix}$, decomp. 191° (corr.). *Methyl α-acetoxymercuri-β-propoxy-β-phenylpropionate*, $C_{15}H_{20}O_5Hg$, m. p. 135·5° (corr.), forms a *mercurichloride*, m. p. 109°, *mercuribromide*, m. p. 84°, *mercuri-iodide*, m. p. 84°, and an internal *anhydride*, decomp. 188° (corr.). *Methyl α-acetoxymercuri-β-*iso*propoxy-β-phenylpropionate*, m. p. 150° (corr.), yields the internal *anhydride*, $C_{12}H_{14}O_3Hg$, decomp. 191° (corr.). *Methyl α-acetoxymercuri-β-*iso*butoxy-β-phenylpropionate*, m. p. 154° (corr.), yields the internal *anhydride*, $C_{13}H_{16}O_3Hg$, decomp. 193° (corr.). *Ethyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, m. p. 107°, and *benzyl α-acetoxymercuri-β-methoxy-β-phenylpropionate*, m. p. 127°, have also been prepared.

A methyl-alcoholic solution of mercuric acetate reacts with allyl cinnamate to form a soluble mercuriacetate, which is precipitated by aqueous sodium chloride as the *dimercurichloride*,

$$OMe{\cdot}CHPh{\cdot}CH(HgCl){\cdot}CO_2{\cdot}CH_2{\cdot}CH(OMe){\cdot}CH_2{\cdot}HgCl,$$

m. p. 169° (decomp.).

The internal anhydride of α-hydroxymercuri-β-methoxy-β-phenylpropionic acid (*loc. cit.*) is moistened with alcohol, suspended in water, and brought into solution by the addition of potassium iodide; by acidifying the solution with *N*-sulphuric acid, a *substance*, $C_{18}H_{16}O_5Hg$, m. p. 200° decomp.), is obtained, which acts as a dibasic acid and does not yield mercuric sulphide by treatment with ammonium sulphide. Probably it has the constitution



$$O{<}\begin{matrix}CHPh{\cdot}CH(CO_2H)\\CHPh{\cdot}CH(CO_2H)\end{matrix}{>}Hg,$$

C. S.

Stannous Alkyl Derivatives. I. PAUL PFEIFFER (*Ber.*, 1911, **44**, 1269—1274. Compare Löwig, *Annalen*, 1852, **84**, 320; Frankland, *ibid.*, 1853, **85**, 329).—[With R. PRADE.]—Pure tin diethyl is most readily prepared by reducing tin diethyl chloride with 4% sodium amalgam and ether, and filtering rapidly, all the work being carried on in an atmosphere of hydrogen. It forms a pale yellow, odourless oil, and decomposes when distilled under reduced pressure. It combines readily with oxygen, yielding a white, amorphous precipitate of the oxide, $SnEt_2O$. It also combines readily with chlorine, bromine, or iodine, and with ethyl iodide at 140° yields tin triethyl iodide.

[With H. REKATE.]—Nearly pure tin diethyl can be obtained by the action of a large excess of magnesium ethyl bromide on stannous chloride, provided the Grignard reagent is free from alkyl iodide.

J. J. S.

Hexaphenylsilicoethane and Some Biphenyl-substitution Products of Ordinary Ethane and Ethylene. WILHELM SCHLENK, JULIUS RENNING, and GEORG RACKY (*Ber.*, 1911, **44**, 1178—1182).—The action of metals on triphenylsilicyl chloride has been investigated, in the hope of obtaining the silicon analogue of triphenylmethyl.

The metals usually employed for the removal of halogen in the preparation of triphenylmethyl are without action on triphenylsilicyl chloride. The removal of chlorine from the latter compound may, however, be effected by heating it with sodium in xylene solution. The *hexaphenylsilicoethane*, $SiPh_3{\cdot}SiPh_3$, thus obtained, crystallises in slender prisms, m. p. about 354°. It shows no tendency to dissociate, and remains unchanged when subjected to the action of oxygen in hot xylene solution. From its stability the conclusion is drawn that the total valency of the silicon atom is greater than that of the carbon atom.

Triphenylsilicyl chloride does not form coloured additive products, and remains colourless in contact with phenol. The *sodium* derivative of triphenylsilicol is obtained in a crystalline condition by heating the silicol with sodium in toluene solution.

It has previously been shown that the introduction of phenyl groups into hexaphenylethane greatly increases the tendency to dissociation. In order to ascertain if a similar influence is to be observed in the case of tetraphenylethane and tetraphenylethylene, the authors have prepared and examined the behaviour of some tetraphenyl derivatives of these hydrocarbons; no evidence of dissociation was obtained.

ω-Bromo-di-4-diphenylmethane, $CHBr(C_6H_4Ph)_2$, prepared by brominating di-4-diphenylmethane (Weiler, this Journ., 1875, 151) at 185°, crystallises in colourless leaflets, m. p. 143; it gives a red (in thin layers, blue) coloration with strong sulphuric acid, and is converted by aqueous potassium hydroxide into *di-*p*-phenylbenzhydrol*, $CH(C_6H_4Ph)_2{\cdot}OH$, leaflets or needles, m. p. 150°. When heated with copper-bronze in xylene solution, it yields s-*tetra-4-diphenylethane*, $CH(C_6H_4Ph)_2{\cdot}CH(C_6H_4Ph)_2$. This forms short prisms, m. p. 276—279°, and crystallises from benzene and xylene with one molecule of the solvent. Its solutions in solvents of high boiling point are colourless, do not decolorise iodine, and are unattacked by oxygen, so that no dissociation takes place. *Tetra-4-diphenylethylene*, $C(C_6H_4Ph)_2{:}C(C_6H_4Ph)_2$, prepared by heating ω-bromodi-4-diphenylmethane above its melting point, crystallises in pale yellow needles, m. p. 330°.

F. B.

Organic Chemistry.

$\Delta^{\alpha\kappa}$-Undecadiene and $\Delta^{\alpha o}$-Hexadecadiene. J. N. Reformatsky, E. Grischkewitsch-Frochimowsky, and A. Semenzoff (*Ber.*, 1911, **44**, 1885—1886).—A mixture of undecadiene and hexadecadiene is obtained on adding magnesium ribbon to $\alpha\epsilon$-dibromopentane in ethereal solution, and subsequently boiling with allyl bromide. The hydrocarbons were fractionally distilled under reduced pressure over metallic sodium.

$\Delta^{\alpha\kappa}$-*Undecadiene*, $C_{11}H_{20}$, is a colourless, mobile liquid, b. p. 187°/755 mm. (corr.), D^{20} 0·7671, n_D^{20} 1·43497. It decolorises 4 atoms of bromine in ethereal solution, forming a viscid, colourless tetrabromide.

$\Delta^{\alpha o}$-*Hexadecadiene*, $C_{16}H_{30}$, is a colourless, mobile liquid, solidifying to a mass of crystalline leaflets, m. p. $-14°$ to $-12°$, b. p. 142—147°/6 mm., D_4^{18} 0·8149, n_D^{18} 1·45612. It forms a viscid, faintly red-coloured tetrabromide.

Both hydrocarbons form bright green additive products with liquid nitrogen trioxide. $\Delta^{\alpha\delta}$-Dodecadiene and dimethyldodecadiene have been prepared in a similar manner. E. F. A.

Preparation of Chloro- and Bromo-compounds from Organic Bases. Julius von Braun and W. Sobecki (*Ber.*, 1911, **44**, 1464—1475. Compare Abstr., 1904, i, 731, 841; 1905, i, 206, 341, 596, 634; 1907, i, 79; 1910, i, 25, 119).—A simple method for the preparation of an alkyl chloride, RCl, from an amine, $R{\cdot}NH_2$, is to benzoylate the amine and to decompose this according to the equation: $R{\cdot}NH{\cdot}COPh + PCl_5 = POCl_3 + PhCN + RCl$. This reaction does not proceed quantitatively, and only 60—75% of benzonitrile is formed as a rule. After removing the phosphoryl chloride by means of water, the benzonitrile and alkyl chloride can be separated in certain cases by fractional distillation. If, however, the boiling points are too close for such a separation, the mixture is treated with a slight excess of ethyl alcohol and one equivalent of hydrogen chloride, and on the addition of ether the crystalline benzimino-ethyl ether hydrochloride is completely precipitated at the end of four days.

The following compounds have been prepared by this method: ϵ-Phenylamyl chloride, 73% (Abstr., 1910, i, 844); $\alpha\eta$-dibromoheptane, 65% (Abstr., 1906, i, 577), and $\alpha\epsilon$-dichloropentane. The method is much more convenient than the old one of removing the benzonitrile by hydrolysis to benzoic acid. Nonyl bromide is readily obtained from octyl iodide, by converting the latter into the cyanide, reducing with sodium and alcohol to nonylamine, and then treating according to the general method. Nonylamine has b. p. 201°, and rapidly absorbs moisture and carbon dioxide (compare Hofmann, Abstr., 1882, 1054). It is not identical with the nonylamine prepared from petroleum by Pelouze and Cahours (*Jahres.*, 1863, 529). The *hydrochloride* crystallises well and is not hygroscopic; the *platinichloride*, $C_{18}H_{44}N_2Cl_6Pt$, forms a pale yellow precipitate, and decomposes at 205—207°; the *picrate*, $C_{15}H_{24}O_7N_4$, crystallises from alcohol in brilliant needles, m. p. 111°, and the *benzoyl* derivative, $C_{16}H_{25}ON$, is readily soluble in alcohol and has m. p. 49°. *Nonyl bromide*, $C_9H_{19}Br$, is a colourless liquid, b. p. 91°/9 mm. With magnesium and carbon dioxide in the presence of dry ether, it yields decoic acid together with octadecane.

Pentadecyl chloride can be obtained from palmitic acid by transforming the latter into its amide, and conversion of this into pentadecylamine, the *benzoyl* derivative of which has m. p. 78°. *Pentadecyl chloride*, $C_{15}H_{31}Cl$, is an oil with b. p. 168—171°/10 mm., and on treatment with aniline yields pentadecylaniline (Le Sueur, Trans., 1910, **97**, 2433).

Heptadecyl chloride can also be obtained from cetyl iodide by conversion into the nitrile, reduction of this with sodium and alcohol, and treatment of the benzoyl derivative of the resulting amine with phosphorus pentachloride. *Cetyl cyanide* [*heptadeconitrile*], $C_{16}H_{33}\cdot CN$, has b. p. 208°/10 mm., and m. p. 29°. Heptadecylamine has b. p. 322—324° and m. p. 48°, and *heptadecyl chloride*, $C_{17}H_{35}Cl$, b. p. 192—195°/10 mm. and m. p. 24°.

$\alpha\mu$-Dichlorododecane can be obtained from $\alpha\kappa$-di-iodododecane (Abstr., 1910, i, 26) by a similar method. When the dibenzoyl derivative of $\alpha\mu$-diaminododecamethane (*loc. cit.*) is distilled with phosphorus pentachloride under reduced pressure, and the products decomposed with water, *$\alpha\mu$-dichlorododecane*, $C_{12}H_{24}Cl_2$, is obtained as an oil, b. p. 170—172°/10 mm., which solidifies and then has m. p. 29°. With sodium phenoxide and alcohol it yields $\alpha\mu$-diphenoxydodecane, m. p. 86°. A by-product obtained during the distillation of the dichloro-derivative is *μ-chlorododecylbenzamide*, $CH_2Cl[CH_2]_{11}\cdot NH\cdot COPh$, which crystallises from a mixture of ether and light petroleum in brilliant plates, m. p. 66°. J. J. S.

Preparation of Olefine Alcohols of the General Formula $OH\cdot CHMe\cdot CR\colon CH_2$. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233519).—It is found that unsaturated $\alpha\beta$-ketones can be readily converted into the therapeutically valuable olefine alcohols of the general formula $OH\cdot CHMe\cdot CR\colon CH_2$ (where R is hydrogen or an alkyl group) by a series of operations represented by the following equations:

(1) $COMe\cdot CR\colon CH_2 + NHMe_2 = COMe\cdot CHR\cdot CH_2\cdot NMe_2$.

(2) $COMe\cdot CHR\cdot CH_2\cdot NMe_2 + H_2 = OH\cdot CHMe\cdot CHR\cdot CH_2\cdot NMe_2$, this on methylation and subsequent treatment with silver hydroxide yields $OH\cdot CHMe\cdot CHR\cdot CH_2\cdot NMe_3\cdot OH$, which is readily decomposed by heat into water, trimethylamine, and the required alcohol.

β-Methyl-Δ^{α}-buten-γ-ol, $OH\cdot CHMe\cdot CMe\colon CH_2$, a colourless oil, b. p. 113—115°, sparingly soluble in water, which on oxidation with chromic acid yields the characteristic odour of ethyl vinyl ketone, was obtained by means of the following intermediate compounds: β-Methyl-Δ^{α}-buten-γ-one, $COMe\cdot CMe\colon CH_2$, was converted by dimethylamine into *dimethyl-β-acetylpropylamine*, $CHMeAc\cdot CH_2\cdot NMe_2$, b. p. 51—51·5°/13 mm., a colourless oil readily soluble in water; this on reduction with sodium amalgam or electrolysis yielded *δ-dimethylamino-γ-methylbutan-β-ol*, $OH\cdot CHMe\cdot CHMe\cdot CH_2\cdot NMe_2$, a colourless, soluble

oil, b. p. 64—66°/16 mm., or 166—167° under atmospheric pressure; the *methiodide*, m. p. 154°, furnished, on treatment with silver hydroxide, a syrupy *base*, which decomposed at 140—160° into the required *β-methyl-Δ^{α}-buten-γ-ol.* Methyl vinyl ketone, $CH_3\cdot CO\cdot CH\colon CH_2$, on treatment with dimethylamine yielded *δ-dimethylamino-β-butanone*, $CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot NMe_2$, b. p. 39—45°/14 mm., a colourless oil readily soluble in water, which on reduction furnished *δ-dimethylamino-β-butanol*, $OH\cdot CHMe\cdot CH_2\cdot CH_2\cdot NMe_2$, b. p. 150—155°, a soluble oil with an odour of piperidine, and was subsequently converted into *methylvinylcarbinol*, $OH\cdot CHMe\cdot CH\colon CH_2$, b. p. 98—100°, a colourless oil sparingly soluble in water. F. M. G. M.

Beeswax. III. Are the Alcohols from Psyllawax and Beeswax Identical? ERNST EDW. SUNDWIK (*Zeitsch. physiol. Chem.*, 1911, **72**, 455—458. Compare Abstr., 1899, i, 112; 1907, i, 887).—It is shown that the alcohol from beeswax is not identical with psylla alcohol. When the latter is heated with soda-lime at 360—370°, psyllic acid is formed, whereas the same acid cannot be obtained from the alcohol of beeswax.

Beeswax alcohol and soda lime at 320° yield a compound containing $C = 84{\cdot}05$ and $H = 14{\cdot}60\%$; $(C_{33}H_{67})_2O$ or $(C_{32}H_{65})_2CO$? It crystallises from acetone, has m. p. 56—56·5°, and b. p. 310—314°. The alcohol and soda lime at 220—260° yield a small amount of an *acid* with m. p. 78°. The *silver* salt gave $Ag = 17{\cdot}53\%$. J. J. S.

Acid Sodium Acetates. RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, **3**, 13—17. Compare Vaselieff, Abstr., 1909, i, 756).—The solubility of sodium acetate in acetic acid solutions at 20° has been determined, also the composition of the residues, and the conditions under which the hydrated salt as well as the acid salts come into existence found to be as follows:

Molecular percentage in solution.		Residue.
$NaC_2H_3O_2$.	$C_2H_4O_2$.	
9·5	0	
		$NaC_2H_3O_2,3H_2O$.
10·82	8·28	
		$NaC_2H_3O_2,C_2H_4O_2$.
10·84	32·90	
		$NaC_2H_3O_2,2C_2H_4O_2$.
—	—	

J. D. K.

Solubility of Strontium Acetate and the Transition Point of its Hydrates. YUKICHI OSAKA and RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, **3**, 51—54).—Strontium acetate is well known to crystallise with $\frac{1}{2}H_2O$ at 15°, but with $4H_2O$ at lower temperatures. The solubility has been determined between 0° and 97°, and the transition point found to be 9·4°. Above this temperature the solubility decreases, and seems to reach a minimum at about 83°. The crystals, stable at lower temperatures, were difficult to free completely from the mother liquor on account of their instability at the ordinary temperature. A small quantity of strontium chloride was therefore added to the solution, and the amount of mother liquor adhering to the crystals taken for analysis was estimated from their chloride content. J. D. K.

Catalytic Preparation in the Wet Way of Esters of Saturated Aliphatic Acids. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1911, **152**, 1671—1673. Compare Abstr., 1910, i, 649, 651).—Two hundred c.c. of a mixture of acetic acid and alcohol in equimolecular proportions give on distillation a liquid containing 17·8% of the theoretical amount of ethyl acetate, whereas under the same conditions, but in presence of 10 grams of anhydrous aluminium sulphate or potassium hydrogen sulphate, the yield of ester is 82%. With 1% of sulphuric acid by volume, the yield is 86·5%. The catalytic effect of the latter is attributed to the formation of ethyl hydrogen sulphate; this becomes converted into the relatively unstable ethyl sulphate, which reacts with acetic acid to form the ester and ethyl hydrogen sulphate. The latter is the actual catalyst and not the sulphuric acid. Anhydrous sodium sulphate is without catalytic effect on esterification, and hence the reaction is not entirely dependent on the efficiency of the catalyst as a dehydrating agent. W. O. W.

Ethyl Acetate. A. KURTENACKER and H. HABERMANN (*J. pr. Chem.*, 1911, [ii], **83**, 541—552).—Continuing the experiments of Habermann and Brezina (Abstr., 1909, i, 873), the authors have investigated the formation of ethyl acetate from 96 volume % alcohol and glacial acetic acid in the presence of sodium metaphosphate, or the ignited sulphate of copper, magnesium, nickel, zinc or sodium as the dehydrating agent. A mixture of the alcohol and the acid in approximately molecular proportions is kept for some hours with a quantity of the dehydrating agent in excess of that required to combine with the water produced in the reaction; the whole is then heated for many hours under a reflux condenser, the course of the reaction being followed by siphoning off samples at intervals, cooling, filtering, and titrating the residual acetic acid with $N/2$-sodium hydroxide. Sodium metaphosphate or sodium sulphate has no influence whatever on the yield of ethyl acetate; copper sulphate, zinc sulphate, and magnesium sulphate produce approximately the same effect; nickel sulphate is by far the best dehydrating agent. Having shown that an excess of alcohol or the prolonged heating of the mixture does not improve the yield of purified ethyl acetate, the authors state the following as the best conditions for the preparation of the ester.

A mixture of 200 grams of alcohol, 250 grams of acetic acid, and about 160 grams of anhydrous nickel sulphate is distilled until the temperature begins to exceed 73°. The condenser is then arranged vertically, and the mixture is heated under reflux, until the b. p. has fallen below 73°. The condenser is then reverted, and the mixture again distilled until the temperature begins to exceed 73°. These operations are repeated as long as any liquid distils over below 73°. The distillate containing a molecular compound of ethyl alcohol and ethyl acetate, b. p. about 72° (*loc. cit.*), is purified in the usual way. C. S.

Preparation of Esters of Organic Acids with the Exception of those of Formic Acid. ADMINISTRATION DER MINEN VON BUCHSWEILER AKT.-GES. (D.R.-P. 232818).—It is found that esters can be prepared in quantitative yield by boiling the components together in the presence of anhydrous calcium chloride and a mineral acid; the ester rises to the surface of the liquid, and is thus readily separated from the hydrated calcium chloride. Details for the preparation of ethyl and amyl acetates, methyl butyrate, ethyl benzoate, and ethyl phthalate are given in the patent. F. M. G. M.

Preparation of Tri-iodo-derivatives of Stearic Acid. ERNST ERDMANN (D.R.-P. 233893).—Tri-iodostearic acid derivatives may be obtained by the action of three molecules of iodine monobromide or monochloride or hydrogen iodide in acetic acid on a cooled solution of linoleic acid in the same solvent; excess of halogen is removed with sulphurous acid, the product separated by stirring in petroleum, and then crystallised from acetic acid.

Tribromotri-iodostearic acid has m. p. 122—124°, and by shaking with calcium hydroxide is converted into its *calcium* salt.

Trichlorotri-iodostearic acid is a colourless, crystalline powder, m. p. 144°.

Tri-iodostearic acid is obtained when hydrogen iodide is employed, and forms a *calcium* salt. F. M. G. M.

Preparation of Unsaturated Dihalogenated Aliphatic Acid Chlorides. F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 232459).—It is found that the hitherto unknown unsaturated dihalogenated aliphatic acid chlorides of the general formula $C_nH_{2n-4}X_2O_2$ (X = halogen) can be prepared in quantitative yield by the action of thionyl chloride on the corresponding dihalogenated acid.

Di-iodostearolyl chloride is thus obtained from di-iodostearolic acid (Liebermann and Sachse, Abstr., 1892, i, 470); it forms a yellow oil, which can be distilled under 0·3 mm. pressure without decomposition; the corresponding *dibromostearolyl chloride* is a pale brown, oily fluid, which solidifies at the temperature produced by a mixture of solid carbon dioxide and ether.

Di-iodotaririolyl chloride forms brownish-yellow, spear-shaped crystals, m. p. 28°.

Di-iodobehenolyl chloride has m. p. 19°. F. M. G. M.

Preparation of Stable Bromo- and Iodo-derivatives of Fats Free from Sulphur. ARNOLD VOSWINKEL (D.R.-P. 233857).—Animal and vegetable oils can be conveniently halogenated in alcoholic solution by means of the reaction occurring between chloral hydrosulphide and bromine (or iodine) according to the equation $(C_2HCl_3O)_2,H_2S + 2I = 2HI + S + 2C_2HCl_3O$, when the halogen acid formed at once attacks the oil.

Sesame oil under these conditions yielded a yellow, oily *product* containing 4—5% iodine.

Butylchloral hydrosulphide, obtained by passing hydrogen sulphide into a solution of butylchloral in chloroform, forms leaflets, m. p. 85°.

These oils containing bromine and iodine are therapeutically active.

F. M. G. M.

"Alcoholysis" of Japan Wax. EUGÈNE TASSILLY (*Bull. Soc. chim.*, 1911, [iv], **9**, 608—615. Compare Geitel and van der Want, Abstr., 1900, i, 271, Schaal, Abstr., 1908, i, 3, and Matthes and Heintz, Abstr., 1910, i, 149).—The author has examined the acids furnished by Japan wax when "alcoholysed" by Haller's process (Abstr., 1907, i, 9). It was found necessary to add sufficient ether to keep the material in solution, and under these conditions the process had to be continued thirteen hours to effect complete hydrolysis.

The wax consists principally of palmitin, and by Haller's method a yield of 55% of pure methyl palmitate is readily obtained from it. Other acid constituents detected in the course of the present investigation were pelargonic, stearic, oleic, and japanic acids, and an *acid*, $C_{15}H_{30}O_2$ (or $C_{30}H_{58}O_4$), m. p. 87°, with acids soluble in water and possibly including some *iso*butyric acid. No arachidic acid was found. The unsaponifiable matter amounted to 0·54%. T. A. H.

Keto-enolic Equilibrium of Ethyl Acetoacetate. ARTHUR HANTZSCH (*Ber.*, 1911, **44**, 1771—1776).—Correction of mistakes in, and a more extended discussion of, work already recorded (Abstr., 1910, i, 811; compare also Meyer, this vol., i, 351; Knorr, *ibid.*, i, 516). C. S.

Neutralisation Curve of Oxalic Acid. J. E. ENKLAAR (*Chem. Weekblad*, 1911, **8**, 487—492).—A table is given containing the results of measurements with the gas electrode, obtained in the step-by-step neutralisation of solutions of oxalic acid with sodium hydroxide. A curve is appended showing the relation of the concentration of the hydrogen ions to the quantity of added alkali.

A. J. W.

Improved Method of Preparation of Mono-substituted Malonic and Acetoacetic Esters. HERMANN LEUCHS (*Ber.*, 1911, **44**, 1507—1511).—The formation of the disubstituted ethyl malonate, which is usually obtained as a by-product in the preparation of the mono-substituted ester, can be prevented to a great extent by employing a large excess, usually 1 mol., of ethyl malonate. Thus the following substances have been prepared, the figures in the brackets denoting the yield by the ordinary method: ethyl benzylmalonate, 85% (50—55%); ethyl γ-phenoxyethylmalonate, 89% (55%: Fischer and Blumenthal, Abstr., 1907, i, 191); ethyl δ-chloro-γ-valerolactone-α-carboxylate, 78% (50%: Traube and Lehmann, Abstr., 1901, i, 501); ethyl γ-bromopropylmalonate, 35—38% (25%: Willstätter and Ettlinger, Abstr., 1903, i, 362).

Similarly, by using an excess of ethyl acetoacetate, ethyl benzylacetoacetate has been obtained in 89% yield (55%), and acetyl-δ-chlorovalerolactone in 74% yield (50%: Traube, *loc. cit.*).

C. S.

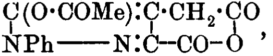
Ethyl Oxalylsuccinate. WILHELM WISLICENUS and MARTIN WALDMÜLLER (*Ber.*, 1911, **44**, 1564—1573).—An ether-alcohol solution of potassium ethoxide reacts with ethyl oxalate to form insoluble ethyl potassio-oxalylsuccinate; this crystallises in very slender, matted needles. On acidifying, the ester is obtained as a colourless oil; it exists in two forms in equilibrium, the enolic, giving a deep red and the ketonic, showing no coloration with ferric chloride. Of the solvents methyl and ethyl alcohols, ether and benzene, the first named contains least, and the last most, of the enolic modification.

With ammonia, ethyl oxalylsuccinate forms a neutral crystalline salt-like additive product, which sinters at 82°, m. p. 88—89°. This substance changes spontaneously, or more quickly on warming, to *ethyl a-amino-β-carboxyglutaconate*,

$$CO_2Et\cdot C(NH_2){:}C(CO_2Et)\cdot CH_2\cdot CO_2Et.$$

This crystallises in colourless, lustrous plates, m. p. 68—69°, b. p. 255—260°/112 mm. or 211—214°/27 mm.

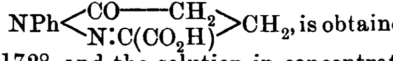
The ammonia compound interacts with copper acetate, forming *ethyl cupro-oxalylsuccinate,* crystallising in slender, green needles, m. p. 64—69°. The corresponding *nickel* compound forms greenish-white needles, m. p. 114—119°; the *zinc* compound separates in colourless needles.

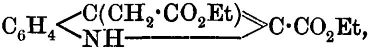
Ethyl oxalylsuccinate phenylhydrazone separates in small, pale yellow crystals, m. p. 85°. At 150°, or on treatment with hydrogen chloride in ethereal solution, ethyl 3-carboxy-1-phenyl-5-pyrazolone-4-acetate is obtained. This forms an *acetyl* derivative crystallising in colourless needles, m. p. 89—90°. The corresponding acid phenylpyrazolone, obtained by hydrolysis of the ester, is converted by acetyl chloride into the *anhydride* of 3-*carboxy*-1-*phenyl*-5-*acetoxy*-*pyrazole*-4-*acetic acid,*  $\begin{array}{l} C(O\cdot COMe){:}C\cdot CH_2\cdot CO \\ NPh\text{———}N{:}C\text{—}CO\text{—}O \end{array}$, which crystallises in lustrous, colourless needles, m. p. 150—151°.

On boiling with alkali and acidifying, 3-carboxy-1-phenylpyrazolone-4-acetic acid, m. p. 232°, is obtained. On boiling with alcohol and precipitating with water, the mono-*ethyl* ester of the acetylated acid is obtained in colourless, lustrous needles, m. p. 178—182°.

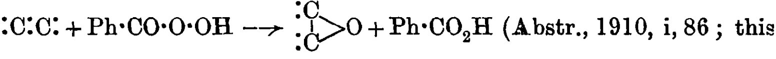
Ethyl oxalylsuccinate forms a crystalline additive product with diphenylhydrazine, m. p. 78—79°; on keeping, this changes into the *diphenylhydrazone,* which is an oil.

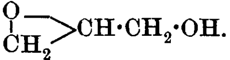
With hydroxylamine an *additive product* consisting of 2 mols. of ester and 1 mol. of hydroxylamine is obtained; it crystallises in slender, colourless needless, which soften at 55°, m. p. 61—62°.

a-Ketoglutaric acid forms colourless crystals, m. p. 115—116°; the *diethyl* ester is a colourless liquid, b. p. 160°/23 mm. The *phenylhydrazone* of the acid crystallises in almost colourless plates, m. p. 152—153°; on keeping or when heated, the anhydride, 1-*phenyl*-6-*pyridazinone*-3-*carboxylic acid,*  $NPh{<}\begin{array}{l} CO\text{———}CH_2 \\ N{:}C(CO_2H) \end{array}{>}CH_2$, is obtained. It forms colourless plates, m. p. 172°, and the solution in concentrated sulphuric acid is not coloured by either ferric chloride or potassium dichromate.

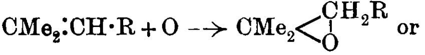
On the introduction of hydrogen chloride into a warm alcoholic solution of the anhydride, ammonium chloride is eliminated and *ethyl 2-carboxyindole-3-acetate*,  $C_6H_4{<}\begin{matrix}C(CH_2\cdot CO_2Et)\\ NH\text{————}\end{matrix}{>}C\cdot CO_2Et$, obtained in colourless plates, m. p. 83—84°. E. F. A.

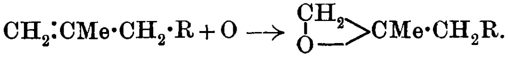
Oxidation of Unsaturated Compounds with Organic Peroxides. II. Oxidation of Derivatives of Unsaturated Hydrocarbons with One Double Linking. NIKOLAUS PRILESCHAEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 609—620).—It has been already shown that the interaction of hydrocarbons of the series, C_nH_{2n-2}, and benzoylhydroperoxide proceeds according to the scheme:


$:C:C: + Ph\cdot CO\cdot O\cdot OH \longrightarrow \begin{matrix}:C\\ |\\ :C\end{matrix}{>}O + Ph\cdot CO_2H$ (Abstr., 1910, i, 86; this vol., i, 255). In the present paper it is shown that the oxidation of derivatives of these hydrocarbons, for example, aldehydes, ketones, alcohols, etc., proceeds in the same way.

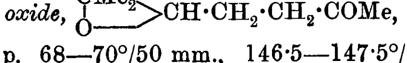
Thus, allyl alcohol yields the corresponding oxide (glycide) (compare Nef, Abstr., 1905, i, 3),  $\begin{matrix}O\text{—}\\ |\\ CH_2\end{matrix}{>}CH\cdot CH_2\cdot OH$.

Oxidation of citronellal (b. p. 103—105°/25 mm., $[\alpha]_D$ +9·79°, D^{16}_{16} 0·8624) gives *citronellal oxide*, $C_{10}H_{18}O_2$, as a colourless liquid, b. p. 126—127°/20 mm., D^{0}_{0} 0·9437, D^{16}_{16} 0·9344, $[\alpha]_D$ +9·63°, n^{16}_D 1·44210, which gives all the aldehyde reactions, but does not form a crystalline oxime or semicarbazone. The oxidation proceeds thus:


$CMe_2{:}CH\cdot R + O \longrightarrow CMe_2{<}\begin{matrix}CH_2R\\ |\\ O\end{matrix}$ or


$CH_2{:}CMe\cdot CH_2\cdot R + O \longrightarrow \begin{matrix}CH_2\\ |\\ O\text{—}\end{matrix}{>}CMe\cdot CH_2R.$

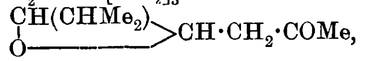
Citronellal oxide readily undergoes hydration to the *glycol*, $C_{10}H_{20}O_3$, which is a viscous, colourless liquid, b. p. 180—182°/18 mm., and forms an *acetyl* derivative, $C_{10}H_{19}O_3Ac$, b. p. 175—176°/13 mm., D^{0}_{0} 1·0418, D^{16}_{4} 1·0295, n^{16}_D 1·4571. From dihydroxydihydrocitronellaldimethylacetal, Harries and Schauwecker (Abstr., 1901, i, 730) also obtained a dihydroxyaldehyde, but the b. p., 158—162°/22 mm., is appreciably lower than that found for the above glycol.

Methylheptenone, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot COMe$, on oxidation gives: (1) The *oxide*,  $\begin{matrix}CMe_2\\ |\\ O\text{—}\end{matrix}{>}CH\cdot CH_2\cdot CH_2\cdot COMe$, as a mobile, colourless liquid, b. p. 68—70°/50 mm., 146·5—147·5°/746 mm., D^{0}_{0} 0·9870, D^{16}_{4} 0·9718, $n^{16\cdot 1}_D$ 1·43031; it is not oxidised by permanganate, reduces Fehling's solution slightly, and does not give a crystalline oxime or semicarbazone. It is readily hydrated, giving the *glycol*,

$$OH\cdot CMe_2\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot COMe,$$

as a mobile liquid, b. p. 139—140°/13 mm., D^{0}_{0} 1·0698, D^{16}_{4} 1·0582, $n^{16\cdot 2}_D$ 1·4610, which slowly crystallises; m. p. 65—66°. Dehydration of the glycol yields the *diketone*, $CHMe_2\cdot CO\cdot CH_2\cdot CH_2\cdot COMe$, b. p. 117—119°/50 mm., 94—95°/15 mm., D^{0}_{0} 0·9538, D^{16}_{4} 0·9396, $n^{16\cdot 2}_D$ 1·4356, which yields a *dioxime*, m. p. 131·5—132°, and a *monosemicarbazone*. m. p. 197—198°. By oxidising methylheptenone with permanganate, Harries (Abstr., 1902, i, 345) obtained a glycol, and from this a diketone, both having similar properties to the above.

(2) The *oxide*, $CH_2{:}CMe{\cdot}[CH_2]_3{\cdot}COMe$ or



$$\begin{array}{l}CH(CHMe_2)\\ |\\ O\end{array}\!\!>CH{\cdot}CH_2{\cdot}COMe,$$

b. p. 115—116°/50 mm., D_0^0 0·9963, D_4^{16} 0·9826, $n_D^{16\cdot3}$ 1·44747. On hydration, it gives a *glycol*,

$$CHMe_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}CH_2{\cdot}COMe(?),$$

b. p. 143—145°/14 mm., D_0^0 1·0700, D_4^{16} 1·0583, $n_D^{16\cdot2}$ 1·4599, m. p. 62—63·5°, which is apparently different from the glycol described under (1). It gives, however, the same diketone on dehydration.

T. H. P.

Oxidation of Hexoses by Air in Presence of Alkali Hydroxides. José I. del Rosario (*Revista Filipina Med. Farm.*, 1910, 1, 191).—The oxidation of lævulose by air in presence of alkali hydroxide gives similar products to those obtained by the oxidation of hexoses by Fehling's solution (compare Nef, Abstr., 1898, i, 7; Anderson, Abstr., 1909, i, 881). The oxidation was carried out by bubbling air freed from carbon dioxide through a solution of 100 grams of lævulose in 3500 c.c. of water in which 300 grams of barium hydroxide were dissolved; 1·22 grams of carbon dioxide, 18·3 grams of formic acid, and 77—80 grams of soluble gum were formed. The latter was resolved by Nef's method into glycollic, *d*- and *l*-glyceric, threonic, *d*-mannonic, and *d*-gluconic acids; in addition there was isolated α-hydroxymethyl-*d*-arabonic acid, which was also obtained by Spoehr (Abstr., 1910, i, 221) on oxidising lævulose with hydrogen peroxide in alkaline solution. No lactic, acetic, or oxalic acid was formed.

W. A. D.

Acetohalogen-glucoses and *p*-Bromophenylosazones of Maltose and Melibiose. Emil Fischer (*Ber.*, 1911, **44**, 1898—1904. Compare Fischer, Abstr., 1910, i, 716).—An optical inversion takes place when anhydrous liquid hydrogen chloride acts on α-pentacetyldextrose, and β-acetochlorodextrose, $[\alpha]_D$ +160·9° in chloroform, is the main product. The conditions for obtaining α-acetochlorodextrose in this manner have not been again realised (Fischer and Armstrong, Abstr., 1901, i, 257, 671). Similarly, with anhydrous hydrogen bromide, β-acetobromodextrose, $[\alpha]_D$ +199·28° in chloroform, is obtained from α-pentacetyldextrose. β-Acetobromodextrose is conveniently prepared in quantity by the action of anhydrous hydrogen bromide in glacial acetic acid on β-pentacetyldextrose.

The preparation of maltosone from phenylmaltosazone by boiling with benzaldehyde is much facilitated by the presence of 10—15% of benzoic acid in the benzaldehyde.

E. F. A.

Glucodecose and α-Glucodecitol. L. H. Philippe (*Compt. rend.*, 1911, **152**, 1774—1776. Compare this vol., i, 12).—Reduction of α-glucodeconic acid, or of the crude mixture of acid and lactone, leads to the production of *α-glucodecose*, $C_{10}H_{20}O_{16}$, m. p. 210°; in aqueous solution it has $[\alpha]_D$ +37°, but after twenty-four hours, or on boiling, shows $[\alpha]_D^{20}$ + 50·4°. The substance crystallises from water in anhydrous needles, but sometimes separates from concentrated solutions as hexagonal lamellæ containing $1H_2O$. The hydrated form shows the same rotation as the anhydrous substance. The *phenylhydrazone* crystallises in colourless, prismatic needles, m. p. 228—229°; the *osazone* in slender, yellow needles, m. p. 278°.

Further treatment of the decose with sodium amalgam converts it into *a-glucodecitol*, $C_{10}H_{22}O_{10}$, small, prismatic needles, m. p. 222° (sublimes), $[\alpha]_D$ +1·2°; the *deca-acetyl* derivative forms rectangular lamellæ, m. p. 149—150°, $[\alpha]_D$ +16·0° in chloroform solution. It combines with benzaldehyde to form an insoluble *acetal*.

W. O. W.

The Solubility of Lime in Solutions of Sucrose. H. CLAASSEN (*Zeitsch. Ver. deut. Zuckerind.*, 1911, 489—509).—To determine the solubility, well-stirred solutions of sucrose were heated with lime at different temperatures for definite intervals of time; the solution was rapidly filtered, and the lime determined in the filtrate, which was also examined polarimetrically.

The solubility of lime in pure solutions of sucrose is independent of the kind of lime when a good commercial sample is used, but it depends on the way in which the lime is added. Most lime dissolves when it is added directly as quicklime, whilst the solubility is the least when an old milk of lime is used. Under the same conditions of experiment the same quantity of lime dissolves.

The solubility increases with the quantity of lime (always in excess) added, until a solubility of 2—2·5% by weight is reached; further increase in the quantity of lime then slightly diminishes the solubility.

Rise in temperature diminishes the solubility, as also does a diminution in the concentration of the sucrose solution. When solutions which have been saturated at 0°, 20°, or 50° are heated in the presence of excess of lime, part of the lime is deposited as such, and not as calcium sucrate. The amount deposited varies with the conditions, but the amount remaining in solution is always greater than that which would be dissolved by direct addition of the lime at the higher temperature.

On warming the filtrates from solutions which have been saturated at 0° or 20°, a deposit is obtained which contains, not only lime, but also calcium sucrate as a gelatinous precipitate. Filtrates from solutions saturated at 50° give practically no deposit on heating to 90—100°.

If sucrose solutions which have been saturated at a high temperature are cooled in the presence of excess of milk of lime, the latter dissolves until the solubility is the same as that which would have been obtained directly at the lower temperature. With quicklime, however, the solubility is less than that obtained directly, but greater than in the case of milk of lime.

Impure sucrose solutions, such as the thin liquor obtained in the manufacture of sucrose, behave in the same manner as pure solutions of the same sucrose content. T. S. P.

Behaviour of Sucrose, and its Decomposition Products on Heating. J. E. Duschsky (*Zeitsch. Ver. Deut. Zuckerind.*, 1911, 581—608).—As the result of a series of experiments in which the change in the polarisation or in the cupric reducing power was studied, the conclusion is drawn that on heating dextrose either at atmospheric or under increased or reduced pressure, there is no marked increase in the polarisation or reduction in the reducing power. In some cases an increase in the polarisation is observed, indicating the formation of new products; this is due to the use of strong solutions or particularly to the presence of acids, for example, lactic and acetic acids. Lactic acid is particularly active, and in addition prevents the further decomposition of the new products formed. Normally the polarisation first increases on heating, and then decreases as the new products are decomposed. Alkalis have a similar decomposing action, and here in no case was an increase in polarisation observed, very small quantities of alkali being enough to reduce materially the polarisation. Heating of dextrose causes a very small reduction of the reducing power.

Under all pressures lævulose is readily decomposed at somewhat low temperatures. A higher temperature has a greater effect than a longer exposure to a lower temperature. A diminution of the pressure protects the lævulose to some extent. Less concentrated solutions of lævulose are more stable. The products of heating are probably optically inactive and have but a weak reducing power. Lactic and acetic acids protect lævulose from decomposition to some extent. E. F. A.

Yeast-Gum. Hans von Euler and Andor Fodor (*Zeitsch. physiol. Chem.*, 1911, 72, 339—346. Compare Salkowski, Abstr., 1894, i, 222, 316; Meigen and Spring, 1908, ii, 315).—The gum was prepared by Salkowski's method by means of the copper derivative, and in aqueous solution gave $[\alpha]_D^{20}$ +86·95°. The solution, purified by dialysis, does not give precipitates with phosphomolybdic or phosphotungstic acid. When hydrolysed with dilute sulphuric acid, the ratio mannose : dextrose lies between 40 : 30 and 40 : 40, the mannose being estimated as its phenylhydrazone. J. J. S.

Action of Hydriodic Acid on Starch and Dextrin. William Oechsner de Coninck and A. Raynaud (*Bull. Soc. chim.*, 1911, [iv], 9, 586—587. Compare this vol., i, 423).—The rate of hydrolysis of starch and dextrin by hydriodic acid is proportional to the concentration of the acid. In both cases complete hydrolysis can be effected, and it is reached more quickly with dextrin than with starch. T. A. H.

Electrolytic Decomposition of Cellulose. R. Oertel (*Chem. Zeit.*, 1911, 35, 713).—By the electrolysis of cellulose in a neutral potassium chloride bath the author has succeeded in transforming it into a product which is soluble in 10% sodium hydroxide, and is probably a new hydroxycellulose. It can be obtained either as retaining the fibrous structure of cellulose, or in such a form that it gives a milky, colloidal solution with water.

Details are reserved for a future communication. T. S. P.

Propylamine Peroxide. Eduard K. Kurovski and L. Nisenman (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 654—655).—In the authors' previous paper, the opinion was expressed that salts of pertitanic acid with organic bases (this vol., i, 183) are really compounds of pertitanic acid and peroxides of amines. They have now been able to prepare propylamine peroxide by the action of propylamine on an ethereal solution of hydrogen peroxide at a low temperature. A heavy, viscous liquid separates, and this, on further cooling, forms a white, crystalline mass. This compound is very unstable and was not completely analysed, but the relation between active oxygen and propylamine indicates that it has the formula $C_3H_7NH_3 \cdot O_2H$. T. H. P.

Perchlorates of the Choline and Neurine Group. Detection of Choline and Neurine. Karl A. Hofmann and K. Höbold (*Ber.*, 1911, **44**, 1766—1771).—The fact that quaternary ammonium perchlorates are less soluble in water than the perchlorates of primary, secondary, or tertiary amines (Abstr., 1910, i, 818) has been applied to the detection and isolation of choline and neurine. Choline perchlorate itself is too soluble (100 parts of water dissolve 290 parts of the salt at 15°) for this purpose. *Nitratocholine perchlorate*, $NO_2 \cdot O \cdot CH_2 \cdot CH_2 \cdot NMe_3 \cdot ClO_4$, m. p. 185—186° (previously described as choline perchlorate, *loc. cit.*), however, answers admirably. It is obtained by evaporating a 0·2% aqueous solution of choline perchlorate with 2 c.c. of 65% nitric acid on the water-bath, dissolving the residue in a little hot water, and adding a few drops of dilute perchloric acid.

Trimethyldibromoethylammonium perchlorate,

$$CH_2Br \cdot CHBr \cdot NMe_3 \cdot ClO_4,$$

large, doubly refracting plates (solubility 2·2 at 15°), and *bromovinyltrimethylammonium perchlorate*, $CH_2{:}CBr \cdot NMe_3 \cdot ClO_4$, elongated plates (solubility 2·65 at 14°), are about half as soluble as neurine perchlorate (*loc. cit.*). C. S.

Molecular State of Organic Ammonium Halides in Non-dissociating Media. Arthur Hantzsch and O. K. Hofmann (*Ber.*, 1911, **44**, 1776—1783).—Owing to the fact that certain organic ammonium halides have, not only different colours, but also different molecular weights in chloroform (Hantzsch and Leupold, Abstr., 1909, ii, 198), polymerism has been regarded as a cause of difference of colour, and Tinkler has attempted to represent the polymerides of pyridine and acridine methiodides by structural formulæ containing tervalent iodine (Trans., 1909, **95**, 921). Now the authors are of opinion that these supposed polymerides are really only molecular associations, because (i) the molecular weights of organic ammonium halides in the same solvent vary with the nature of the anion in such a way that the chlorides always have the smallest, the iodides the largest, molecular weights, the bromides and thiocyanates showing intermediate values; (ii) one and the same salt in different, non-dissociating media has a larger or smaller molecular weight according to the greater or smaller associating power of the solvent; (iii) the molecular weight occasionally increases with the concentration in one and the same solvent.

The preceding generalisations have been established by the following experiments. Examined by the ebullioscopic method in dry chloroform, tetrapropylammonium iodide is always quinquemolecular independently of the concentration, tetrapropylammonium chloride is most probably termolecular, whilst triethylammonium chloride is bimolecular and dimethyl- and diethyl-ammonium chlorides are quinquemolecular; the molecular weights of the last three, however, increase with increasing concentration. *iso*Amylammonium chloride does not produce any appreciable rise of the b. p. The degree of association of alkylammonium salts in chloroform does not depend on their molecular weights, but on the amount of the substitution (of the ammonium hydrogen atoms) and the nature of the halogen. The degree of association also depends largely on the solvent; thus, tetra-ethylammonium iodide, which by analogy with tetrapropylammonium iodide should be quinquemolecular in chloroform (actually its solubility is too small for experimental purposes), is almost unimolecular in pyridine.

The molecular weights in chloroform of the 5-phenyl-10-methylacridonium halides given by Hantzsch and Leupold (*loc. cit.*) are too small. The chloride and bromide are bi- to ter-molecular, the thiocyanate is ter- to quadri-molecular, whilst the iodide is constantly quinquemolecular. The simple 5-phenylacridonium halides, however, are only slightly associated in chloroform, whatever the halogen atom. Moreover, 5-phenyl-10-methylacridonium iodide is unimolecular in pyridine or phenol.

A comparison of the preceding results shows that aliphatic and aromatic ammonium halides of the same degree of substitution are about equally strongly associated in the same solvent.

The chloroform used for ebullioscopic measurements must be absolutely free from alcohol or water. A satisfactory quality can be obtained by shaking commercial chloroform with concentrated sulphuric acid for fifteen minutes, washing thoroughly with dilute sodium carbonate and with water, and drying over ignited potassium carbonate; the purified chloroform should be kept in a full bottle over potassium carbonate, in the dark (see further, this vol., i, 673).

C. S.

[Preparation of Quaternary Ammonium Bases.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 231806).—The salts obtained by the exhaustive alkylation of polyacidic bases are converted into quaternary ammonium bases, which are then decomposed by heat.

Hexamethylbutylene-aδ-diammonium iodide,

$$Me_3NI\cdot CH\ \cdot CH_2\cdot CH_2\cdot CH_2\cdot NMe_3I,$$

on treatment with silver oxide yields the corresponding *hydroxide*, a faintly coloured, strongly basic oil, which is decomposed by heat into erythrene (divinyl) and trimethylamine, whilst β-methylbutylene-$\alpha\delta$-diamine yields methyldivinyl (isoprene) when treated in a similar manner. F. M. G. M

Decomposition of Quaternary Ammonium Hydroxides. I.

JULIUS VON BRAUN (*Annalen*, 1911, **382**, 1—49).—The thermal decomposition of quaternary ammonium halides is analogous to that of the trialkylcyanoammonium bromides (compare Abstr., 1910, i, 189). As a rule, the smallest alkyl group is eliminated in the form of alkyl halide, but exceptions are met with when an olefine linking or a phenyl group is present in the alkyl group, and is adjacent to the nitrogen atom. The following are the common alkyl groups arranged in order of decreasing tendency to be eliminated as alkyl halide: allyl, benzyl, methyl, ethyl, propyl, butyl, amyl, phenyl (compare Collie and Schryver, Trans., 1890, **57**, 767; Meyer, this Journ., 1877, ii, 190). Other quaternary ammonium salts, for example, cyanides, thiocyanates, phenoxides, benzoates, and *p*-toluenesulphinates, behave in a similar manner. Experiments made with a number of quaternary ammonium hydroxides show that the behaviour is somewhat different; the order of the groups is: allyl, benzyl, ethyl, propyl, *iso*amyl, hexyl, methyl, *iso*butyl, phenyl (compare Collie and Schryver, *loc. cit.*; Claus and Rautenberg, Abstr., 1881, 584; Claus and Hirzel, 1887, 134; Merling, 1891, 1506). The following numbers give the percentage of the hydroxide transformed into methyl alcohol and dimethylalkylamine: $NMe_3Et{\cdot}OH$, 0%; $NMe_3Pr{\cdot}OH$, 5—10%; $C_4H_9{\cdot}NMe_3{\cdot}OH$, 50%; $C_5H_{11}{\cdot}NMe_3{\cdot}OH$, 60%; $C_6H_{13}{\cdot}NMe_3{\cdot}OH$, 73%; $C_7H_{15}{\cdot}NMe_3{\cdot}OH$, 75%; $C_8H_{17}{\cdot}NMe_3{\cdot}OH$, 75%, and $C_{16}H_{33}{\cdot}NMe_3{\cdot}OH$, 75%, and in each case a decomposition into trimethylamine and an alcohol or olefine also occurs. The following numbers also give the percentage of the hydroxide transformed into methyl alcohol and mixed tertiary base:

$OPh{\cdot}[CH_2]_3{\cdot}NMe_3{\cdot}OH$, 10%; $OPh{\cdot}[CH_2]_4{\cdot}NMe_3{\cdot}OH$, 55%;
$OMe{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%; $OPh{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%;
$NH_2{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%; $COPh{\cdot}NH{\cdot}[CH_2]_5{\cdot}NMe_3{\cdot}OH$, 60%.

The amount of olefine tends to diminish, and the amount of corresponding alcohol to increase, with an increase of the molecular weight of the alkyl group present in the trimethylalkylammonium hydroxide, so that trimethylcetylammonium hydroxide yields practically no cetene. The formation of an olefine or unsaturated compound is regarded as a primary decomposition, and is not attributed to a secondary decomposition of an alcohol. The following numbers are also given:

$CH_2Ph{\cdot}NMe_3{\cdot}OH$, little; $CH_2Ph{\cdot}CH_2{\cdot}NMe_3{\cdot}OH$, 0%;
$CH_2Ph{\cdot}[CH_2]_2{\cdot}NMe_3{\cdot}OH$, 70%; $CH_2Ph{\cdot}[CH_2]_4{\cdot}NMe_3{\cdot}OH$, 75%,

where the number indicates the percentage of the hydroxide decomposed into methyl alcohol and mixed tertiary amine. The general conclusion drawn is, that the manner in which a quaternary ammonium hydroxide decomposes depends first on the tendency of the mobile light groups to be eliminated as alcohols, and, secondly, on the tendency by means of the elimination of water to form olefines of symmetrical structure. The influence of the second factor is seen by a comparison of the products of decomposition of *n*-heptyl- and *n*-octyl-trimethylammonium hydroxide with the corresponding *cyclo*heptyl and *cyclo*octyl hydroxides (compare Willstätter, Abstr., 1901, i, 223; Willstätter and Waser, 1910, i, 366). Hexenyltrimethylammonium hydroxide (Merling) gives 80% of trimethylamine, owing to the fact that a symmetrical diolefine, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2$, can be formed.

As quaternary ammonium hydroxides are readily prepared, the manner in which they decompose on heating is of importance in connection with the preparation of mixed tertiary amines. The simplest method of preparing butyl-, amyl-, hexyl-, heptyl-, octyl-, and cetyl-dimethylamines and similar compounds is probably by decomposing the corresponding alkyltrimethylammonium hydroxides.

The quaternary ammonium salts can be prepared by the complete methylation of the primary amine, or, in some cases, by the union of trimethylamine with the necessary alkyl iodide or bromide. As a rule, the quaternary hydroxides can be distilled under atmospheric pressure, and the basic products separated from the neutral compounds by means of dilute acid.

Trimethyl-n-*butylammonium iodide,* $C_7H_{18}NI$, can be separated from potassium iodide as it dissolves in warm chloroform; it softens at 225°, and has m. p. 230° (decomp.). The corresponding hydroxide is syrupy, and when heated yields dimethylbutylamine, $NMe_2{\cdot}C_4H_9$, as a mobile oil, b. p. 96°, sparingly soluble in water. The *platinichloride,*

$$2C_6H_{15}N,H_2PtCl_6,$$

crystallises in brilliant, reddish-yellow plates, m. p. 110°, and the *picrate* separates from alcohol in similar plates, m. p. 98°.

Trimethylamylammonium iodide has m. p. 215° (Willstätter and Waser give 222°), and when decomposed gives Δ^{α}-amylene, but no amyl alcohol. α-Dimethylaminopentane yields a *picrate,*

$$C_7H_{17}N,C_6H_3O_7N_3,$$

which crystallises from alcohol in brilliant, long needles, m. p. 100°. Cyanogen bromide reacts with an ethereal solution of the tertiary base, yielding trimethylamylammonium bromide and *methyl*-n-*amylcyanamide,* $C_5H_{11}{\cdot}NMe{\cdot}CN$. The latter is an oil with a fragrant odour, has b. p. 109°, and when boiled with 30% aqueous alcoholic sulphuric acid yields methyl-*n*-amylamine (Löffler, Abstr., 1910, i, 632; the picrate has m. p. 121°, not 119—120°).

Trimethylhexylammonium iodide, $C_6H_{13}{\cdot}NMe_3I$, prepared from *n*-amylamine (Braun and Sobecki, this vol., i, 128), has m. p. 167°; the corresponding *hydroxide* is a solid, and when distilled yields Δ^{α}-hexylene, b. p. 62—63°/740 mm. and D^{20}_{20} 0·6686. *Dimethyl*-n-*hexylamine,* $C_6H_{13}{\cdot}NMe_2$, has b. p. 147°; the *platinichloride* is readily soluble in water and has m. p. 126—127°, and the *picrate* has m. p. 101°. *Trimethyl*-n-*heptylammonium iodide,* $C_{10}H_{24}NI$, forms crystalline plates, which soften at 143° and melt at 145°. The *hydroxide* is a solid, and when distilled yields Δ^{α}-heptylene, heptyl alcohol, and *dimethyl*-n-*heptylamine,* $C_9H_{21}N$. The tertiary base has b. p. 172°, yields a *platinichloride* in the form of felted, reddish-yellow needles, m. p. 139°, and a *picrate,* m. p. 83°. When treated with cyanogen bromide the tertiary base yields *methylheptylcyanamide,* $C_7H_{15}{\cdot}NMe{\cdot}CN$, as a colourless oil with b. p. 142°/15 mm., and this on hydrolysis with 33% sulphuric acid gives the secondary base, *methylheptylamine*, $C_8H_{19}N$, with b. p. 168°. The *picrate* crystallises in yellow needles, m. p. 97°, and the *platinichloride* in orange plates, m. p. 168°. The *carbamide*, $C_7H_{15}\cdot NMe\cdot CO\cdot NH_2$, crystallises from a mixture of ether and light petroleum in colourless, glistening plates, m. p. 100°.

Trimethyl-*n*-octylammonium iodide, prepared from trimethylamine and *n*-octyl iodide, has m. p. 138° (Mugdan, Abstr., 1898, i, 157, gives 139—141°); the *hydroxide* is a solid, and yields a mixture of octylene and octyl alcohol, together with *dimethyl*-n-*octylamine*, $C_8H_{17}\cdot NMe_2$, b. p. 194°. The *platinichloride* of the tertiary base forms long needles, m. p. 120°, and the *picrate* has m. p. 62—65°.

Trimethylcetylammonium iodide, $C_{19}H_{42}NI$, crystallises in felted needles, m. p. 222°, and on treatment with moist silver oxide shows a great tendency to form colloidal silver iodide, and this complicates the preparation of the quaternary hydroxide. The hydroxide when heated does not melt, and yields *dimethylcetylamine*, $C_{16}H_{33}\cdot NMe_2$, with b. p. 193—205°/18 mm. The base contains small amounts of non-nitrogenous products, and is best purified by means of the *picrate*, $C_{18}H_{39}N,C_6H_3O_7N_3$, which crystallises in long needles, m. p. 69°. The pure base has b. p. 203—205°/17 mm., and its *platinichloride* has m. p. 83°, and is practically insoluble in hot water. Cetyl alcohol is also formed during the decomposition of the hydroxide.

γ-Phenoxypropyltrimethylammonium iodide, $OPh\cdot[CH_2]_3\cdot NMe_3I$, is best prepared from trimethylamine and γ-phenoxypropyl iodide, and crystallises from alcohol in glistening plates, m. p. 174°. The hydroxide on distillation yields trimethylamine and phenyl allyl ether, together with a small amount of phenyl γ-dimethylaminopropyl ether (compare Knorr and Roth, Abstr., 1906 ,i, 457). *δ-Phenoxybutyltrimethylammonium iodide*, $C_{13}H_{22}ONI$, is sparingly soluble, and has m. p. 169°. When distilled the *hydroxide* yields *phenyl Δ^a-butenyl ethcr*,

$$CH_2:CH\cdot CH_2\cdot CH_2\cdot OPh,$$

b. p. 208—210°, together with *phenyl δ-dimethylaminobutyl ether*, $OPh\cdot[CH_2]_4\cdot NMe_2$, with b. p. 139—140°/13 mm. The *platinichloride* is oily, and the *picrate* has m. p. 108°.

ε-Phenoxyamyltrimethylammonium iodide, $OPh\cdot[CH_2]_5\cdot NMe_3I$, has m. p. 185°, and its oily *hydroxide* when distilled yields phenyl amylenyl ether (Braun and Trümpler, Abstr., 1910, i, 26) and *phenyl ε-dimethylaminoamyl ether*, $OPh\cdot[CH_2]_5\cdot NMe_2$. The latter is a colourless oil with b. p. 149°/11 mm., and yields a *picrate*, m. p. 99°.

Methyl ε-benzoylaminoamyl ether and phosphorus pentachloride yield benzonitrile and methyl ε-chloroamyl ether, together with αε-dichloropentane. When a mixture of the two latter compounds is boiled with an alcoholic solution of potassium iodide a mixture of the corresponding iodo-compounds is obtained, and these with trimethylamine yield *hexamethylamylenediammonium iodide*,

$$NMe_3I\cdot[CH_2]_5\cdot NMe_3I,$$

and a small amount of *ε-methoxyamyltrimethylammonium iodide*, $OMe\cdot[CH_2]_5\cdot NMe_3I$. The former is sparingly soluble in alcohol, turns brown at 200°, and decomposes between 268° and 273°. The latter dissolves readily in alcohol, and has m. p. 123—124°. When the hydroxide corresponding with the methoxy-salt is distilled, the products are methyl amylenyl ether and *methyl ε-dimethylaminoamyl ether*, $OMe\cdot[CH_2]_5\cdot NMe_2$.

ε-Benzoylaminoamyltrimethylammonium hydroxide (Abstr., 1910, i, 820) has to be decomposed under reduced pressure, and gives a 60% yield of benzoyldimethylamylenediamine and a 40% yield of pentenylbenzamide.

The *hydrochloride* of *aminoamyltrimethylammonium chloride*,

$$HCl,NH\cdot[CH_2]_5\cdot NMe_3Cl,$$

obtained by hydrolysing the corresponding benzoyl derivative with concentrated hydrochloric acid at 160°, forms hygroscopic crystals, and the *platinichloride* forms red crystals, m. p. 218°. To obtain the hydroxide, the chloride is transformed into the sulphate by means of silver sulphate, and this is then decomposed with barium hydroxide solution. *Aminoamyltrimethylammonium hydroxide* is a sticky mass, and when distilled under atmospheric pressure yields *as*-dimethylcadaverine and methyl alcohol, together with trimethylamine, water, and Δ^{α}-*pentenylamine*. The unsaturated amine is a colourless oil with an intense odour, has b. p. 91—94°, absorbs water and carbon dioxide, and yields a *platinichloride*, $C_{10}H_{24}N_2PtCl_6$, in the form of red plates, m. p. 166° (decomp.). The *aurichloride* sinters at 180° and has m. p. 195°, and the *benzenesulphonyl* derivative is oily and readily soluble in alkalis. The quaternary salt, *trimethylpentenylammonium iodide*, $C_5H_9NMe_3I$, has m. p. 195°.

β-Phenylethyltrimethylammonium bromide (this vol., i, 35) is readily prepared from β-phenylethyl bromide and trimethylamine, and the corresponding hydroxide decomposes into trimethylamine and styrene when its aqueous solution is heated on the water-bath (compare Freund, Abstr., 1899, i, 308; Pschorr, 1904, i, 767; 1905, i, 590).

γ-Phenylpropyltrimethylammonium hydroxide (compare Tafel and Senfter, Abstr., 1894, i, 579) is more stable, and is decomposed when strongly heated, giving a 70% yield of phenylpropyldimethylamine, b. p. 225°, and a 28% yield of propenylbenzene, b. p. 169—171°.

ε-Phenylamyltrimethylammonium hydroxide (Abstr., 1910, i, 844) gives a 75% yield of *ε-phenylamyldimethylamine*, $CH_2Ph\cdot[CH_2]_4\cdot NMe_2$, as a colourless liquid with b. p. 134—135°; its *picrate* and platinichloride are both oily. A 20% yield of *phenylamylene*,

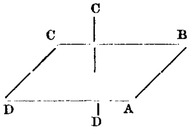
$$CH_2Ph\cdot CH_2\cdot CH_2\cdot CH{:}CH_2\ (?),$$

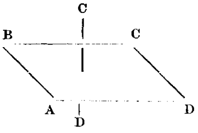
is also formed. It is a colourless liquid with b. p. 197—198°, D_4^{20} 0·8851, and n_D 1·5064. The position of the olefine linking has not been settled.

J. J. S.

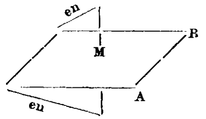
The Asymmetric Cobalt Atom. I.

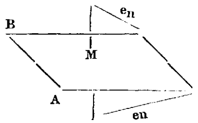
Alfred Werner [with V. L. King and E. Scholze] (*Ber.*, 1911, **44**, 1887—1898).—According to the author's co-ordination theory, compounds containing the following complex radicles should give optical isomerides: (1) $\left[{}^{B}_{C}M^{A_3}_{D}\right]$, when B, C, and D occupy the corners of one of the faces of an octahedron. (2) $\left[\begin{matrix}A\\B\end{matrix}M\begin{matrix}C_2\\D_2\end{matrix}\right]$, when the groups combined with the metal atom, M, take up the following positions:





In the second case it is not necessary for the groups C and D to be different, and one of the simplest cases would be when the groups CC and DD are replaced by ethylenediamine, giving compounds of the type $\left[\begin{matrix}A\\B\end{matrix}M\ en_2\right]$. When the groups A and B are in the *cis*-position, the two optical isomerides would be represented by the space formulæ:





The compounds 1-chloro-2-amminediethylenediaminecobalt salts, $\left[\begin{matrix}Cl\\H_3N\end{matrix}Co\ en_2\right]X_2$, and 1-bromo-2-ammine-diethylenediaminecobalt salts, $\left[\begin{matrix}Br\\H_3N\end{matrix}Co\ en_2\right]X_2$, have been prepared and resolved into their optically-active isomerides by means of *d*-bromocamphorsulphonic acid. The salts of the bromo-ammine series are the more easily resolved, because of the great difference in solubility between the isomeric *d*-bromocamphorsulphonates. In both series the *d*-bromocamphorsulphonate of the *d*-isomeride is the more sparingly soluble.

The active compounds are very stable. The aqueous solutions of the bromides of the bromo-ammine series can be kept for a long time at the ordinary temperature, or even heated just to boiling without undergoing racemisation. The activity is also maintained when the bromine atom in the complex is taken out with silver nitrate, according to the equation:

$$\left[\begin{matrix}Br\\H_3N\end{matrix}Co\ en_2\right]Br_2 + 3AgNO_3 + H_2O = \left[\begin{matrix}H_2O\\H_3N\end{matrix}Co\ en_2\right](NO_3)_3 + 3AgBr,$$

showing that the aquo-amminediethylenediaminecobalti-salts also give optical isomerides. No racemisation takes place when various salts are formed in the two series, as will be seen in the experimental part.

The fact that such active compounds have been prepared shows that the distinction between valency compounds and molecular compounds can be maintained no longer.

Optically-active Chloro-amminediethylenediaminecobalti-salts, YX_2, where $Y = \left[\begin{matrix}Cl\\H_3N\end{matrix}Co\ en_2\right]$.—The starting point for the preparation of these salts was the racemic compound 1-chloro-2-amminediethylenediaminecobalti-chloride, $\left[\begin{matrix}(1)\\(2)\end{matrix}\begin{matrix}Cl\\H_3N\end{matrix}Co\ en_2\right]Cl_2$, which was prepared by triturating acid-free 1 : 6-dichlorodiethylenediaminecobalti-chloride with concentrated ammonia. The green salt first dissolves and then the solution sets to a mass of red crystals of the required salt. Forty grams of this salt were dissolved in 250 c.c. of water, and a solution of 115 grams of silver *d*-bromocamphorsulphonate in 350 c.c. of water added. After collecting the silver bromide, the filtrate, on keeping, deposits short, slender, red prisms. These are collected as soon as felted, silky needles begin to form alongside them, and the filtrate, after four to six hours, solidifies to a mass of these needles. The former compound consists of d-1-*chloro-2-amminediethylenediaminecobalti*-d-*bromocamphorsulphonate*, $Y(O_3S{\cdot}O{\cdot}C_{10}H_{14}Br)_2$, and after recrystallisation from water forms flat, slender, prismatic crystals; $[\alpha]_C = +69{\cdot}5°$ and $[M]_C = +592{\cdot}14°$. The latter compound is l-1-*chloro-2-amminediethylenediaminecobalti*-d-*bromocamphorsulphonate*, and forms bluish-red, long, slender needles, with $[\alpha]_C = +31{\cdot}25°$ and $[M]_C = +362{\cdot}1°$. The d-*bromide*, YBr_2, was prepared from the bromocamphorsulphonate either by direct treatment with concentrated hydrobromic acid, or else by forming the sparingly soluble *dithionate*, and triturating that compound with concentrated hydrobromic acid. It forms cherry-red, small, leaf-like crystals, which have $[\alpha]_C = +43{\cdot}1°$ and $[M]_C = +172{\cdot}34°$. The rotatory power was unchanged when the bromide was again obtained after being transformed successively into the dithionate, bromide, platinichloride, nitrate and bromide, neither did heating the solution to 70° alter the rotation. The l-*bromide* was obtained in the same way as the d-*bromide*, and corresponded completely with the latter in colour, shape of crystals, and solubility; $[\alpha]_C = -43{\cdot}1°$ and $[M]_C = -168{\cdot}43°$.

Optically-active 1-*bromo-2-amminediethylenediaminecobalti-salts*, YX_2, where $Y = \left[\begin{matrix}\mathrm{Br}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\ en_2}\right]$, were prepared from 1:2-bromoamminediethylenediaminecobalti-bromide, $\left[\begin{matrix}(1)\ \mathrm{Br}\\ (2)\ \mathrm{H_3N}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Br_2}$. This salt was obtained according to the following two methods: (1) 1 : 6-Dibromodiethylenediaminecobalti-bromide is moistened with water and treated with 1 : 1 ammonia at a low temperature until the green salt is completely transformed into reddish-violet:

$$\left[\begin{matrix}(1)\ \mathrm{Br}\\ (6)\ \mathrm{Br}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Br} + \mathrm{NH_3} = \left[\begin{matrix}(1)\ \mathrm{Br}\\ (2)\ \mathrm{H_3N}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Br_2}.$$

(2) Ten grams of tetraethylenediaminediaquotetroldicobalticobaltosulphate and 30 grams of ammonium bromide are covered with water and the mixture heated. A reddish-violet solution results, which on cooling and saturating with sodium bromide deposits the required salt:

$$\left[\mathrm{en_2\,Co}\begin{matrix}\cdot\mathrm{OH}\cdot\\ \cdot\mathrm{OH}\cdot\end{matrix}\mathrm{Co(OH_2)_2}\begin{matrix}\cdot\mathrm{OH}\cdot\\ \cdot\mathrm{OH}\cdot\end{matrix}\mathrm{Co\ en_2}\right](\mathrm{SO_4})_2 + 6\mathrm{NH_4Br} + 2\mathrm{H_2O} =$$

$$[\mathrm{Co(OH_2)_6}]\mathrm{SO_4} + 2\left[\begin{matrix}\mathrm{Br}\\ \mathrm{H_3N}\end{matrix}\mathrm{Co\ en_2}\right]\mathrm{Br_2} + (\mathrm{NH_4})_2\mathrm{SO_4} + 2\mathrm{NH_3}.$$

The resolution of this salt by means of the *d*-bromocamphorsulphonate was carried out in a manner similar to that described for the chloroammine salt. The d-1-*bromo-2-amminediethylenediaminecobalti*-d-*bromocamphorsulphonate*, $Y(O_3S{\cdot}O{\cdot}C_{10}H_{14}Br)_2$, crystallises out first in the form of dark, thick, long, reddish-violet needles; $[\alpha]_C = +65{\cdot}7°$ and

$[M]_C = +588{\cdot}7°$. The addition of sodium dithionate to the mother liquors gives a precipitate of a racemic dithionate; this is collected, and further addition of sodium dithionate to the filtrate produces, on standing, a deposit of the active *dithionate*, which serves as the starting point for salts of the *l*-series.

The d-*chloride*, YCl_2, was obtained from the *d*-bromocamphorsulphonate by treatment with concentrated hydrochloric acid. It forms dark reddish-violet, shining, flat crystals, and has $[\alpha]_C = +50{\cdot}6°$ and $[M]_C = +175{\cdot}6°$. The solution shows no signs of racemisation after keeping for six days. The d-*bromide*, YBr_2, was obtained similarly, using hydrobromic acid, and forms small, shining, dark violet needles; $[\alpha]_C = +46{\cdot}25°$ and $[M]_C = +201{\cdot}65°$. The 0·8% aqueous solution was not racemised when heated for a short time at the boiling point. The d-*nitrate*, $Y(NO_3)_2,H_2O$, prepared from the bromocamphorsulphonate and fuming nitric acid, forms dark violet columns. It loses $1H_2O$ at 100°, and has $[\alpha]_C = +45{\cdot}0°$ and $[M]_C = +188°$.

The l-*bromide*, YBr_2, was obtained as dark reddish-violet, needle-shaped crystals by treating the *l*-dithionate with concentrated hydrobromic acid. It has $[\alpha]_C = -45°$ and $[M]_C = -196{\cdot}2°$. T. S. P.

Oxidation of the Amino-acids. I. Glycine and Cystine. W. Denis (*J. Biol. Chem.*, 1911, **9**, 365—374).—Glycine on complete oxidation with alkaline potassium permanganate yielded oxalic acid, carbon dioxide, ammonia, and nitric acid. If the oxidation was incomplete, traces of formic and glyoxylic acids could be detected. A modification of the existing methods for the preparation of cystine is described; on complete oxidation it yields sulphuric, oxalic, acetic, and nitric acids, carbon dioxide, ammonia, and free sulphur; if the oxidation was incomplete, traces of pyruvic acid were found.

W. D. H.

Action of *iso*Butylamine and Di-*iso*butylamine on α-Bromobutyric Acid. Jean Nivière (*Compt. rend.*, 1911, **152**, 1673—1674).—α-Hydroxybutyric acid is the only product when di-*iso*butylamine acts on α-bromobutyric acid. *iso*Butylamine reacts, forming iso*butylamine* α-iso*butylaminobutyrate*. α-iso*Butylaminobutyric acid*, $C_4H_9{\cdot}NH{\cdot}CHEt{\cdot}CO_2H$, occurs in pearly lamellæ, which sublime and decompose without melting. Heated in hydrogen chloride at 180—200° it does not form a piperazine derivative, but loses carbon dioxide, yielding the corresponding secondary amine. The amino-acid forms a *hydrochloride*, crystallising with $1{\cdot}5H_2O$, a *platinichloride* crystallising in red needles with $2H_2O$, decomp. 100—110°, an *aurichloride*, a *picrate*, and *copper* and *silver* salts. The *hydrochloride*, *platinichloride*, and *picrate* of the *ethyl* ester are uncrystallisable. W. O. W.

Action of Oxalyl Chloride on Amines and Amides. J. Th. Bornwater (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 42—46).—Oxalyl chloride in ethereal solution at the ordinary temperature gives with piperidine, oxalylpiperidide; with aniline, oxanilide, and with *o*- and *m*-nitranilines, the corresponding dianilides. With 2 : 4-dinitroaniline in boiling benzene, oxalyldi-2 : 4-dinitroanilide resulted.

Oxalyl chloride reacts *directly* in boiling benzene with the hydrochlorides of the amines, such as aniline and piperidine, also with those of the amino-acid esters. Of the latter, the following compounds have been prepared:

Oxalyldiglycine ethyl ester, $C_2O_2(NH{\cdot}CH_2{\cdot}CO_2Et)_2$, m. p. 143°.

Oxalyldiglycylglycine ethyl ester,

$$C_2O_2(NH{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et)_2,$$

lustrous leaflets, giving the biuret reaction, m. p. 250°.

Oxalyldi-diglycylglycine ethyl ester,

$$C_2O_2(NH{\cdot}CH_2{\cdot}[CO{\cdot}NH{\cdot}CH_2]_2{\cdot}CO_2Et_2,$$

forming silky needles, giving a reddish-violet biuret reaction, m. p. 302°.

As an example of the amino-derivatives of dibasic acids, the hydrochloride of the diethyl ester of glutamic acid was found to give *oxalyldi-glutaminic diethyl* ester,

$$C_2O_2[NH{\cdot}CH(CO_2Et){\cdot}CH_2{\cdot}CH_2{\cdot}CO_2Et]_2,$$

m. p. 94·5°.

The author suggests the possibility of obtaining similar oxalyl compounds from polypeptides in general, and of the ultimate synthesis of the proteins, which, as shown by Schützenberger many years ago, all yield oxalic acid by resolution with barium hydroxide.

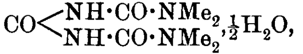
With simple amides, oxalyl chloride yields in some cases carbonyl and not oxalyl derivatives. For example, with benzamide, di-benzoylcarbamide, and with chloroacetamide, *dichloroacetylcarbamide*,

$$CO(NH{\cdot}CO{\cdot}CH_2Cl)_2,$$

white needles, m. p. 171°, is produced, but benzanilide gives *oxalyl di-benzanilide*, $C_2O_2(NPh{\cdot}COPh)_2$, m. p. 210°.

Ethyl urethane yields carbonyl diethylurethane, but methylethyl urethane gives *oxalyldimethylethylurethane*, $C_2O_2(NMe{\cdot}CO_2Et)_2$, m. p. 67°. Carbamide gives, in ether at the ordinary temperature, parabanic acid and, apparently *oxalyldiureide*, $C_2O_2(NH{\cdot}CO{\cdot}NH_2)_2$, which is quite different from Grimaux's compound (Abstr., 1880, 105) wrongly termed oxalyldiureide in German literature. It is quite insoluble in the ordinary solvents, and gives no biuret reaction.

s-Dimethylcarbamide gives cholestrophan, but *as*-dimethylcarbamide (in boiling benzene) gives *carbonyldi*-as-*dimethylcarbamide*,



$$CO{<}\begin{matrix}NH{\cdot}CO{\cdot}NMe_2\\NH{\cdot}CO{\cdot}NMe_2\end{matrix},\tfrac{1}{2}H_2O,$$

in beautiful prisms, m. p. 140°. J. D. K.

Iodogorgonic Acid. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1911, **72**, 505—506).—Polemical. A point of priority, Wheeler and Jamieson having claimed that they and not the author were the first to describe di-iodotyrosine as a decomposition product of iodogorgonic acid. W. D. H.

Reduction of Potassium Cyanate with Hydrogen. A. P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 650—651).—When dry hydrogen is passed through a tube heated at 400° in an electric furnace and containing a platinum boat filled with potassium cyanate, the latter undergoes reduction to the cyanide. The reaction is apparently complicated by secondary reactions, since the loss in weight of the cyanate often exceeds the increase in weight of a calcium chloride tube situate at the far end of the tube. T. H. P.

Formation of Cyanates from Nitrites. A. P. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 651—652).—If a mixture of sodium nitrite (5 grams) with 3—5 times the calculated quantity of finely divided carbon (5 grams) is introduced, in small portions, into a heated platinum dish or crucible, energetic reduction of the nitrite occurs, an aqueous solution of the fused mass no longer developing nitric oxide when shaken with mercury and sulphuric acid. The products formed are cyanate, a small proportion of cyanide and sodium carbonate, together with other cyanogen compounds of an acid character. One of the latter forms a barium salt which is soluble in a neutral solution, but is immediately deposited in shining scales on addition of a small quantity of potassium hydroxide; when freshly prepared, this salt does not give any evolution of gas when treated with acid, but it darkens later and then yields with acids, "carbon acid" gas, the weight of which is rather less than that of carbon dioxide.

T. H. P.

Oxidation of Sodium Cyanamide and Cyanates with Hydrogen Peroxide and Alkaline Bromine Solution. A. P. Lidoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 652—653).—By the interaction of sodium cyanamide solution and a solution of bromine in sodium hydroxide, free from carbon dioxide, in a nitrometer, only about 15—25% of the nitrogen is evolved. Decomposition of the alkaline solution with phosphoric acid results in the development of "carbon acid" gas with a small admixture of hydrogen bromide.

A 5% solution of sodium cyanamide was oxidised by hydrogen peroxide, the latter being added first in the cold and finally on boiling until the solution, which originally gave a yellow precipitate of lead cyanamide with lead acetate, gave a pure white precipitate. On boiling the liquid, a distinct smell of ammonia was observed. To the cooled liquid, lead acetate was added as long as a precipitate was formed, this being then washed with water, alcohol and ether. The lead salt weighed 12 grams, and the gas evolved with potassium hydroxide, 1·902 grams.

When potassium cyanate and an alkaline solution of bromine are allowed to react and barium chloride is added to the liquid, a precipitate is obtained which, with phosphoric acid, gives a quantity of "carbon acid" gas, 1·872—1·915, corresponding closely with that obtained from the cyanamide; similar results are obtained when the oxidation is effected by hydrogen peroxide.

The conclusion is drawn that, under the above conditions, the cyanogen group undergoes oxidation to oxycyanogen, CNO.

T. H. P.

Constitution of Prussian Blue. Arnaldo Brioni (*Boll. Chim. Farm.*, 1911, **50**, 165—169).—Polemical. The author furnishes arguments and experimental evidence against the view put forward by

Tarugi and Revello (*Atti VI Congr. Chim. appl.*, 1906) that Prussian blue is to be regarded as a ferrous or ferrous potassium salt of an oxyferrohydrocyanic acid. R. V. S.

Cobaltinitrites. ARTHUR ROSENHEIM and ABRAHAM GARFUNKEL (*Ber.*, 1911, **44**, 1865—1873).—The authors show that the complex cobaltinitrites previously investigated by Rosenheim and Koppel (Abstr., 1898, ii, 430), and salts of a cobalt-3-hydroxo-3-nitrite anion studied by Hofmann and Buchner (Abstr., 1909, i, 775) belong to the same class. Two cobalt-3-guanidinium-3-hydroxo-3-nitrites have also been obtained, these probably being isomerides, as predicted by Werner's theory, and the first of their kind. Furthermore, a new class of compounds, the cobalt-2-acetylacetonato-2-nitrites, has been prepared.

Cobalt-3-hydroxo-3-nitrites.—When a concentrated solution of cobalt-3-sodium-6-nitrite, $Na_3Co(NO_2)_6$, to which an equimolecular proportion of guanidine carbonate has been added, is evaporated over sulphuric acid, amber-coloured, tabular crystals are obtained, having the composition $(CN_3H_6)_2Na[Co(NO_2)_6]$, which show all the reactions of the cobalt-6-nitrites. When 3 mols. of guanidine carbonate are used to 1 mol. of the cobaltinitrite, a deep red solution results, from which garnet-red, shining crystals, having the composition $(CN_3H_6)_3[Co(OH)_3(NO_2)_3]$, are obtained. They agree, in all their properties, with the crystals described by Hofmann and Buchner as having the composition $(CN_3H_6)_2Na[Co(OH)_3(NO_2)_3]$, but do not contain sodium.

The mother liquors from the garnet-red crystals give a further deposit of dark brick-red needles, having the formula

$$(CN_3H_6)_3[Co(OH)_3(NO_2)_3],$$

and agreeing in properties and composition with the compound previously obtained by Hofmann and Buchner.

The two compounds of the same composition (garnet-red crystals = A; brick-red = B) differ in appearance, solubility, and some precipitation reactions. With a solution of thallous nitrate, A gives immediately a microcrystalline, cinnabar-red precipitate, having the composition $Tl_2H[Co(OH)_3(NO_2)_3]$, whereas B, after a few minutes, deposits brownish-red crystals of the formula $Tl_2(CN_3H_6)[Co(OH)_3(NO_2)_3]$.

The *zinc* salt, previously prepared by Rosenheim and Koppel (*loc. cit.*), is now found to have the formula

$$ZnH[Co(OH)_3(NO_2)_3],4H_2O;$$

with thallous nitrate the solution deposits the above-mentioned cinnabar-red thallium salt, proving that the zinc salt belongs to the cobalt-3-hydroxo-3-nitrites. The *silver* salt has the formula

$$Ag_2H[Co(OH)_3(NO_2)_3].$$

Cobalt-2-hydroxo-4-nitrites.—The strontium salt,

$$SrH[Co(OH)_2(NO_2)_4],4H_2O,$$

is the only one which has been obtained pure. It is prepared by leading nitrous gases into a cooled suspension of cobalt carbonate and strontium carbonate, and forms small, garnet-red prisms, which are unstable as such, and in solution, nitrous acid being liberated.

Cobalt-2-acetylacetonato-2-nitrites.—When concentrated solutions of sodium acetylacetonate and sodium cobaltinitrite are mixed and kept, purple-red crystals are deposited, having the composition

$$Na[Co(C_5H_7O_2)_2(NO_2)_2],5H_2O,$$

which lose $5H_2O$ in a vacuum over sulphuric acid. The anhydrous salt is also obtained as slender, bright-red needles, when the solution crystallises at 30°. The aqueous solution gives characteristic precipitates with salts of the alkali metals, of thallium and of silver. The *potassium* salt, $K[Co(C_5H_7O_2)_2(NO_2)_2],H_2O$, forms hair-like, light brownish-red needles; the *ammonium*, *caesium*, and *rubidium* salts are similar in appearance to the potassium salt. The *thallium* salt, $Tl[Co(C_5H_7O_2)_2(NO_2)_2]$, forms a microcrystalline, brownish-yellow precipitate. Dilute solutions of the sodium salt give, with silver nitrate, reddish-brown, shining needles of the composition

$$Ag[Co(C_5H_7O_2)_2(NO_2)_2],$$

whereas a saturated solution gives a dark yellow precipitate of the composition $Ag_2[Co(C_5H_7O_2)_2(NO_2)_3]$.

A solution of the sodium salt, on being boiled, deposits deep green crystals, together with brown, flocculent decomposition products. The crystals are soluble in ether, and consist of cobaltiacetylacetonate, $Co(C_5H_7O_2)_3$. When sodium acetylacetonate is added to the mother liquors from which the salt $Na[Co(C_5H_7O_2)_2(NO_2)_2]$ has crystallised, bright red, hair-like needles having the composition $Na[Co(C_5H_7O_2)_3]$ are obtained. This compound gives the colour reaction of acetylacetone with ferric chloride, whereas the complex cobalt-2-acetylacetonato-2-nitrites do not.

Other 1 : 3-diketones, such as benzoylacetone, as also acetoacetic ester, give compounds analogous to those obtained with acetylacetone.

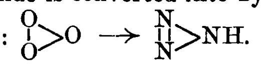
Zinc and *cadmium acetylacetonates*, $Zn(C_5H_7O_2)_2$ and $Cd(C_5H_7O_2)_2$, were obtained as white needles by the action of sodium acetylacetonate on zinc and cadmium sulphates respectively. T. S. P.

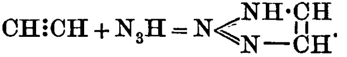
Synthesis of Pentamethylenediguanidine. OTTO RIPKE (*Zeitsch. physiol. Chem.*, 1911, 72, 484—485).—When an aqueous solution of pentamethylenediamine is left in contact with a large excess of cyanamide for seventeen days in a desiccator at the ordinary temperature, the solution then treated with sulphuric acid and silver sulphate, then neutralised with barium hydroxide and filtered, and the filtrate saturated with barium hydroxide, a precipitate is obtained, which, after treatment with sulphuric acid and hydrogen sulphide, yields pentamethylenediguanidine sulphate. This forms well developed crystals, sparingly soluble in water, and is not molten at 300°.

The *aurichloride*, $C_7H_{18}N_6,2HAuCl_4$, crystallises well, and has m. p. 161°. The structural formula suggested for the base is

$$CH_2[CH_2{\cdot}CH_2{\cdot}NH{\cdot}C(NH_2){:}NH]_2.$$

The reaction between cyanamide and pentamethylenediamine is quite different from that between cyanamide and tetramethylenediamine (Kossel, Abstr., 1910, i, 655). J. J. S.

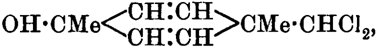
Relations between Certain Derivatives of Oxygen and of Nitrogen. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 625—627. Compare Abstr., 1910, ii, 844, 948).—Harries (Abstr., 1910, i, 607) has shown that the action of ozone on an oxime results in the formation of an ozonide, which has a ring structure, and which can be resolved into a ketone and nitric acid. The latter contains the grouping O·N(OH)·O in place of the O·O·O grouping of the ozone. Nitric acid can further be transformed into the amino-compound, $O\cdot N(NH_2)\cdot O$, which readily loses a molecule of water, giving nitrous oxide, N·N·O, two of the oxygen atoms of ozone now having been replaced by nitrogen atoms. Then, by the action of ammonia in the form of its sodium derivative, nitrous oxide is converted into hydrazoic acid, the total change from ozone being:  $\overset{O}{\underset{O}{|}}{>}O \longrightarrow \overset{N}{\underset{N}{\|}}{>}NH$. These two extreme terms of this series of changes exhibit considerable similarity. Thus, they are both formed with absorption of heat and are explosive, and both are poisonous and have suffocating odours. Both react with compounds having multiple linkings, ozone forming ozonides and hydrazoic acid the analogous triazoles:

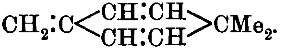


$$CH{:}CH + N_3H = N{<}\begin{matrix}NH\cdot CH\\ \qquad \|\\ N—CH\end{matrix}.$$

T. H. P.

Hydroaromatic Compounds. Hydrocarbon, C_9H_{12}, of the Semibenzene Series. KARL AUWERS and KARL MÜLLER (*Ber.*, 1911, **44**, 1595—1608).—The previously described semibenzene derivatives all contain chlorine, whilst hydroaromatic ketones unite with hydrogen and form phenols with the elimination of methylene chloride when attempts are made to prepare semibenzene derivatives from them. The alcohols obtained from these ketones by the Grignard reaction behave differently.

The alcohol,  $OH\cdot CMe{<}\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}{>}CMe\cdot CHCl_2$, is converted on treatment with sodium and moist ether into 1 : 1 : 4-*trimethyl*cyclo-$\Delta^{2,5}$-*hexadiene*-4-*ol*, although the yield is unsatisfactory, and this is readily converted into 1 : 1-*dimethyl*-4-*methylene*cyclo-$\Delta^{2,5}$-*hexadiene*,



$$CH_2{:}C{<}\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}{>}CMe_2.$$

The alcohol, *trimethyl*cyclo*hexadienol*, crystallises in colourless, lustrous needles, m. p. 43—44°, b. p. 169—170°/760 mm., and is characterised by the fact that when pure it distils without decomposition. On the other hand, it is very sensitive to acids, and even pure preparations decompose slowly on keeping. Strong and weak acids and acid salts all bring about the decomposition to the hydrocarbon, which, being insoluble in water, has its presence made evident by the aqueous solution of the alcohol becoming cloudy.

The physical constants of the new hydrocarbon are compared with those of the isomeric benzene derivatives mesitylene, ψ-cumene and *p*-methylethylbenzene. Owing to the ease with which it undergoes polymerisation or rearrangement, the purification is a matter of great difficulty; it is best accomplished by rapid distillation in steam under reduced pressure.

The hydroaromatic hydrocarbon has a lower density, D_4^{20} 0·839, than its aromatic isomerides. Spectrochemically the high exaltation of the specific refractive and dispersive powers of the hydrocarbon is of interest.

Unlike the chlorinated semibenzene, the hydrocarbon is only slowly changed by heat even at 160°, and the products are mainly condensation products, D_4^{20} 0·8837, n_D^{20} 1·51209.

Aromatic products were obtained by distilling the methylene derivative in hydrogen under reduced pressure, amongst which ψ-cumene was identified. It is undecided whether this is formed during distillation or at the time of decomposition of the hydroaromatic alcohol. The methylene derivative is immediately oxidised in the cold by potassium permanganate; it unites with bromine, but a mixture of products is formed. Several hydrocarbons are formed on reduction with sodium and moist ether. E. F. A.

Old and New Benzene Formulæ. ISRAEL LIFSCHITZ (*Zeitsch. angew. Chem.*, 1911, **24**, 1153—1161).—An account of the various structural formulæ which have been put forward for the benzene molecule. The author favours Werner's formula, but considers that it will be possible to combine it with that of Stark in such a way that all the various reactions and phenomena can be accounted for.

T. S. P.

Bromination of *cyclo*Hexane. F. BODROUX and FELIX TABOURY (*Bull. Soc. chim.*, 1911, [iv], **9**, 592—594. Compare Markownikoff, Abstr., 1898, i, 637).—In diffused sunlight bromine acts extremely slowly on *cyclo*hexane at its boiling point, but in direct sunlight the boiling hydrocarbon decolorises bromine rapidly, forming *cyclo*hexyl bromide and some polybromo-derivatives. In quartz vessels and exposed to ultra-violet rays from a mercury lamp, the hydrocarbon does not react with bromine. *cyclo*Hexyl bromide at the boiling point, 162°, reacts with bromine, forming some dibromo*cyclo*hexane, b. p. 144—145°/100 mm., which is probably the 1 : 2-isomeride. T. A. H.

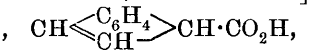
Additive Compounds of *m*-Dinitrobenzene. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 46—47).—A solution of *m*-dinitrobenzene in aniline deposits on cooling red crystals, m. p. 41—42°, losing aniline on exposure to air. Similarly, dimethyl-*p*-toluidine yields a black, unstable compound, m. p. 43°. With α-naphthylamine in alcoholic solution are produced red needles, m. p. 57°. Similarly, dimethyl-β-naphthylamine gives dark red needles, m. p. 52—53°. Tetramethyl-*m*-phenylenediamine yields a very dark garnet-red substance, m. p. 58°. With benzidine are obtained black crystals, m. p. 128°, decomposed by hydrochloric acid. All the foregoing compounds contain an equal number of molecules of amine and dinitrobenzene.

4 : 4′-Tetramethyldiaminodiphenylmethane gives garnet-red plates or crystals, m. p. 76°, containing 2 mols. of amine per mol. of dinitrobenzene.

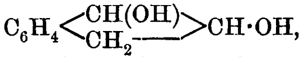
4 : 4′-Tetramethyldiamidobenzophenone in alcoholic solution gives red plates, m. p. 91°, containing 2 mols. of dinitrobenzene per mol. of the base. J. D. K.

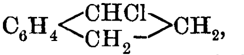
Indene Series. RUDOLF WEISSGERBER (*Ber.*, 1911, **44**, 1436—1448). [With F. KRAFT.]—1-Alkyl derivatives of indene (compare Marckwald, Abstr., 1900, i, 434) can be prepared by the action of alkyl halides on sodioindene (Abstr., 1909, i, 219). As a rule, not readily volatile tarry products are also formed. With benzyl chloride and toluene a 30% yield of 1-benzylindene is obtained. It has b. p. 185°/18 mm., and crystallises from alcohol in yellow prisms, m. p. 33—34°.

[With P. BREHME.]—*Di-indene*, $C_{18}H_{16}$, can be obtained by boiling indene for ten to twenty-four hours with its own weight of glacial acetic acid; it has b. p. 235—245°/16 mm., and crystallises from glacial acetic acid in nodular masses, m. p. 51°. It is stable towards oxidising agents, and a quantitative yield can also be obtained by boiling indene for fifteen hours with syrupy phosphoric acid.

[With M. VOGEL, A. DOMBROWSKY, and F. KRAFT.]—A 75% yield of indene-1-carboxylic acid,  $\mathrm{CH}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CH}\end{matrix}{>}\mathrm{CH{\cdot}CO_2H}$, is obtained by passing dry carbon dioxide into the fused sodium indene from heavy benzene, and a theoretical yield by passing carbon dioxide into a xylene suspension of the finely divided sodioindene. It crystallises from toluene in needles, m. p. 156—157°, has b. p. 193—195°/12 mm. (compare Grignard and Courtot, this vol., i, 538), and differs entirely from the acid described by Perkin and Révay (Trans., 1894, **65**, 238). It combines with bromine slowly, and the additive *compound* has m. p. 136—137° (decomp.). The *methyl* ester, $C_{11}H_{10}O_2$, is a pale yellow oil, b. p. 153—154°/23 mm., with a fragrant odour; the *ethyl* ester has b. p. 164°/24 mm. When heated for several hours at 180° in an oil-bath, the acid yields *di-indenedicarboxylic acid*, $C_{20}H_{16}O_4$, which crystallises from boiling glacial acetic acid in compact needles, m. p. 265° (decomp.).

[With P. BREHME.]—Chlorohydroxyhydrindene (Spilker, Abstr., 1893, i, 519) is readily obtained by the addition of hypochlorous acid prepared by Wohl and Schweitzer's method (Abstr., 1907, i, 194) to indene.

Dihydroxyhydrindene,  $\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CH(OH)}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH{\cdot}OH}$, obtained by heating the chlorohydroxy-derivative with potassium acetate and acetic anhydride and then hydrolysing with potassium hydroxide solution (D 1·3), crystallises from water in brilliant needles, m. p. 158°. The products described by Spilker, m. p. 120°, and by Heusler and Schieffer, m. p. 98—99° (Abstr., 1899, i, 365), are evidently impure. The glycol yields β-hydrindone when warmed with dilute sulphuric acid.

1-*Chlorohydrindene*,  $\mathrm{C_6H_4}{<}\begin{matrix}\mathrm{CHCl}\\ \mathrm{CH_2}\end{matrix}{>}\mathrm{CH_2}$, is readily formed by passing hydrogen chloride into well cooled indene, and forms a colourless oil which reacts with the greatest readiness with water, yielding indene, 1-hydroxyhydrindene (compare König, Abstr., 1893, i, 587), and 1-hydrindyl ether. 1-Hydroxyhydrindene is odourless and crystallises with great readiness. The *methyl ether*, $C_9H_9{\cdot}OMe$, prepared by the action of sodium methoxide on the chloro-derivative, is a colourless oil with b. p. 98°/10 mm., and has an intense odour of acetal.

The *ethyl ether*, $C_{11}H_{14}O$, has b. p. 106—109°/16 mm., and 1-*acetoxyhydrindene*, $C_{11}H_{12}O_2$, has b. p. 135°/15 mm. or 241° under atmospheric pressure.

1-*Hydrindyl ether*, $(C_9H_9)_2O$, crystallises from alcohol and has m. p. 51—53°. J. J. S.

Ketens. XXIII. The Reactivity of Halogen Atoms Towards Metals. HERMANN STAUDINGER, KARL CLAR, and E. CZAKO (*Ber.*, 1911, **44**, 1640—1647).—The authors have investigated the behaviour of several halogen derivatives of methane, and of benzyl chloride, benzylidene dichloride, ω-chlorodiphenylmethane, benzotrichloride, di-ω-chlorodiphenylmethane, and ω-chlorotriphenylmethane towards zinc in ethereal solution, and find that the removal of halogen takes place readily only in the case of the three compounds last mentioned. From these observations the conclusion is drawn that the substitution of hydrogen by phenyl or chlorine increases the reactivity of the halogen atom. The influence exerted by the chlorine atom is, however, less than that of the phenyl group.

The entrance of substituents into the phenyl groups considerably modifies the reactivity of the chlorine atoms in di-ω-chlorodiphenylmethane. Whilst di-ω-chloro-4 : 4′-dimethoxydiphenylmethane reacts with zinc even more vigorously than di-ω-chlorodiphenylmethane, di-ω-chlorodiphenylmethane-4 : 4′-dicarboxyl chloride and methyl di-ω-chlorodiphenylmethane-4 : 4′-dicarboxylate are without action towards this metal.

Attention is also called to the fact that acyl chlorides do not react with zinc in ethereal solution, and, therefore, contrary to the usual view, the chlorine atom must be firmly combined with the carbonyl group. A similar behaviour is exhibited by many other halogen compounds, in which the halogen is attached to an unsaturated carbon atom. The apparent mobility of the chlorine atom of acyl chlorides is due, not to its feeble attachment, but to the presence of the unsaturated carbonyl group, which readily combines with water, alcohol, and amines.

The interaction of acyl chlorides with these compounds is represented by the following scheme:

$$R\cdot COCl + H\cdot R' \longrightarrow OH\cdot CRR'Cl \longrightarrow R\cdot COR' + HCl.$$

It is also found that acyl chlorides do not react with magnesium to give Grignard compounds, and this is explained by the chlorine atom being firmly combined with the carbonyl group.

The method previously described (Staudinger, Abstr., 1908, i, 654) for the preparation of aldehydes by the action of magnesium on imino-chlorides has been extended to *iso*butyrophenylimino-chloride, diphenylacetophenylimino-chloride, and triphenylacetophenylimino-chloride, but in no case could a reaction either with magnesium or with zinc be induced. The halogen atom of imino-chlorides is, therefore, firmly attached to the C⁚N group, and its apparent mobility in many reactions is referred to the intermediate formation of additive compounds, according to the scheme:

$$R\cdot CCl⁚NPh + H\cdot R' \longrightarrow CRR'Cl\cdot NHPh \longrightarrow R\cdot CR'⁚NPh + HCl.$$

The greater reactivity of imino-chlorides, as compared with acyl chlorides, towards alcohol, water, and amines is due to the greater additive power of the C:N group.

Di-ω-chlorodiphenylmethane reacts vigorously with zinc in ethereal solution, yielding αβ-dichlorotetraphenylethane, $CPh_2Cl{\cdot}CPh_2Cl$, together with tetraphenylethylene; if the mixture is heated, tetraphenylethylene is the sole product. According to the authors, ω chlorodiphenylmethyl is formed as an intermediate product in the reaction, but attempts to convert this into a peroxide by the passage of oxygen into the mixture during the reaction proved unsuccessful. Di-ω-chlorodiphenylmethane yields with zinc chloride a yellowish-green *additive* compound.

When treated with zinc in ethereal solution, benzotrichloride gives tolane dichloride (αβ-dichloro-*s*-diphenylethylene).

*Di-ω-chloro-*4 : 4′*-dimethoxydiphenylmethane,* obtained by the action of oxalyl chloride on dimethoxybenzophenone, has m. p. 101—102°, and gives with zinc chloride and mercuric chloride in ethereal solution red *additive* compounds, which are decomposed by water, yielding the original ketone. It reacts with zinc or mercury in ethereal solution, yielding 4 : 4′ : 4″ : 4‴*-tetramethoxytetraphenylethylene.*

*Methyl di-ω-chlorodiphenylmethane-*4 : 4′*-dicarboxylate,*

$$CCl_2(C_6H_4{\cdot}CO_2Me)_2,$$

prepared by the interaction of phosphorus pentachloride and methyl benzophenone-4 : 4′-dicarboxylate, crystallises in colourless needles, m. p. 73°.

iso*Butyrophenylimino-chloride,* $CHMe_2{\cdot}CCl{:}NPh$, prepared from phosphorus pentachloride and *iso*butyranilide, is a colourless liquid, b. p. 102—104°/11 mm.

Diphenylacetylphenylimino-chloride, $CHPh_2{\cdot}CCl{:}NPh$, forms colourless crystals, m. p. 90°.

Triphenylacetylphenylimino-chloride, $CPh_3{\cdot}CCl{:}NPh$, has m. p. 132°.

F. B.

Hydrogenation by means of Calcium and Alcohol. PIERRE BRETEAU (*Bull. Soc. Chim.*, 1911, [iv], **9**, 585—586, and *J. Pharm. Chim.*, 1911, [vii], **3**, 580—582).—The process depends on the utilisation of a reaction recorded by Doby (Abstr., 1903, i, 546), in which calcium reacts with ammonia to form hydrogen and calcium amide, the latter being then decomposed by alcohol, giving calcium ethoxide. The application of the method to phenanthrene, which is not reduced by calcium and alcohol alone, is as follows: Fifteen grams of calcium filings are placed in a litre flask provided with a reflux condenser. To this are added 5 grams of phenanthrene in 200 c.c. of alcohol, and the mixture is heated to boiling. Dry ammonia gas is then led into the mixture, and the flame extinguished as soon as hydrogen begins to be evolved. After the calcium is dissolved, the solution is boiled during one hour and then acidified with dilute hydrochloric acid. On cooling, tetrahydrophenanthrene separates as an oil, and may be separated and purified by distillation.

T. A. H.

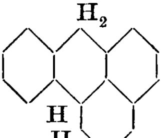
Phenanthrene Series. XXXI. Nitro- and Amino-phenanthrenes. JULIUS SCHMIDT and EUGEN HEINLE (*Ber.*, 1911, 44, 1488—1503).—1-Nitrophenanthrene has not yet been prepared. The four other possible isomerides are produced by the addition of a mixture of acetic anhydride and nitric acid, D 1·45, to a solution of phenanthrene in hot glacial acetic acid. The separation of the four compounds necessitates a tedious fractional crystallisation from alcohol, whereby 60% of pure 9-nitrophenanthrene, 2% of pure 3-nitrophenanthrene, and 20% each of approximately pure 2-*nitrophenanthrene*, m. p. 99°, and 4-*nitrophenanthrene*, m. p. 80—82°, are obtained, the yields being calculated on the crude nitrophenanthrenes; a very small amount of 2-nitrofluorene, produced from a trace of fluorene in the phenanthrene, has also been isolated. 2-Nitrophenanthrene crystallises in pale yellow rosettes, and yields 2-nitrophenanthraquinone when oxidised by chromic and acetic acids. 4-Nitrophenanthrene crystallises in yellow needles, and is oxidised to 4-nitrophenanthraquinone.

A methyl-alcoholic solution of 9-nitrophenanthrene is reduced by zinc dust and methyl-alcoholic ammonia, yielding two modifications of 9-aminophenanthrene, which are separated by crystallisation from alcohol. The less soluble α-form, m. p. 137—138°, which is the principal product, has been described by Schmidt and Strobel (Abstr., 1903, i, 691). The β-modification, m. p. 104°, forms a benzoyl derivative, m. p. 199°, identical with that obtained from the α-modification, yields 9-phenanthrylphenylcarbamide with phenylcarbimide much more slowly than does the α-modification, and is converted into the α-modification by acetylation and subsequent hydrolysis. The suggestion is made that the isomerism of the two modifications is due to the different distributions of the double linkings in the phenanthrene nucleus. In large quantities, 9-nitrophenanthrene is reduced most conveniently by tin and hydrochloric acid. 9-Aminophenanthrene forms a *picrolonate*, $C_{14}H_{11}N,C_{18}H_8O_5N_4$, m. p. 230—231° (decomp.), and a *perchlorate*, m. p. 185°.

4-*Aminophenanthrene*, m. p. 105°, obtained by reducing 4-nitrophenanthrene with stannous chloride and acetic acid, does not exist in two modifications, and forms a *hydrochloride*, *picrate*, m. p. 216° (decomp.), *picrolonate*, m. p. 195°, decomp. 232°, *benzoyl* derivative, m. p. 224°, and *acetyl* derivative, m. p. 190°; with ethereal phenylcarbimide, it yields s-*phenyl*-4-*phenanthrylcarbamide*, $C_{14}H_9\cdot NH\cdot CO\cdot NHPh$, m. p. 219—220°, resolidifying and subsequently melting at 279—280°.

C. S.

Identity of Graebe's *iso*Chrysofluorene with Dihydrobenzanthrene. ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1911, 44, 1671—1674).—Graebe's "*iso*chrysofluorene" (Abstr., 1894, i, 336), obtained by pyrogenic synthesis from 1-benzylnaphthalene, has the formula $C_{17}H_{14}$, and not $C_{17}H_{12}$. After purification by means of the picrate, it has m. p. 79—80°, and is identical with dihydrobenzanthrene (annexed formula: see this vol., i, 676). The red oxidation



product described by Graebe is probably a mixture of benzanthrone and anthraquinone-1-carboxylic acid. F. B.

New Method of Preparation of Benzylamine and Hexahydrobenzylamine.

PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, 153, 160—162).—The authors' method of preparing amines from aliphatic alcohols (Abstr., 1909, i, 292) has been applied by heating the vapour of benzyl alcohol and ammonia in the presence of thorium dioxide; at 330°, benzylamine is the chief product; at 370—380°, dibenzylamine. In practice, a resinous hydrocarbon is gradually deposited on the oxide, and the reaction must be interrupted from time to time in order to revive the catalyst by heating it at a dark red heat in the air.

When the vapour of the benzylamine produced by this method is passed, together with hydrogen, over nickel at 170—180°, considerable quantities of ammonia and toluene are formed, but also a fairly good yield of hexahydrobenzylamine is obtained, identical with that obtained by Démianoff. The experiment fails with benzylamine produced by other methods, probably owing to traces of impurities which destroy the activity of the catalyst. C. S.

Preparation of Sulphonated Naphthalene Derivatives.

KALLE & Co. (D.R.-P. 233934).—When naphthalenepolysulphonic acids are boiled with zinc dust in aqueous solution (preferably in the presence of alkali or ammonium chloride), the sulphonic groups which would be attacked in the case of an alkali fusion are eliminated and replaced by hydrogen. By this means α-naphthylamine-3 : 6 : 8-trisulphonic acid yielded the 3 : 6-disulphonic acid; α-naphthylamine-4 : 6 : 8-trisulphonic acid, the 4 : 6-disulphonic acid; α-naphthylamine-3 : 5 : 7-trisulphonic acid, the 3 : 7-disulphonic acid; α-naphthylamine-2 : 5 : 7-trisulphonic acid, the 2 : 7-disulphonic acid; β-naphthylamine-3 : 6 : 8-trisulphonic acid was converted into the 3 : 6-disulphonic acid; α-naphthol-3 : 5 : 7-trisulphonic acid into 3 : 7-disulphonic acid; α-naphthylamine-3 : 8-disulphonic acid into 3-monosulphonic acid; α-naphthylamine-4 : 8-disulphonic acid yielded naphthionic acid; β-naphthylamine-4 : 8-disulphonic acid a mixture of the 4- and the 8-monosulphonic acids; and α-naphthol-8-amino-4 : 6-disulphonic acid, the α-naphthol-8-amino-6-sulphonic acid. F. M. G. M.

Preparation of Sulphonated Aromatic Ammonium Compounds.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 233328).—The sulphonation of aromatic quaternary ammonium bases yields crystalline compounds soluble in water, which probably have the constitution of inner anhydrides.

Phenylnaphthylmethyldimethylammonium chloride, m. p. 124°, prepared from dimethylaniline and ω-chloro-β-methylnaphthalene, yields a crystalline *sulphonic acid.*

Phenylbenzyldimethylammonium hydroxide sulphonic anhydride, large, colourless crystals, is obtained by treating a cooled solution of *phenylbenzyldimethylammonium chloride* in concentrated sulphuric acid with fuming acid (23% SO_3), and heating the mixture at 25—30°; when acid containing 70% SO_3 is employed, a somewhat soluble *disulphonic acid* is produced.

When the *phenylbenzyldimethylammonium hydroxide sulphonic anhydride* prepared from benzyl chloride and dimethylaniline-*m*-sulphonic acid is sulphonated, an isomeric disulphonic acid is obtained.

F. M. G. M.

The Influence of the Medium and of Light on the Rate of Decomposition of Quaternary Ammonium Salts. Edgar Wedekind, F. Paschke, and, in part, W. Mayer (*Ber.*, 1911, **44**, 1406—1415. Compare Abstr., 1908, i, 723).—The racemisation of *d*-phenylbenzylmethylpropylammonium bromide in chloroform and in chloroform mixed with other solvents has been studied.

The addition of 20% of a hydroxylic compound, such as methyl or ethyl alcohol, retards racemisation, as does acetone, whereas benzene and carbon disulphide favour decomposition. Solutions of phenylbenzylmethylethylammonium bromide in mixtures of ethyl alcohol and chloroform, or of ethyl alcohol and ethylene dibromide, have smaller electrical conductivities than solutions of the same concentration in ethyl alcohol alone.

The fact that the racemisation is less in hydroxylic solvents is probably due to the fact that in such solvents the salts are largely ionised, and that for racemisation (thermal dissociation) complete molecules are necessary. Labile salts, such as *l*-phenylbenzylmethyl (methylanilinoethyl) ammonium iodide (Wedekind and Mayer, Abstr., 1909, i, 186), can undergo decomposition in ionising media, but the reaction here is less rapid than in such solvents as chloroform. The reaction has been studied by both polarimetric and electrical conductivity determinations, and the results indicate that autoracemisation is to be attributed to a decomposition into tertiary amine and alkyl halide: $C_7H_7{\cdot}NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh^{\cdot} + I' \rightleftarrows C_7H_7{\cdot}NMePhI{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh \rightleftarrows C_7H_7I + NMePh{\cdot}CH_2{\cdot}CH_2{\cdot}NMePh$.

In determining the molecular conductivity it was noticed that the value for this fell to a minimum after about 103 hours, and then increased again, until after 1650 hours the original value was again reached. This is probably due to the fact that the benzyl iodide formed reacts with the solvent alcohol, forming hydrogen iodide and benzyl ethyl ether (compare Halban, Abstr., 1909, i, 627). The solid quaternary ammonium iodide also decomposes when kept, it loses in weight, owing to evolution of benzyl iodide, and its optical activity diminishes from $-95{\cdot}98°$ to $-91{\cdot}07°$ after 230 days.

The accelerating influence of light on the racemisation of quaternary ammonium salts appears to be of a purely thermal and non-actinic nature (compare Abstr., 1906, i, 419).

When a solution of *d*-phenylbenzylmethylallylammonium hydroxide in chloroform and a little alcohol is kept for forty-eight hours, a slight diminution in the rotation is observable (compare Abstr., 1905, i, 520). This is attributed, not to the decomposition of the base itself, but of a small amount of quaternary chloride formed by the reaction of the base with the chloroform. J. J. S.

Preparation of Hydroxyphenylethyldialkylamines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233069. Compare Abstr., 1906, i, 204, 761, 979; 1907, i, 151, 234, 336).—When the quaternary ammonium salts of *p*-hydroxyphenylethylamines are distilled, they furnish hydroxyphenylethyldialkylamines, and thus confirm the work of Gaebel and Léger, who formulated hordenine as *β*-*p*-hydroxyphenylethyldimethylamine (Abstr., 1907, i, 151); in the present instance hordenine methiodide, m. p. 230° (prepared from *p*-hydroxyphenylethylamine), furnished on distillation hordenine identical with the product described by these authors.

Hordenine methochloride has m. p. 285° (decomp.).

m-*Ethoxyphenylethylamine hydrochloride*, m. p. 160—165° (prepared from *m*-ethoxyphenylpropionamide and sodium hypochlorite), when heated at 100° with alcoholic sodium hydroxide and methyl chloride yields m-*ethoxyphenylethyltrimethylammonium chloride*, m. p. 130°; the *methiodide* forms colourless needles, m. p. 185—190°, and on distillation in a vacuum furnishes a quantitative yield of m-*ethoxyphenylethyldimethylamine*, a colourless liquid, b. p. 130—133°/15 mm., and convertible by the action of hydrogen iodide into m-*hydroxyphenylethyldimethylamine*, m. p. 103°. F. M. G. M.

Preparation of Hydroxyphenylethylamines and their Alkyl Ethers. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233551).—It is found that Hofmann's reaction for the conversion of amides into amines can be applied for the preparation of hydroxyphenylethylamines from hydroxyphenylpropionic acids.

β-*p*-Methoxyphenylpropionic acid, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO_2H$, was converted by known methods into p-*methoxyphenylpropionamide*, $OMe\cdot C_6H_4\cdot CH_2\cdot CH_2\cdot CO\cdot NH_2$, needles, m. p. 120°, which by treatment with sodium hypochlorite yielded *p*-methoxyphenylethylamine (its hydrochloride has m. p. 210°), and was subsequently converted with hydrogen iodide into *p*-hydroxyphenylethylamine.

Ethyl β-p-*hydroxyphenylpropionate*, m. p. 45°, b. p. 185°/13 mm., furnished an *amide*, m. p. 125°, and subsequently *β*-*p*-hydroxyphenylethylamine.

m-*Ethoxyphenylethylamine hydrochloride* has m. p. 160—165°, and m-*hydroxyphenylethylamine hydrochloride*, m. p. 145°.

o-*Ethoxyphenylethylamine* and o-*hydroxyphenylethylamine hydrochloride* have m. p. 210° and m. p. 155° respectively. F. M. G. M.

The Separation of 6-Chloro-*m*-cresol by the Chlorination of Pure *m*-Cresol, or of the Technical Mixture of *m*- and *p*-Cresols. ARTHUR LIEBRECHT (D.R.-P. 233118. Compare this vol., i, 537).—Pure 6-chloro-*m*-cresol can be isolated from the technical mixture of *m*- and *p*-cresol by chlorination and subsequent sulphonation of the mixed products with sulphuric acid at 100°. Any 3-chloro-*p*-cresol obtained in the first operation escapes sulphonation, whilst the sulphonated 6-chloro-*m*-cresol is separated in the form of its sparingly soluble sodium salt, and the sulphonic group eliminated by known methods. F. M. G. M.

Preparation of 6-Amino-α-naphthol-5-sulphonic Acid.

KALLE & Co. (D.R.-P. 233105).—β-Naphthylamine-1 : 5-disulphonic acid (prepared by further sulphonation of β-naphthylamine-1-sulphonic acid) when fused at 210—230° with potassium hydroxide yields 6-*amino-α-naphthol-5-sulphonic acid*, which crystallises from water in slender needles or compact crystals and combines very readily (in alkaline solution) with diazonium salts; its solution in sodium carbonate exhibits a green fluorescence. F. M. G. M.

Preparation of Sulphaminobenzoylaminonaphthols and their Sulphonic Acids.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233117).—Sulphaminobenzoylaminonaphthols, prepared by the action of sulphurous acid on the salts of the corresponding nitrobenzoylaminonaphthols, are readily converted by dilute mineral acid into the corresponding aminobenzoylaminonaphthols; this reaction is capable of extended application, and can be successfully employed in the case of substituted halogen derivatives.

Details for the preparation of sulphaminobenzoyl-5-amino-β-naphthol (from *m*-nitrobenzoyl-1 : 6-aminonaphthol) and of *p*-sulphaminobenzoyl-6-amino-α-naphthol-7-sulphonic acid are given in the patent.

F. M. G. M.

Preparation of Phenyl Esters of Iodoparaffin Acids.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 233327).—*Phenyl iodoacetate*, glistening needles, m. p. 75—77°, is prepared by boiling together iodoacetic acid, phenol, and carbonyl chloride in benzene-pyridine solution.

Thymol iodoacetate, b. p. 176—178°/10 mm., is an oil at the ordinary temperature.

*Guaiacol α-bromo*iso*valerate*, colourless, odourless, tasteless crystals, has m. p. 69—70°, and when boiled with potassium iodide yields *guaiacol α-iodo*iso*valerate*, m. p. 76—79°.

*Tolyl α-iodo*iso*valerate* is a viscous, oily fluid which slowly solidifies.

Guaiacol α-iodo-β-methylhexoate, $C_3H_7·CHMe·CHI·CO_2·C_6H_4·OMe$, and its *bromo*-analogue form oily, yellow, tasteless, odourless, fluids. *Guaiacol α-iodo*-n-*butyrate* has b. p. 185°/10 mm., and *guaiacol α-bromo*-n-*butyrate*, b. p. 165°/10 mm.

Guaiacol iodobehenate, a thick, honey-like oil, is prepared from iodobehenic acid and guaiacol in the presence of phosphorus trichloride.

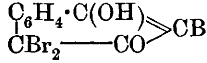
*Quinol di-α-bromo*iso*valerate*, $(C_4H_8Br·CO_2)_2C_6H_4$, odourless, tasteless needles, has m. p. 53°; *quinol di-α-iodo*iso*valerate* has similar properties and m. p. 85—87°.

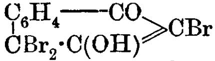
Guaiacol iodostearate is a yellowish-red oil, and *guaiacol α-iodo*iso*butyrate* has b. p. 160—175°/15 mm. These compounds are of therapeutic value. F. M. G. M.

Naphtharesorcinol [1 : 3 - Dihydroxynaphthalene] and 4-Amino-β-naphthol. RICHARD MEYER and KURT WOLFSLEBEN (*Ber.*, 1911, **44**, 1958—1966).—An account of the preparation and properties of some derivatives of 1 : 3-dihydroxynaphthalene and of 4-amino-β-naphthol, obtained in an unsuccessful attempt to prepare a meta-quinone of the naphthalene series.

When 1 : 3-dihydroxynaphthalene (1 mol.) is treated with bromine (4 atoms) in glacial acetic acid solution at a low temperature, 2 : 4-*dibromo*-1 : 3-*dihydroxynaphthalene*, $C_{10}H_4Br_2(OH)_2$, crystallising in needles, m. p. 128—129°, is produced; the *acetyl* derivative, $C_{10}H_4Br_2(OAc)_2$, has m. p. 125°.

Tribromo-1 : 3-*dihydroxynaphthalene*, $C_{10}H_3Br_3(OH)_2$, prepared by the action of bromine (8 atoms) on 1 : 3-dihydroxynaphthalene in a similar manner, crystallises in silvery needles, m. p. 186°; the *acetyl* derivative, $C_{10}H_3Br_3(OAc)_2$, crystallises in needles or prisms of a monoclinic habit, m. p. 182°; the *benzoyl* derivative, felted needles, has m. p. 129° (not sharp).

When the bromination is carried out in the presence of water at 0°, an *isomeride* having the constitution  $\begin{array}{l}C_6H_4\cdot C(OH)\\ |\\ CBr_2\text{——}CO\end{array}\!\!>\!CBr$ or



$$\begin{array}{l}C_6H_4\text{——}CO\\ |\\ CBr_2\cdot C(OH)\end{array}\!\!>\!CBr$$

is obtained. This forms yellow crystals, m. p. 85° (decomp.), and when heated with acetyl chloride loses bromine and yields the above-mentioned acetyl derivative of 2 : 4-dibromo-1 : 3-dihydroxynaphthalene.

Zincke and Egly's 2 : 4-tetrachloro-1 : 3-diketotetrahydronaphthalene (Abstr., 1898, i, 439) is obtained by the action of chlorine on 1 : 3-dihydroxynaphthalene in glacial acetic acid solution.

When air is passed through an alkaline solution of 1 : 3-dihydroxynaphthalene, β-hydroxy-α-naphthaquinone is produced.

Attempts to oxidise substituted derivatives of 1 : 3-dihydroxynaphthalene yielded tarry products.

4-*Benzoylamino-β-naphthyl benzoate*, $NHBz\cdot C_{10}H_6\cdot OBz$, forms colourless needles, m. p. 188°.

Ethyl 3-*hydroxy-α-naphthyloxamate*, $OH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CO_2Et$, prepared by the interaction of 4-amino-β-naphthol and ethyl oxalate, crystallises in pale yellow, felted needles, m. p. 171°. When hydrolysed with aqueous sodium hydroxide, this yields 3-*hydroxy-α-naphthyloxamic acid*, which crystallises in stellar aggregates of needles, m. p. 219° (decomp.); the *amide*, $OH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CO\cdot NH_2$, forms yellow, flat needles, m. p. 260°.

N-3-*Hydroxy-α-naphthylphthalamic acid*,

$$OH\cdot C_{10}H_6\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H,$$

obtained by heating 4-amino-β-naphthol with phthalic anhydride in xylene solution, has m. p. 220° (decomp.).

N-α-Naphthylphthalamic acid, $C_{10}H_7\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, and *N*-β-naphthylphthalamic acid may be prepared from the corresponding naphthylamines in a similar manner (compare Piutti, Abstr., 1886, 472, 473).

1(or 3)-*Bromo*-4-*benzoylamino*-β-*naphthyl benzoate*,

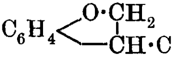
$NHBz\cdot C_{10}H_5Br\cdot OBz$,

obtained by brominating the benzoyl derivative of 4-amino-β-naphthol in alcoholic solution forms colourless crystals.

1 : 3-*Dibromo*-4-*acetylamino*-β-*naphthol*, $NHAc\cdot C_6H_4Br_2\cdot OH$, is prepared by the interaction of bromine and 4-acetylamino-β-naphthol in glacial acetic acid solution ; it crystallises in stout needles, m. p. 210° (decomp.), and on treatment with acetic anhydride and a little sulphuric acid yields 1 : 3-*dibromo*-4-*acetylamino*-β-*naphthyl acetate*, $NHAc\cdot C_6H_4Br_2\cdot OAc$, m. p. 230°, which is also obtained by brominating and subsequently acetylating 4-amino-β-naphthol. F. B.

Action of Phenol on Methylcoumaric Acid Dibromide and the Constitution of Werner's "Hydroxyphenylcoumaran."

RICHARD STOERMER and C. FRIEMEL (*Ber.*, 1911, **44**, 1838—1853. Compare Werner, Abstr., 1906, i, 180).—The supposed 2-hydroxyphenylcoumaran,



$C_6H_4{<}\begin{matrix}O\cdot CH_2\\ |\\ CH\cdot C_6H_4\cdot OH\end{matrix}$,

prepared by Werner (*loc. cit.*) by the action of phenol on methylcoumaric acid dibromide, is shown to be 4′-*hydroxy*-2-*methoxystilbene*, $OMe\cdot C_6H_4\cdot CH{:}CH\cdot C_6H_4\cdot OH$. On oxidation, *o*-methoxybenzoic acid and anisic acid are formed. The chief product of the interaction of the dibromide and phenol is β-bromo-α-methoxyphenylhydrocoumaric acid. This amounts to 65% ; some is decomposed into hydroxystilbene during the reaction, and it is readily converted into this by treatment with sodium carbonate.

The constitution of 4′-hydroxy-2-methoxystilbene is established by its synthesis from *p*-hydroxyphenylacetic acid and *o*-methoxybenzaldehyde ; these condense to hydroxymethoxystilbenecarboxylic acid, which is heated with soda lime.

4′-*Hydroxy*-2-*methoxystilbene*, $C_{15}H_{14}O_2$, regarded by Werner as hydroxyphenylcoumaran, $C_{14}H_{12}O_2$, is prepared by mixing equal parts of methylcoumaric acid dibromide and phenol and heating on the water-bath ; it has m. p. sharp at 149°.

β-*Bromo*-α-*methoxyphenylhydrocoumaric acid*,

$OMe\cdot C_6H_4\cdot CHBr\cdot CH(C_6H_4\cdot OH)\cdot CO_2H$,

crystallises in colourless, rhombic plates, m. p. 185—186°.

2 : 4′-Dimethoxystilbene, obtained by the action of methyl sulphate on the monomethyl ether, forms blue fluorescing platelets, m. p. 93° (compare Werner, *loc. cit.*).

2-*Methoxy*-4′-*ethoxystilbene* crystallises in blue, fluorescing, broad needles, m. p. 70°.

4′-*Benzoyloxy*-2-*methoxystilbene* separates in colourless needles of silky lustre, m. p. 123°. The corresponding p-*nitrobenzoyl* derivative forms lustrous, golden-yellow plates, m. p. 148°.

The *dibromide* of the above dimethoxy-derivative is a colourless powder, m. p. 133° ; the *dibromide* of the acetyl derivative crystallises in small, colourless plates, m. p. 170°.

On reduction of dimethoxystilbene in alcohol with sodium, 2 : 4′-*dimethoxydibenzyl* is obtained as a clear, transparent oil, which becomes solid in ice, m. p. 45°.

The reduction of methoxyhydroxystilbene is more difficult, and is carried out in amyl alcohol. *4′-Hydroxy-2-methoxydibenzyl* forms colourless, long needles, m. p. 63°. Methyl sulphate converts it into the dimethyl ether, m. p. 45°. The p-*nitrobenzoyl ether* crystallises in creamy-yellow plates, m. p. 135°.

Oxidation of both methoxyhydroxystilbene and its dihydro-derivative with permanganate gave *o*-methoxybenzoic acid; the oxidation of the dimethoxystilbene gave a mixture of *o*- and *p*-methoxybenzoic acids.

p-*Methoxy-a-*o-*anisylcinnamic acid*,

$$OMe\cdot C_6H_4\cdot C(CO_2H)\colon CH\cdot C_6H_4\cdot OMe,$$

prepared by the Perkin synthesis from anisaldehyde and sodium *o*-methoxyphenylacetate, crystallises in colourless needles, m. p. 191°. On distillation with soda lime, 2 : 4′-dimethoxystilbene is obtained.

*a-*p-*Methoxyphenylcoumaric acid*, $OMe\cdot C_6H_4\cdot CH\colon C(C_6H_4\cdot OH)\cdot CO_2H$, from sodium *p*-hydroxyphenylacetate and *o*-methoxybenzaldehyde, crystallises in renniform aggregates of needles, m. p. 202°. On distillation with soda lime, methoxyhydroxystilbene, m. p. 149°, is obtained. Methyl sulphate converts it into the di-ether, and, on hydrolysis, *a*-*p*-methoxymethylcoumaric acid, m. p. 198°, is formed.

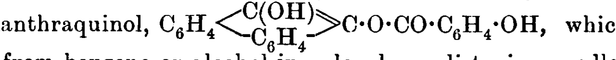
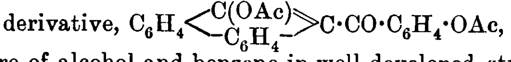
On condensation of ethylcoumaric acid dibromide with phenol, *β-bromo-a-ethoxyphenylhydrocoumaric acid*,

$$OEt\cdot C_6H_4\cdot CHBr\cdot CH(C_6H_4\cdot OH)\cdot CO_2H,$$

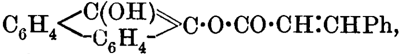
is obtained, crystallising in needles, m. p. 166°. On treatment with sodium carbonate, *4′-hydroxy-2-ethoxystilbene* is obtained; it crystallises in blue, fluorescing needles, m. p. 107°. The compound *2-methoxy* forms short, blue, fluorescing plates, m. p. 60°. E. F. A.

Syntheses by means of Sunlight. HEINRICH KLINGER [with WALTER ROERDANSZ] (*Annalen*, 1911, **382**, 211—221. Compare Klinger and Standke, Abstr., 1891, 900; Klinger and Kolvenbach, 1898, i, 467).—Valeroylquinol and benzoylquinol can be prepared by the action of zinc chloride on quinol and valeric or benzoic acid. The yields, however, are not good, as appreciable amounts of dark-coloured products are also formed. The dibenzoyl derivative of quinol, $C_6H_4(O\cdot COPh)_2$, is also formed when benzoic acid is used.

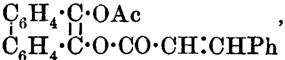
Mixtures of phenanthraquinone, benzene, and various aldehydes when exposed to bright sunlight in narrow sealed tubes undergo condensation. Most of the experiments were conducted in tubes 70 cm. long and 2 cm. wide.

Phenanthraquinone (10 grams), salicylaldehyde (6 c.c.), and benzene (50 c.c.) at the end of twenty days yield the *monosalicyloyl* derivative of phenanthraquinol,  $C_6H_4{<}\begin{matrix}C(OH)\\C_6H_4\end{matrix}{>}C\cdot O\cdot CO\cdot C_6H_4\cdot OH$, which crystallises from benzene or alcohol in colourless, glistening needles, m. p. 188°. It is hydrolysed by alkalis to the quinol, and this, on shaking in contact with air and the alkaline liquid, gives the quinone. The *diacetyl* derivative,  $C_6H_4{<}\begin{matrix}C(OAc)\\C_6H_4\end{matrix}{>}C\cdot CO\cdot C_6H_4\cdot OAc$, crystallises from a mixture of alcohol and benzene in well-developed, strongly refractive octahedra, m. p. 143°, or from hot alcohol in colourless, glistening needles, m. p. 151°. The corresponding *dibenzoyl* derivative, $C_{35}H_{22}O_5$, prepared by heating the salicyloylphenanthraquinol with five times its weight of benzoic anhydride at 150—160° for thirty minutes, crystallises from benzene or glacial acetic acid in colourless, flat needles, m. p. 216—217°. Cold anhydrous nitric acid reacts with the salicyloyl derivative, yielding phenanthraquinone and 3 : 5-dinitrosalicylic acid.

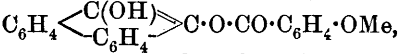
Phenanthraquinone, cinnamaldehyde, and benzene, at the end of fourteen days, yield the *monocinnamoyl* derivative,



$$C_6H_4\Big<\begin{matrix}C(OH)\\ -C_6H_4-\end{matrix}\Big>C\cdot O\cdot CO\cdot CH{:}CHPh,$$

which crystallises from benzene or glacial acetic acid in colourless needles, m. p. 193°, or from alcohol in canary-yellow needles. Its *acetyl* derivative,  $\begin{array}{l}C_6H_4\cdot C\cdot OAc\\ \vert\qquad\ \ \vert\\ C_6H_4\cdot C\cdot O\cdot CO\cdot CH{:}CHPh\end{array}$, crystallises in colourless prisms, m. p. 154°, and yields a *dibromide*, $C_{25}H_{18}O_4Br_2$, in the form of colourless, slender needles, m. p. 211°. The corresponding *benzoyl* derivative, $C_{50}H_{20}O_4$, forms colourless crystals, m. p. 218°.

The *monoanisoyl* derivative of phenanthraquinol,



$$C_6H_4\Big<\begin{matrix}C(OH)\\ -C_6H_4-\end{matrix}\Big>C\cdot O\cdot CO\cdot C_6H_4\cdot OMe,$$

crystallises from benzene in slender, glistening plates, m. p. 232°, and yields an *acetyl* derivative, $C_{24}H_{18}O_5$, in the form of colourless, rhombic plates, m. p. 175°, and a *benzoyl* derivative, $C_{29}H_{20}O_5$, m. p. 193°.

Monofurfuroylphenanthraquinol, $C_{19}H_{12}O_4$, crystallises from benzene in well-developed, ruby-red prisms, m. p. 193°, or in orange-coloured crystals with the same m. p. The crystals have $a : c = 1 : 0{\cdot}3111$.

J. J. S.

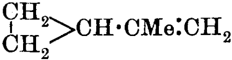
New Derivatives in the Triphenylmethane Series. TIBOR SZÉKI (*Ber.*, 1911, **44**, 1476—1481).—In consequence of the labile character of the hydrogen atom in the para- position to a methoxy-group in hydroxyquinol trimethyl ether (Abstr., 1907, i, 45; 1910, i, 837), the ether condenses readily with aromatic aldehydes to form derivatives of triphenylmethane of the type $CHR[C_6H_2(OMe)_3]_2$. The condensation is effected in glacial acetic acid by hydrochloric acid, D 1·19, at the ordinary temperature. Thus benzaldehyde, *m*-nitrobenzaldehyde, and *p*-nitrobenzaldehyde respectively yield 2 : 4 : 5 : 2′ : 4′ : 5′-*hexamethoxytriphenylmethane*,

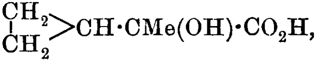
$$CHPh[C_6H_2(OMe)_3]_2,$$

m. p. 130·5°, 3-*nitro*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 117°, citron-yellow needles, and 4-*nitro*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 117°, citron-yellow crystals. The following compounds have been obtained from vanillin, salicylaldehyde, *p*-hydroxybenzaldehyde, piperonal, and protocatechualdehyde respectively: 4-*hydroxy*-3 : 2′ : 4′ : 5′ : 2″ : 4″ : 5″-*heptamethoxytriphenylmethane*, m. p. 187·5°; 2-*hydroxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 176° (*acetate*, m. p. 148—149°); 4-*hydroxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m.p. 205°; 3 : 4-*methylenedioxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 137°; 3 : 4-*dihydroxy*-2′ : 4′ : 5′ : 2″ : 4″ : 5″-*hexamethoxytriphenylmethane*, m. p. 202° (*diacetate*, m. p. 124°).

The preceding compounds, excepting those prepared from the nitrobenzaldehydes and salicylaldehyde, react with bromine in benzene to form bromotrimethoxybenzene and brown or bluish-violet substances, which are very probably derivatives of diphenylmethane. C. S.

Transformations of *cyclo*Propyldimethylcarbinol. Nicolai M. Kijner and W. Klawikordoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 595—608).—In the synthesis of *cyclo*propyldimethylcarbinol by the action of magnesium methyl iodide on ethyl *cyclo*propylcarboxylate (compare Zelinsky, Abstr., 1901, i, 660; 1902, i, 70), an appreciable proportion of an unsaturated *iodide*, $C_6H_{11}I$, b. p. 176—180°/752 mm. (decomp.), D_0^{20} 1·4305, is obtained. When freed from all traces of this iodide, *cyclo*propyldimethylcarbinol has b. p. 124·5—125°/752 mm., D_0^{20} 0·8844, n_D^{20} 1·4330 (compare Bruylants, Abstr., 1909, i, 226).

The hydrocarbon obtained by Alexéeff (Abstr., 1905, i, 639) by the action of acetic anhydride on *cyclo*propyldimethylcarbinol, and described by this author as dimethylmethylenetrimethylene, is found to be *β-*cyclo*propyl-Δ^α-propylene*,  $\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH\cdot CMe{:}CH_2$, b. p. 71·1—71·5°/772 mm., D_0^{20} 0·7523, n_D^{20} 1·4252, and is accompanied by acetyl derivatives giving on hydrolysis a mixture of alcohols, b. p. 124—160°, the nature of which was not investigated. Oxidation of this hydrocarbon by means of permanganate yields: (1) acetyltrimethylene; (2) *α-hydroxy-α-*cyclo*propylpropionic acid*,



$$\begin{matrix}CH_2\\|\\CH_2\end{matrix}\!\!>CH\cdot CMe(OH)\cdot CO_2H,$$

which forms colourless, acicular needles, m. p. 75·5°, gives a *hydrate*, $2C_6H_{10}O_3,H_2O$, m. p. 54—55°. This oxidation probably takes place according to the scheme:

$$C_3H_5\cdot CMe{:}CH_2 \longrightarrow C_3H_5\cdot CMe(OH)\cdot CH_2\cdot OH \longrightarrow$$
$$C_3H_5\cdot CMe(OH)\cdot CO_2H \longrightarrow C_3H_5\cdot COMe.$$

By the action of fuming hydrobromic acid, hydroxy*cyclo*propylpropionic acid yields (1) in the cold, *α-methylene-δ-bromovaleric acid*, $CH_2Br\cdot CH_2\cdot CH_2\cdot C({:}CH_2)\cdot CO_2H$, colourless, rhombic plates, m. p. 68°; (2) in a sealed tube at 100°, *δ-bromo-α-bromomethylvaleric acid*, $CH_2Br\cdot CH_2\cdot CH_2\cdot CH(CH_2Br)\cdot CO_2H$, plates, m. p. 88—90°.

When heated with dilute sulphuric acid in a sealed tube, *β-cyclo*propyl-Δ^α-propylene yields the hexylene oxide obtained by Zelinsky (Abstr., 1902, i, 70). Treatment of this oxide or of *cyclo*propyldimethylcarbinol by fuming hydrobromic acid yields *βε-dibromo-β-methylpentane*, $CH_2Br\cdot CH_2\cdot CH_2\cdot CMe_2Br$, b. p. 104—104·5°/23 mm., D_0^{20} 1·5865—1·5902, n_D^{20} 1·5045—1·5051. The action of alcoholic potassium hydroxide on this dibromo-derivative yields:

(1) *δ-Methyl-Δ^αγ-pentadiene*, $CH_2{:}CH\cdot CH{:}CMe_2$, b. p. 76—77·5°/766 mm., D_0^{20} 0·7193, n_D^{20} 1·4491. The structure of this hydrocarbon is decided by the considerable excess of the experimental (30·59) value of the molecular refraction over the calculated value (28·93) (compare Brühl, Trans., 1907, 115; Reif, Abstr., 1908, i, 847). δ-Methyl-Δ^αγ-pentadiene is found to be identical with the compound described by Bruylants (*loc. cit.*) as *β-cyclo*propylpropylene.

(2) *ε-Ethoxy-β-methyl-Δ^β-amylene*, $OEt\cdot CH_2\cdot CH_2\cdot CH:CMe_2$, b. p. 142·5—143·5°/766 mm., D_0^{20} 0·7975, n_D^{20} 1·4182. On oxidation with permanganate, it yields acetone and other products.

The action of hydriodic acid on *cyclo*propyldimethylcarbinol and reduction of the iodo-derivative thus obtained by means of sodium yields β-methylpentane. T. H. P.

Dehydration of Alkyl- and Benzylphenyl-*tert.*-butylcarbinols. (Mlle.) PAULINE LUCAS (*Compt. rend.*, 1911, **152**, 1771—1774. Compare Abstr., 1910, i, 378).—A further examination of the hydrocarbons obtained previously by dehydrating the product of the action of an organo-magnesium halide on a trialkylacetophenone. The substance to which the formula $CMe_3\cdot CPh:CH_2$ was ascribed appears to be a mixture of a liquid having this constitution with *1-phenyl-2 : 2-dimethyl*cyclo*propane*, since on oxidation with chromic acid it furnishes acetone, acetophenone, and trimethylacetophenone; the latter ketone was characterised by its *semicarbazone*, m. p. 195°.

Magnesium ethyl iodide acts on trimethylacetophenone to give *γ-phenyl-ββ-dimethylpentan-γ-ol*, $CMe_3\cdot CEtPh\cdot OH$, b. p. 115—116°/15 mm. When this is boiled with formic acid, it yields a single hydrocarbon, *γ-phenyl-δδ-dimethyl-Δ^β-hexene*, $CMe_3\cdot CPh:CHMe$, b. p. 90—95°/12 mm., the constitution of which follows from the formation of carbon dioxide and trimethylacetophenone on oxidation.

The hydrocarbon from γδ-diphenyl-ββ-dimethylbutan-γ-ol similarly gives carbon dioxide, benzoic acid, trimethylacetophenone, and a *substance*, $C_{18}H_{20}O$, b. p. 195—200°/15 mm. It is, therefore, probably *αβ-diphenyl-γγ-dimethyl-Δ^α-butylene*, $CMe_3\cdot CPh:CHPh$. The unidentified product of oxidation appears not to contain a carbonyl group.

W. O. W.

Preparation of Hydroxybenzyl Alcohol, Hydroxybenzaldehyde, and Hydroxybenzoic Acids. FRITZ RASCHIG (D.R.-P. 233631).—When substituted phenols containing an acid radicle in place of the hydroxyl hydrogen are quantitatively chlorinated at a temperature of 150—180°, derivatives containing chlorine in the side-chain only are obtained.

*ω-Chloro-*o*-tolyl carbonate*, $CO(O\cdot C_6H_4\cdot CH_2Cl)_2$, m. p. 79°, prepared from *o*-tolyl carbonate, furnishes when boiled with calcium carbonate and water under 4—5 atmospheres pressure a satisfactory yield of *o*-hydroxybenzyl alcohol (saligenin).

*ω-Dichloro-*o*-tolyl carbonate*, $CO(O\cdot C_6H_4\cdot CHCl_2)_2$, m. p. 73°, b. p. 247°/30 mm., when similarly treated furnishes salicylaldehyde.

*ω-Dichloro-*p*-tolyl carbonate*, m. p. 108°, is decomposed into *p*-hydroxybenzaldehyde, whilst *ω-trichloro-m-tolyl carbonate*, $CO(O\cdot C_6H_4\cdot CCl_3)_2$, an unstable oil, yields *m*-hydroxybenzoic acid.

o-*Tolyl phosphate*, $PO(O\cdot C_6H_4Me)_3$, an oil, b. p. 410°/760 mm., prepared from *o*-cresol and phosphoryl chloride, yields *ω-dichloro-*o*-tolyl phosphate*, m. p. 78°, and subsequently salicylaldehyde.

o-*Tolyl phosphite*, $P(O\cdot C_6H_4Me)_3$, prepared from *o*-cresol and phosphorus trichloride on chlorination, yields first an additive product, $(CH_3\cdot C_6H_4O)_3PCl_2$, and subsequently a viscous oil consisting chiefly of ω-*dichloro*-o-*tolyl dichlorophosphate*, $(CHCl_2\cdot C_6H_4\cdot O)_3PCl_2$, and on hydrolysis, salicylaldehyde.

o-Tolyl benzenesulphonate, $C_6H_4Me\cdot O\cdot SO_2Ph$, yields ω-*dichloro*-o-*tolyl benzenesulphonate*, needles, m. p. 73°, and salicylaldehyde on hydrolysis.

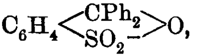
ω-*Dichloro*-m-*tolyl benzoate*, $OBz\cdot C_6H_4\cdot CHCl_2$, obtained from *m*-tolyl benzoate, is an unstable oil, which cannot be distilled even in a vacuum, and on hydrolysis yields a mixture of benzoic acid and *m*-hydroxybenzaldehyde. F. M. G. M.

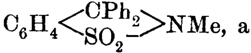
Catalytic Esterification of Aromatic Acids in the Wet Way. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1911, **152**, 1855—1857. Compare this vol., i, 600).—Contrary to what has been noticed in the case of the aliphatic acids, the extent and rapidity of the esterification of benzoic acid increases with the amount of sulphuric acid employed as a catalyst, but not with that of potassium hydrogen sulphate or hydrated aluminium sulphate, which only give poor yields of the ester. The same observation applies to salicylic acid and the toluic acids, but phenylacetic and phenylpropionic acids more closely resemble acetic acid in this respect. W. O. W.

Alkyl Chloro- and Bromo-anthranilates. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], **9**, 605—608).—Methyl 5-chloroanthranilate (Abstr., 1907, i, 158) is readily obtained by direct chlorination by Flürscheim's method (Trans., 1908, **93**, 1772), using a mixture of acetic and hydrochloric acids as a solvent. A small amount of the 3 : 5-dichloro-ester is formed in the reaction, but this is easily separated owing to its insolubility in dilute hydrochloric acid. *Methyl* 3 : 5-*dichloroanthranilate*, m. p. 63—64°, crystallises in colourless needles, and is very soluble in alcohol.

The process used by Wheeler (Abstr., 1909, i, 382) for the bromination of anthranilic acid gives good results for the methyl ester. *Methyl* 5-*bromoanthranilate*, m. p. 74°, crystallises in yellowish-white prisms. The *dibromo*-ester (? 3 : 5) formed simultaneously has m. p. 84°, crystallises in slender needles, and is soluble in alcohol.

T. A. H.

Further Investigation of Certain Derivatives of *o*-Sulphobenzoic Acid. PHILIP H. COBB and GEORGE P. FULLER (*Amer. Chem. J.*, 1911, **45**, 605—611).—It has been shown by Cobb (Abstr., 1906, i, 499) that the substance, m. p. 162—163°, obtained by Remsen and Saunders (Abstr., 1895, i, 474) and List and Stein (Abstr., 1898, i, 584) by the action of benzene and aluminium chloride on a mixture of the chlorides of *o*-sulphobenzoic acid, is diphenylbenzylsulphone,  $C_6H_4<\begin{matrix}CPh_2\\SO_2\end{matrix}>O$, and can be prepared by the action of magnesium phenyl bromide on *o*-sulphobenzoic anhydride.

Sachs (Abstr., 1904, i, 877) has stated that when "methylsaccharin" is treated with magnesium phenyl bromide, triphenylcarbinol-*O*-sulphonmethylamide is produced, which, when heated with concentrated hydrochloric acid in a sealed tube at 150°, yields a compound, m. p. 210°, which he regarded as diphenylbenzylsulphone. On repeating these experiments, it has been found that Sachs' compound (m. p. 210°) is not diphenylbenzylsulphone, but the *lactam*,  $C_6H_4<\begin{matrix}CPh_2\\SO_2\end{matrix}>NMe$, and that the same substance is produced when triphenylcarbinol-*O*-sulphonemethylamide is treated with concentrated sulphuric acid for twelve hours at 50°.

When *di-p-tolylphenylcarbinol-O-sulphonmethylamide*,

$$OH\cdot C(C_6H_4Me)_2\cdot C_6H_4\cdot SO_2\cdot NHMe,$$

m. p. 243° (uncorr.), obtained by the action of magnesium *p*-tolyl bromide on "methylsaccharin," is heated with concentrated hydrochloric acid for fourteen hours at 150°, or with concentrated sulphuric acid at 70°, no change takes place and the substance can be recovered.

E. G.

Ketens. XX. Attempts to Prepare Quinoketens. HERMANN STAUDINGER and KARL CLAR (*Ber.*, 1911, **44**, 1623—1633).—An account of unsuccessful attempts to synthesise the following quinonoid ketens: (I) $CO{:}C_6H_4{:}CO$, (II) $CPh_2{:}C_6H_4{:}CO$, (III) $CO{:}C_6H_4{:}C{:}C_6H_4{:}CO$.

Terephthaloyl bromide, prepared by the action of phosphorus pentabromide on the corresponding acid in the presence of phosphoryl bromide, crystallises from light petroleum in long, colourless needles, m. p. 85°. When heated with zinc in ethereal solution, it yields ethyl terephthalate; no evidence of the formation of dioxoquinodimethane (I) was obtained.

Diphenyl-*p*-tolylcarbinol is prepared most readily by the interaction of magnesium phenyl bromide and phenyl *p*-tolyl ketone (compare Bistrzycki and Gyr, Abstr., 1904, i, 315; Acree, *ibid.*, 409). It is converted by prolonged boiling with dilute nitric acid into triphenylcarbinol-*p*-carboxylic acid, m. p. 203—205° (compare Bistrzycki and Gyr, *loc. cit.*), which, on treatment with phosphorus pentachloride or thionyl chloride, yields *ω-chlorotriphenylmethane-4-carboxyl chloride*, $CPh_2Cl\cdot C_6H_4\cdot COCl$. The latter forms colourless crystals, m. p. 80—81°, is very stable towards water, and, when treated with aniline in ethereal solution, yields *ω-anilinotriphenylmethane-4-carboxylic acid*, $C_6H_5\cdot NH\cdot CPh_2\cdot C_6H_4\cdot CO_2H$, m. p. 182°.

Triphenylmethane-4-carboxylic acid, m. p. 165° (compare O. Fischer and Albert, Abstr., 1893, i, 196), obtained by reducing triphenylcarbinol-*p*-carboxylic acid with phosphorus and iodine in glacial acetic acid solution, is converted by thionyl chloride into the corresponding *chloride*, $CHPh_2\cdot C_6H_4\cdot COCl$, which forms white crystals, m. p. 89—90°; the *anilide*, $C_{26}H_{21}ON$, has m. p. 196°. All attempts to prepare diphenyloxoquinodimethane (II) either by the removal of hydrogen chloride from triphenylmethane-4-carboxyl chloride by means of quinoline and tripropylamine, or by the action of zinc on ω-chlorotriphenylmethane-4-carboxyl chloride, proved unsuccessful.

When an ethereal solution of the last-named compound is heated with zinc, or shaken with mercury in an atmosphere of carbon dioxide, an intense reddish-violet coloration, due to the formation of *triphenylmethyl-4-carboxyl chloride*, $-CPh_2\cdot C_6H_4\cdot COCl$, is produced. The violet solution of the triphenylmethyl derivative is at once decolorised on exposure to air, or by the addition of bromine; when treated with aniline it yields *triphenylmethyl-4-carboxylanilide.*

The *peroxide*, $C_{40}H_{28}O_4Cl_2$, obtained by passing a stream of air through an ethereal solution of the chloride, crystallises in white plates, m. p. 168° (decomp.), and gives the usual peroxide reactions. It is decomposed by concentrated sulphuric acid, yielding triphenylcarbinol-*p*-carboxylic acid.

Methyl triphenylcarbinol-4-carboxylate, $C_{21}H_{18}O_3$, prepared by the action of methyl iodide on the corresponding silver salt, has m. p. 119°, and, on treatment with phosphorus pentachloride or oxalyl chloride, yields *methyl ω-chlorotriphenylmethane-4-carboxylate*, which forms a pale yellow, amorphous mass. When an ethereal solution of the chloro-ester is shaken with mercury, a reddish-violet solution of *methyl triphenylmethyl-4-carboxylate* is obtained.

The solution is stable towards water and aniline, but is decolorised on exposure to air, or by the addition of bromine. The *peroxide* forms a white powder, m. p. 171·5° (decomp.).

Benzophenone-4 : 4′-dicarboxylic acid is best prepared by heating di-*p*-tolyl ketone with dilute nitric acid and subsequently oxidising the monocarboxylic acid thus obtained with potassium permanganate in alkaline solution.

With phosphorus pentachloride it yields *di-ω-chlorodiphenylmethane-4 : 4′-dicarboxyl chloride*, $CCl_2(C_6H_4 \cdot COCl_2)_2$, which forms colourless crystals, m. p. 78°, and undergoes no change when heated with zinc in ethereal or ethyl acetate solution.

Benzophenone-4 : 4′-dicarboxylanilide, $C_{27}H_{20}O_3N$, has m. p. 302°.

F. B.

Action of Sunlight on *allo*-Cinnamic Acid.

ANNE W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 100—101. Compare Riiber, Abstr., 1902, i, 785).—*allo*-Cinnamic acid (m. p. 41—42°) exposed to sunlight for some days became opaque and was no longer completely soluble in ether. The insoluble portion, dissolved in ammonia, gave a heavy precipitate with barium chloride. The acid from the barium salt melted at 206°, the m. p. being unchanged by mixing with β-truxillic acid from the coca-acids. The ether extract yielded, in addition, ordinary cinnamic acid, α-truxillic acid, and a trace of oil.

J. D. K.

Ketens. XXI. Attempts to Prepare Alleneketens.

HERMANN STAUDINGER and E. OTT (*Ber.*, 1911, **44**, 1633—1637).—Attempts to synthesise allene-ketens of the type $CR_2\!:\!C\!:\!CO$ by the action of zinc on α-bromo-αβ-unsaturated acyl chlorides were unsuccessful.

α-Bromocinnamoyl bromide, obtained by the interaction of phosphorus pentabromide and the corresponding acid in benzene solution, has b. p. 170°/23 mm. The chloride is best prepared by the action of thionyl chloride on the acid (compare Anschütz and Selden, Abstr., 1887, 829); when heated with zinc in ethyl acetate solution, it yields a brown, amorphous *substance*, m. p. 206°, which contains chlorine, but is free from bromine.

In the preparation of ββ-dimethylacrylic acid from ethyl α-bromo*iso*valerate, the removal of hydrogen bromide is most readily effected by means of quinoline; the *chloride* has b. p. 145—150°; the *anilide*, m. p. 126—127°.

α-Bromo-ββ-dimethylacrylic acid is obtained in almost quantitative yield by the action of alcoholic sodium ethoxide on αβ-dibromo*iso*valeric acid (compare Massot, Abstr., 1894, i, 356); on treatment with thionyl chloride, it yields the *chloride*, $CMe_2\colon CHBr\cdot COCl$, which has b. p. 178° or 73°/16 mm., and when heated in ethyl acetate solution with zinc gives brown, amorphous products; the *anilide*,

$$C_{11}H_{12}ONBr,$$

has m. p. 90°.

Benzylidenemalonyl chloride, prepared by the action of phosphorus pentachloride on the corresponding acid in the presence of light petroleum, crystallises in white needles, m. p. 37°. It yields with pyridine an *additive* compound, $C_{20}H_{16}O_2N_2Cl_2$, which forms a pale yellow powder, m. p. 95—100° (decomp.).

Attempts to prepare benzylidenemalonic anhydride by the action of silver oxide on the chloride in ethereal solution yielded ethyl benzylidenemalonate. F. B.

Addition of Hydrogen Cyanide to Unsaturated Compounds. PHILIP H. COBB (*Amer. Chem. J.*, 1911, **45**, 604—605).—During the course of some work on phenylmaleic and phenylfumaric acids, it was found that when an alcoholic solution of ethyl phenylpropiolate is treated with an aqueous solution of potassium cyanide and the mixture boiled for some hours on the water-bath, potassium carbonate and phenylsuccinonitrile are produced in accordance with the equation:

$$CPh\colon C\cdot CO_2Et + 2KCN + 2H_2O = CN\cdot CHPh\cdot CH_2\cdot CN + K_2CO_3 + EtOH.$$

This reaction is being extended to other unsaturated compounds.

E. G.

Esters of Boric Acid. GEORG COHN (*Pharm. Zentr.-h.*, 1911, **52**, 479—485).—Esters of boric acid can be readily prepared by treating the acid with an excess of the alcohol in presence of hydrogen chloride or of sulphuric acid. A large excess of alcohol (five or six times the weight of boric acid) gives the best yield, and sulphuric acid is preferable to hydrogen chloride. In this way the methyl, ethyl, propyl, and *iso*butyl esters have been prepared.

Attempts to employ these esters for the alkylation of bases, phenols, and acids were unsuccessful, except in the case of salicylic acid, which, when boiled for a long time with methyl borate, yielded methyl salicylate quantitatively. *p*-Hydroxybenzoic acid remains unchanged under these conditions, and no reaction was observed with aniline, dimethylaniline, phenol, or resorcinol.

Aromatic hydroxy-acids react readily with boric esters, yielding substances of the type of *trisalicylboric acid*, $B(O\cdot C_6H_4\cdot CO_2H)_3$, which is formed initially in the above-mentioned esterification. The compound crystallises in long prisms, which on heating begin to sinter at about 230°, and are completely melted (with energetic decomp.) at 260—270°. When trisalicylboric acid is boiled with phenylhydrazine, a substance, m. p. 223°, is obtained, which crystallises in light brown laminæ, and reduces copper sulphate even in the cold. *m*- and *p*-Hydroxybenzoic acids do not give analogous compounds. *Tri-*o*-hydroxytoluoylboric acid* sinters at 220°, and has m. p. 245—247° (decomp.). *Tri-*m*-hydroxytoluoylboric acid* sinters at 175°, but melts sharply at 261° (decomp.). *Tri-*p*-hydroxytoluoylboric acid* sinters at 143°, and has m. p. 210—212° if slowly heated; if plunged into a bath at 155° the substance froths up, crystallises, and melts then at 210—212°.

Tri-α-hydroxynaphthoylboric acid sinters at 250°, m. p. 255° (decomp.). *Tri-β-hydroxynaphthoylboric acid* is still solid at 263°.

Triresorcinoylboric acid (from carefully dried resorcinic acid) becomes yellow at 220°, but suffers no further change below 260°.

Gallic acid does not react. Tartaric acid and methyl or ethyl borate yield a small quantity of a white, crystalline *substance*.

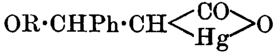
Salicylamide and boric ester yield a white, crystalline *substance*, which begins to sinter at 220°, and melts at about 265°. The analyses indicate the composition $B(O\cdot C_6H_4\cdot CO\cdot NH_2)_3$. R. V. S.

Ketens. XXII. Attempts to Prepare ω-Methoxyphenylketen. Hermann Staudinger and Otto Kupfer (*Ber.*, 1911, **44**, 1638—1640).—Attempts to remove hydrogen chloride from phenylmethoxyacetyl chloride by means of tripropylamine, with the formation of phenylmethoxyketen, proved fruitless.

ω-Methoxyphenylacetyl chloride, OMe·CHPh·COCl, prepared by the action of thionyl chloride on the corresponding acid, is a colourless liquid, b. p. 80—81°/0·1 mm. At temperatures above 120°, it decomposes into carbon monoxide, methyl chloride, and benzaldehyde.

F. B.

Ether Derivatives of β-Phenylhydracrylic Acid (β-Hydroxy-β-phenylpropionic Acid). Walther Schrauth, Walter Schoeller, and Richard Struensee (*Ber.*, 1911, **44**, 1432—1436).—The anhydrides of α-hydroxymercuri-β-alkyloxy-β-phenylpropionic acids,



$$OR\cdot CHPh\cdot CH{<}{}^{CO}_{Hg}{>}O$$

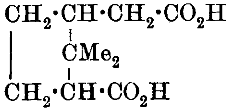
(this vol., i, 595), when hydrolysed with mineral acids are completely decomposed, yielding cinnamic acids, and when the esters of the α-acetoxymercuri-β-alkyloxy-β-phenylpropionic acids are treated with an alcoholic solution of hydrogen sulphide, esters of cinnamic acid are formed. By using an alcoholic solution of ammonium sulphide the esters of the mercuriacetate derivatives can be transformed into esters of β-alkyloxy-β-phenylpropionic acids. The corresponding acids can be obtained by hydrolysing the esters or by the action of hydrogen sulphide on solutions of the anhydro-compounds in dilute sodium hydroxide.

Methyl β-methoxy-β-phenylpropionate, $OMe\cdot CHPh\cdot CH_2\cdot CO_2Me$, prepared from the methyl α-acetoxymercuri-β-methoxy-β-phenylpropionate, is an oil with b. p. 253° (corr.), and the corresponding *acid*, $C_{10}H_{12}O_3$, crystallises from light petroleum in stout, colourless plates, m. p. 98°.

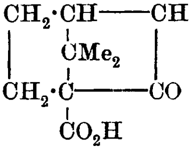
Methyl β-ethoxy-β-phenylpropionate, $OEt\cdot CHPh\cdot CH_2\cdot CO_2Me$, is a colourless oil with an unpleasant odour, and has b. p. 256° (corr.). The corresponding *acid*, $C_{11}H_{14}O_3$, crystallises from light petroleum in colourless plates, m. p. 75°, and when boiled for a short time with hydrochloric acid yields cinnamic acid.

β-Propoxy-β-phenylpropionic acid, $OPr\cdot CHPh\cdot CH_2\cdot CO_2H$, crystallises from water in colourless plates, m. p. 59°, and the corresponding iso*propoxy*-acid from light petroleum in plates, m. p. 73°. *β-*iso-*Butoxy-β-phenylpropionic acid*, $C_{13}H_{18}O_3$, has m. p. 67·5°. J. J. S.

Complete Synthesis of Pinophanic Acid and the Constitution of Ketopinic and Tricyclenic Acid. GUSTAV KOMPPA (*Ber.*, 1911, **44**, 1536—1541).—The homo*apo*camphoric acid (annexed formula), prepared by reduction of *apo*camphoric anhydride to *apo*campholide, addition of potassium cyanide to this, and hydrolysis, is identical with pinophanic acid (Gilles and Rennwick, Proc., 1897, **13**, 65), but not with camphenecamphoric acid. Accordingly, ketopinic acid, from which pinophanic acid is obtained by heating with alkali or with sodium ethoxide, has the annexed formula, and not that suggested by Bredt and May. It follows, further, from this that tricyclenic [dehydrocamphenylic] acid has the constitution suggested by Semmler and by Komppa and Hintikka (Abstr., 1908, i, 852), which readily explains the conversion into ketopinic acid. The corresponding cyclic ketone has been obtained from homo*apo*camphoric acid in small quantities; the semicarbazone has m. p. 209—211°, and the ketone is probably identical with fenchocamphorone.



$$\begin{array}{l} CH_2\cdot CH\cdot CH_2\cdot CO_2H \\ |\quad\ \ CMe_2 \\ CH_2\cdot CH\cdot CO_2H \end{array}$$



$$\begin{array}{lll} CH_2\cdot CH & — & CH_2 \\ |\quad\ CMe_2 & & | \\ CH_2\cdot C & — & CO \\ \quad\ \ CO_2H & & \end{array}$$

dl-apo*Campholide*, obtained by reducing *apo*camphoric anhydride, crystallises in long, indefinite, feathery masses or short, thick, triclinic prisms, m. p. 164°. When kept with hydrogen bromide in acetic acid, *bromo*apo*campholic acid*, $CH_2Br\cdot C_7H_{12}\cdot CO_2H$, is obtained, crystallising in aggregates of indefinite crystals, m. p. 139°.

*Cyano*apo*campholic acid*, prepared by heating *apo*campholide with potassium cyanide, forms short, many-faced, but indefinite crystals, m. p. 141·5—142° (corr.). On hydrolysis, homo*apo*camphoric acid is obtained in rhombic plates, m. p. 203—204°, in every way identical with pinophanic acid prepared from ketopinic acid. The *dianilide* crystallises in slender needles, m. p. 194—195°. E. F. A.

Action of Benzoyl Chloride and Potassium Cyanide on Benzoyloxybenzoic Acids and on Acylated Hydroxybenzoyloxybenzoic Acids. FRANCIS E. FRANCIS and MAX NIERENSTEIN (*Annalen*, 1911, **382**, 194—210. Compare Francis and Davis, Trans., 1909, **95**, 1404; Davis, *ibid.*, 1910, **96**, 949).—By the action of benzoyl chloride and potassium cyanide on hydroxybenzoyloxybenzoic acids, it was thought that acids of the type of galloylgallic acid (digallic acid), that is, compounds of the depside type (Fischer and Freudenberg, Abstr., 1910, i, 266), might be produced according to the equation: $OAc\cdot R\cdot CO\cdot O\cdot R'\cdot CO_2H + PhCO\cdot Cl + KCN =$

$$OAc\cdot R\cdot CO\cdot CN + PhCO\cdot O\cdot R'\cdot CO_2H + KCl.$$

The reaction takes place when the nucleus contains negative substituents, for example, 3-*m*-nitrobenzoyloxybenzoic acid, 4-*m*-nitrobenzoyloxybenzoic acid, 4-*m*-nitro-*p*-ethylcarbonatobenzoyloxybenzoic acid, diethylcarbonatoprotocatechuoyl-*o*-nitrosalicylic acid, 4-nitro-2-*p*-ethylcarbonatobenzoyloxybenzoic acid, and penta-acetylgalloylgallic acid, but not with the following acids: 4-benzoyloxybenzoic acid, 4-*p*-ethylcarbonatobenzoyloxybenzoic acid and the corresponding 3-oxy-acid, 4-*mp*-diethylcarbonatobenzoylbenzoic acid, and 3-nitro-4-dimethylcarbonatobenzoyloxybenzoic acid.

3-m-*Nitrobenzoyloxybenzoic acid*, $NO_2\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, obtained by the action of *m*-nitrobenzoyl chloride on *m*-hydroxybenzoic acid at 40° in the presence of 10% sodium hydroxide solution, crystallises from dilute alcohol in stout needles, m. p. 241°. The isomeric 4-m-*nitrobenzoyloxybenzoic acid* crystallises from methyl alcohol in long needles, m. p. 273—274° (decomp.). When shaken with benzoyl chloride and an aqueous solution of potassium cyanide, the two acids yield respectively *m*-benzoyloxybenzoic acid and *p*-benzoyloxybenzoic acid together with *m*-nitrobenzoylformic acid (Claisen and Thompson, Abstr., 1880, 253).

3-*Nitro*-4-*ethylcarbonatobenzoic acid*, $CO_2Et\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H$, prepared from 3-nitro-4-hydroxybenzoic acid, ethyl chlorocarbonate, and *N*-sodium hydroxide solution, crystallises from dilute alcohol in stellate masses of needles, m. p. 117°. The corresponding *acid chloride*,

$$CO_2Et\cdot O\cdot C_6H_3(NO_2)\cdot COCl,$$

crystallises from a mixture of chloroform and light petroleum in long needles, m. p. 72°, and condenses with *p*-hydroxybenzoic acid in the presence of alkali, yielding 3-*nitro*-4-p-*ethylcarbonatobenzoyloxybenzoic acid*, $CO_2Et\cdot O\cdot C_6H_3(NO_2)\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H$, which crystallises from aqueous acetone in plates or from dilute alcohol in short, stout needles, m. p. 194—196° after beginning to sinter at 184°. Its decomposition into *m*-nitro-*p*-ethylcarbonatophenylglyoxylonitrile and *p*-benzoyloxybenzoic acid proceeds smoothly. The nitrile could not be isolated, but the crude oil when hydrolysed with concentrated hydrochloric acid gave 3-*nitro*-4-*hydroxyphenylglyoxylic acid*,

$$NO_2\cdot C_6H_3(OH)\cdot CO\cdot CO_2H,$$

which crystallises from chloroform in glistening prisms, m. p. 61° after sintering at 59°.

3 : 4-*Diethylcarbonatobenzoic acid*, $C_6H_3(O\cdot CO_2Et)_2\cdot CO_2H$, crystallises from dilute acetone in brilliant plates, m. p. 122—123° (decomp.); the corresponding *chloride*, $C_{13}H_{13}O_7Cl$, crystallises from a mixture of chloroform and light petroleum, has m. p. 55°, and reacts with *o*-nitrosalicylic acid in the presence of ether and dilute sodium hydroxide solution, yielding *nitro*-2-mp-*diethylcarbonatobenzoyloxybenzoic acid*, $C_6H_3(O\cdot CO_2Et)_2\cdot CO\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H$, which crystallises from dliute alcohol in brilliant, glistening needles, m. p. 212—214°

(decomp.) when quickly heated. With benzoyl chloride and potassium cyanide solution it yields o-*nitro-2-benzoyloxybenzoic acid*,

$$OBz\cdot C_6H_4(NO_2)\cdot CO_2H,$$

m. p. 117°, and a nitrile which on hydrolysis gave 3 : 4-*dihydroxyphenylglyoxylic acid*, $C_6H_3(OH)_2\cdot CO\cdot CO_2H$. This acid crystallises from a mixture of chloroform and light petroleum in needles, m. p. 92°.

3 : 4-*Diethylcarbonatophenylglyoxylonitrile*, $C_6H_3(O\cdot CO_2Et)_2\cdot CO\cdot CN$, prepared from an ethereal solution of the corresponding chloride and an aqueous solution of potassium cyanide, crystallises from light petroleum in glistening needles, m. p. 38°. 4-*Nitro*-2-p-*ethylcarbonatobenzoyloxybenzoic acid*, $CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H$, crystallises in small prisms, m. p. 194—196° (decomp.), and with benzyl chloride and potassium cyanide yields p-*ethylcarbonatophenylglyoxylonitrile*, $CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot CN$, as small needles, m. p. 34°, and volatile under 10—12 mm. pressure. The nitrile when hydrolysed with concentrated hydrochloric acid yields p-*hydroxyphenylglyoxylic acid*, $OH\cdot C_6H_4\cdot CO\cdot CO_2H$, which crystallises from benzene in small cubes, m. p. 84°.

Penta-acetylgalloylgallic acid (Abstr., 1909, i, 402) reacts with benzoyl chloride and potassium cyanide, yielding 5-*benzoyl*-3 : 4-*diacetylgallic acid*, $C_6H_2(O\cdot COPh)(OAc)_2\cdot CO_2H$, which crystallises from methyl alcohol in small, pointed needles, m. p. 178—179°. The nitrile which was also formed when hydrolysed with concentrated hydrochloric acid gave *galloylformic acid*, $C_6H_2(OH)_3\cdot CO\cdot CO_2H$, which crystallises from dilute alcohol in glistening needles, m. p. 114—116°. It gives the same coloration with ferric chloride as does gallic acid, but with potassium cyanide solution it gives a violet coloration.

3 : 4 : 5-*Triethylcarbonatophenylglyoxylonitrile*,

$$C_6H_2(O\cdot CO_2Et)_3\cdot CO\cdot CN,$$

obtained from the corresponding chloride, crystallises from light petroleum in small, glistening needles, m. p. 98°.

3-p-*Ethylcarbonatobenzoyloxybenzoic acid*,

$$CO_2Et\cdot O\cdot C_6H_4\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H,$$

crystallises from dilute acetone in colourless needles, m. p. 148°, and 3-*nitro*-4-*dimethylcarbonatobenzoyloxybenzoic acid*,

$$(CO_2Me\cdot O)_2C_6H_3\cdot CO\cdot O\cdot C_6H_3(NO_2)\cdot CO_2H,$$

prepared from 2 : 4-dimethylcarbonatobenzoyl chloride (Fischer, Abstr., 1909, i, 162) and *m*-nitro-*p*-hydroxybenzoic acid, crystallises from alcohol in small needles, m. p. 172° (decomp.). J. J. S.

Compounds of the Propane Series. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 1905—1915. Compare Hildesheimer, Abstr., 1910, i, 891). —Hildesheimer (*loc. cit.*) has described the compound obtained by the action of red phosphorus and bromine on α-phthaliminobutyric acid as αβ-dibromo-α-phthaliminopropane. A compound of this constitution has now been prepared independently, and found not to be identical with Hildesheimer's compound, which, accordingly, must have the composition of an αγ-dibromo-α-phthaliminopropane,

$$C_8H_4O_2{:}N\cdot CHBr\cdot CH_2\cdot CH_2Br.$$

By the action of bromine on phthaliminoacetone, mono-, di-, tri-, and tetra-bromo-derivatives have been obtained.

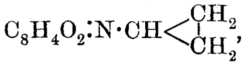
Phthaliminobromoacetone, $C_8H_4O_2{:}N\cdot CH_2\cdot CO\cdot CH_2Br$, prepared either by the action of phosphorus pentabromide or of bromine in chloroform solution on phthaliminoacetone, crystallises in colourless, slender, matted needles, m. p. 147—148°. When fused with potassium phthalimide, diphthaliminoacetone is obtained, proving the position of the bromine atom, whilst on heating with sodium acetate at 170°, *phthaliminohydroxyacetone*, crystallising in needles of silky lustre, m. p. 141—142°, is formed.

On hydrolysis of phthaliminobromoacetone by boiling with water, phthalimide and methylglyoxal are the main products.

Phthaliminodibromoacetone, $C_8H_4O_2{:}N\cdot CHBr\cdot CO\cdot CH_2Br$, produced on bromination in benzene solution or further bromination of the monobromo-compound, forms long needles, m. p. 126—127°. On hydrolysis, phthalimide and bromomethylglyoxal are obtained.

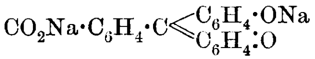
Phthaliminotribromoacetone, $C_8H_4O_2{:}N\cdot CHBr\cdot CO\cdot CHBr_2$, crystallises in obliquely-cut rods, m. p. 146—147°. On hydrolysis phthalimide and dibromomethylglyoxal are obtained, the latter being identified as the phenylhydrazone, crystalling in citron-yellow needles, m. p. 174°—175°.

Phthaliminotetrabromoacetone, $C_8H_4O_2{:}N\cdot CHBr\cdot CO\cdot CBr_3$, crystallises in rhombic plates, m. p. 153—154°. On hydrolysis bromoform is obtained.

On distillation of phthalimino-*n*-butyryl chloride, propenylphthalimide, m. p. 151°, is obtained (compare Johnson and Jones, this vol., i, 455). The isomeric *phthaliminocyclopropane*,  $C_8H_4O_2{:}N\cdot CH\Big\langle\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, prepared from amino*cyclo*propane and phthalic acid, forms colourless, rhombic plates, m. p. 135—136°. It does not form an additive compound with bromine.

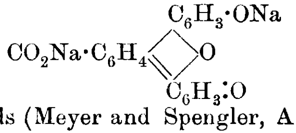
Propenylphthalimide combines with bromine in chloroform solution, forming *phthalimino-αβ-dibromopropane*, $C_8H_4O_2{:}N\cdot CHBr\cdot CHBr\cdot CH_3$, which crystallises in flat, hexagonal crystals, m. p. 105—106°, and differs from Hildesheimer's compound (*loc. cit.*), m. p. 147°. On hydrolysis, phthalimide and acetylcarbinol are obtained. E. F. A.

Composition of Phthalein Salts. RICHARD MEYER and FERD. POSNER (*Ber.*, 1911, **44**, 1954—1957).—The authors have carefully re-investigated the composition of the red sodium salt of phenolphthalein and the violet sodium salt of hydroquinonephthalein, and obtain results which are in agreement with the formulæ:



$$CO_2Na\cdot C_6H_4\cdot C\Big\langle\begin{matrix}C_6H_4\cdot ONa\\ C_6H_4{:}O\end{matrix}$$

and



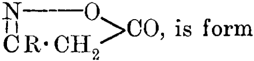
$$CO_2Na\cdot C_6H_4\Big\langle\begin{matrix}C_6H_3\cdot ONa\\ \rangle O\\ C_6H_3{:}O\end{matrix}$$

previously assigned to these compounds (Meyer and Spengler, Abstr., 1905, i, 440; compare Baeyer, Abstr., 1910, i, 249; Kehrmann, *ibid.*, 406).

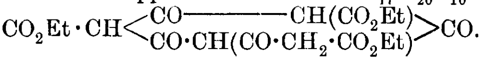
The calcium salt of phenolphthalein is obtained crystalline by shaking phenolphthalein with water and calcium hydroxide at the ordinary temperature, and heating the resulting solution to boiling. It has the composition $C_{20}H_{12}O_4Ca,1\frac{1}{2}H_2O$, and forms reddish-brown, flat prisms with a green lustre; the anhydrous salt has a metallic-green colour (compare D.R.-P. 223969). F. B.

By-products of the Preparation of Ethyl Phloroglucinol-dicarboxylate. HERMANN LEUCHS and FRITZ SIMION (*Ber.*, 1911, **44**, 1874—1884. Compare Leuchs and Geserick, Abstr., 1909, i, 106).—In the preparation of ethyl phloroglucinol dicarboxylate by the Baeyer synthesis, ethyl malonate and ethyl acetate are present in the reaction mixture, and there is the possibility of 3 mols. of acetate uniting to form phloroglucinol, or of 3 mols. of malonate uniting to form a tricarboxylate, or of the formation of phloroglucinolmonocarboxylate from 2 mols. of acetate and 1 mol. of malonate. The by-products of the reaction have been examined from this point of view, and five such isolated, namely, an *ester*, $C_{17}H_{20}O_{10}$, m. p. 96°, an *acid*, $C_{15}H_{16}O_{10}$, and an *ester*, $C_{14}H_{16}O_8$, both derived from this by secondary changes, a compound, $C_{22}H_{20}O_{12}$, and a compound, $C_{18}H_{18}O_{11}$, formed by the combination of 4 mols. of ethyl malonate.

Neither phloroglucinol-mono- nor -tri-carboxylate is formed, although the latter may represent an intermediate stage in the formation of some of the compounds mentioned. More probably the molecules are first united in chains, and the closing of the ring takes place subsequently.

The *ester*, $C_{17}H_{20}O_{10}$, has been more fully investigated. With hydroxylamine, an *iso*oxazolone,  $\left.\begin{array}{l}N\text{———}O\\ \|\\ CR\cdot CH_2\end{array}\right>CO$, is formed. With concentrated nitric acid, the side-chain is hydrolysed, and the ester, $C_{14}H_{16}O_8$, formed.

On acetylation, a *triacetate* is formed, water being at the same time eliminated. On complete hydrolysis with hydrogen iodide, an *acid*, $C_9H_6O_5$, is obtained. Cold sodium hydroxide eliminates a molecule of alcohol.

The formula attached is applied to the ester $C_{17}H_{20}O_{10}$ to express this behaviour:  $CO_2Et\cdot CH\left<\begin{array}{l}CO\text{————————}CH(CO_2Et)\\ CO\cdot CH(CO\cdot CH_2\cdot CO_2Et)\end{array}\right>CO$.

It crystallises in long, matted, colourless needles, m. p. 95·5—96·5°, and shows a deep reddish-brown coloration with ferric chloride.

The iso*oxazolone*, $C_{15}H_{15}O_9N$, produced on boiling with hydroxylamine, forms four-sided, glistening tablets or prisms, m. p. 203—204° (decomp.).

The *acetate*, $C_{23}H_{24}O_{12}$, crystallises in yellow, dome-like prisms, m. p. 109—110°. The mother liquors contain the *sodium* salt, four-sided, yellow plates, m. p. 260° (decomp.), of an *ester*, $C_{21}H_{20}O_{12}$ or $C_{19}H_{18}O_{11}$, which crystallises in needles, m. p. 145—146°. By the action of hydrogen iodide on the acetate, an *acid*, $C_9H_6O_3$, crystallising in feathery needles, is obtained, m. p. above 300°.

The *anhydride*, $C_{17}H_{18}O_9$, of the ester, $C_{17}H_{20}O_{10}$, crystallises in long, hexagonal needles, m. p. 153—154°.

With the ester, sodium hydroxide gives a product, $C_{15}H_{14}O_9$, crystallising in massive prisms, m. p. 162—163°.

Concentrated nitric acid forms from the ester, glistening, broad needles, m. p. 128—129°, of the *compound*, $C_{14}H_{16}O_8$, identical with that formed during the original condensation. A second *product*, $C_{16}H_{18}O_{10}$, crystallises in needles or prisms, m. p. 99—100°.

The *condensation product*, $C_{15}H_{16}O_{10}$, consists of colourless, glistening, obliquely-cut prisms, m. p. 165° (decomp.). When fused, it forms the compound, $C_{14}H_{16}O_8$, just described.

The by-product, $C_{22}H_{20}O_{12}$, forms pale yellow needles, m. p 196—197°.

The fifth condensation product, the ester, $C_{18}H_{18}O_{11}$, crystallises in yellow, pointed, four-sided plates, m. p. 177—178°, and is identical with a substance isolated by Willstätter (Abstr., 1899, i, 577). It yields phloroglucinol when fused with potassium hydroxide, and is considered to be formed by the condensation of 4 mols. of ethyl malonate. E. F. A.

Synthesis of Glucovanillic Acid and of Gluco-*p*-hydroxybenzoic Acid. FERDINAND MAUTHNER (*J. pr. Chem.*, 1911, [ii], **83**, 556—560. Compare Abstr., 1910, i, 677).—*Methyl tetra-acetylglucovanillate*, $C_{23}H_{28}O_{13}$, m. p. 144—145°, obtained by shaking a solution of methyl vanillate in dilute sodium hydroxide with ethereal β-acetobromoglucose for twenty-six hours, is hydrolysed by aqueous barium hydroxide at the ordinary temperature, yielding Tiemann and Reimer's glucovanillic acid.

In a similar manner, methyl *p*-hydroxybenzoate and β-acetobromoglucose yield *methyl tetra-acetylgluco-*p*-hydroxybenzoate*, $C_{22}H_{26}O_{12}$, m. p. 159—160°, which is converted into *gluco-*p*-hydroxybenzoic acid*, $C_{13}H_{16}O_8$, m. p. 211—212°, by shaking with 6% barium hydroxide for twenty-four hours at the ordinary temperature. C. S.

Chemical Action of Light. XXI. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, **44**, 1558—1564).—By the action of light on benzaldehyde a *trimeride*, m. p. 144—145°, is obtained, isomeric with that of Mascarelli, m. p. 247—248°, which is also formed in this reaction. The new polymeride crystallises in chalk-white, microcrystalline crusts, and does not combine with semicarbazide. Cinnamaldehyde after a year's exposure to light gives a reddish-brown, transparent resin, which after purification forms an almost colourless powder, m. p. 115°; this is probably a *polymeride* of four or five molecules.

A mixture of benzophenone and benzaldehyde when exposed to light forms a *compound*, $C_{27}H_{22}O_3$, composed of two molecules of benzaldehyde and one of benzophenone. This crystallises in colourless, voluminous needles, m. p. 245°.

A mixture of benzophenone and diethyl dihydrocollidinedicarboxylate in benzene yields after a year's exposure a mixture of benzopinacone and ethyl collidinedicarboxylate. The *picrate* of the latter forms large, yellow needles, m. p. 164°; the *aurichloride* is oily, and the *platinichloride* yields orange-red platelets, m. p. 181°.

Quinaldine and acetone unite to a condensation product, $C_{23}H_{22}N_2$, composed of 2 mols. of quinaldine and 1 mol. of acetone, which crystallises in light yellow, slender needles, m. p. 212°. It is a diacid base; on the addition of hydrochloric acid it becomes orange-red, but on stirring the solution becomes colourless. When this is evaporated a barely yellow-coloured residue is obtained, which immediately becomes orange-red on the addition of water.

The *dihydrochloride* is colourless; the *monohydrochloride* is orange-red, m. p. 270°. The *platinichloride* is orange-red; the *aurichloride* is at first a golden-yellow, crystalline precipitate, but with water a brown mass is obtained and the filtrate is violet-brown. E. F. A.

Rate of Transformation of *syn*- into *anti*-Oximes. THOMAS S. PATTERSON and ANDREW MCMILLAN (*Proc. Phil. Soc. Glasgow*, 1911, Reprint 7 pp.).—In continuation of previous work (Trans., 1907, **91**, 504; 1908, **93**, 1042), the authors have determined the velocity of transformation of a number of substituted benz*syn*aldoximes into the *anti*-forms in ethyl tartrate solution.

The following are the mean values for 1000 *k* at 26°: Benz*syn*aldoxime, 6·38; *p*-tolyl*syn*aldoxime, 5·18; anis*syn*aldoxime, 6·82; piperonal*syn*aldoxime, 3·59; *o*-nitrobenz*syn*aldoxime, 1·10; *m*-nitrobenz*syn*aldoxime, 4·16; *p*-iodobenz*syn*aldoxime, 5·335.

In the case of *p*-nitrobenz*syn*aldoxime the transformation into the *anti*-oxime takes place so rapidly that no measurements of the rate of change could be made. F. B.

Synthesis of α-Amino-ketones by means of Hexamethylenetetramine. CARL MANNICH and FRIEDRICH L. HAHN (*Ber.*, 1911, **44**, 1542—1552).—A large number of α-halogen ketones readily form crystalline additive products with hexamethylenetetramine, iodides reacting more readily than bromides or chlorides. These compounds are colourless, soluble salts, which tend to decompose when crystallised and decompose also on warming. When hydrolysed with a large excess of alcohol and 38% hydrochloric acid, the corresponding amines are obtained, but the reaction is complicated by the formation of condensation products with the formaldehyde derived from hexamethylenetetramine. In the case of those bases which are stable in the free state, the formaldehyde can be fixed by adding sodium hydrogen sulphite.

Two of the amino-ketones, ω-amino-*p*-hydroxyacetophenone,

$$OH\cdot C_6H_4\cdot CO\cdot CH_2\cdot NH_2,$$

and aminoacetylcatechol, $C_6H_3(OH)_2\cdot CO\cdot CH_2\cdot NH_2$, were obtained as free bases, although α-amino-ketones usually condense to form dihydropyrazines. The condensation is possibly hindered by the phenolic nature of the compounds, or more probably it depends on the solubility of the amino-ketones. When they are sparingly soluble, condensation does not take place.

ω-Chloroacetophenone and hexamethylenetetramine form a salt-like additive product, m. p. 145°. The similar compound from ω-bromoacetophenone and hexamethylenetetramine has m. p. 165°. Either product on treatment for three days with hydrochloric acid and alcohol gives the *hydrochloride* of *aminoacetophenone*, m. p. 186—187°; the *hydrobromide* has m. p. 217—218° (decomp.).

ω-*Carbethoxyaminoacetophenone*, $C_6H_5\cdot CO\cdot CH_2\cdot NH\cdot CO_2Et$, prepared by the interaction of the aminoacetophenone salts with ethyl chlorocarboxylate, crystallises in slender needles, m. p. 58°. It is reduced by sodium amalgam and alcohol to *ω-carbethoxyaminomethylphenylcarbinol*, which crystallises in colourless plates, m. p. 86°.

ω-Chloro-*p*-methoxyacetophenone and hexamethylenetetramine condense to a product, m. p. 170°, which is decomposed into *ω-amino-*p*-methoxyacetophenone hydrochloride*, m. p. 197° (decomp.); this becomes red in solution on the addition of ammonia, and orange needles of a dihydropyrazine separate.

*ω-Amino-*p*-hydroxyacetophenone hydrochloride* crystallises in colourless platelets, m. p. 242° (decomp.). The free *base* is stable, crystallising in glistening plates.

Ethyl carbonato-ω-carbethoxyaminoacetophenone,

$$CO_2Et{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}NH{\cdot}CO_2Et,$$

forms slender, colourless plates, m. p. 85—86°.

ω-Chloroacetylcatechol, m. p. 173°, is best prepared by heating equal quantities of catechol, chloroacetic acid, and phosphoryl chloride in a large flask on the water-bath until the liberation of hydrogen chloride ceases. The *diacetate* has m. p. 110—111°, but the additive product with hexamethylenetetramine could not be obtained pure.

ω-Iodoacetylcatechol diacetate, obtained by interaction of the chloride with sodium iodide, has m. p. 110—111°; it forms a hexamethylenetetramine *additive product*, m. p. 171°.

ω-Aminoacetylcatechol is a heavy powder, decomp. above 200°; the hydrochloride crystallises in lustrous plates, which become brown at 230°, m. p. 252° to a dark red liquid.

ω-Bromoacetoveratrone, $C_6H_3(OMe)_2{\cdot}CO{\cdot}CH_2Br$, obtained by bromination of acetoveratrone in chloroform, has m. p. 80—81°; the *additive product* with hexamethylenetetramine crystallises in needles.

ω-Aminoacetoveratrone hydrochloride forms colourless, lustrous needles, m. p. 221°.

ω-Chloroacetylpyrogallol triacetate, $C_6H_2(OAc)_3{\cdot}CO{\cdot}CH_2Cl$, has m. p. 100—101°. When oxidised with potassium permanganate in acetone, an acid containing acetyl is obtained, which is hydrolysed to pyrogallolcarboxylic acid, thus proving the positions 1, 2, 3, 4 for the substituting groups in chloroacetylpyrogallol. The triacetate does not combine with hexamethylenetetramine.

ω-Iodoacetylpyrogallol triacetate has m. p. 139—140°; it forms an additive product with hexamethylenetetramine, m. p. 130°, but ω-aminoacetylpyrogallol could not be obtained from this.

Acetylpyrogallol trimethyl ether has b. p. 165°/12 mm., m. p. 14—15°. *Bromoacetylpyrogallol trimethyl ether* is a viscid oil, m. p. 174—176°, forming colourless crystals, m. p. 50—51°; it does not form a hexamethylenetetramine additive compound. E. F. A.

Isolation of an Enolic Dibromide and the Course of the Reaction in the Bromination of Acetophenone and Similar Ketones. FRIEDRICH L. HAHN (*Ber.*, 1911, **44**, 1552—1553).—When bromine is passed into a well cooled solution of acetoveratrone in a little chloroform or ether, a yellowish-red *dibromide*, $C_{10}H_{12}O_3Br_2$, separates. This is very unstable, and decomposes completely within twelve hours. When covered with ether and well shaken with dilute sodium hydroxide, both layers remain colourless; the ether on evaporation yields ω-bromoacetoveratrone, an indication that the ketone reacts in the enolic form, and that the dibromide has the formula $C_6H_3(OMe)_2\cdot CBr(OH)\cdot CH_2Br$.

When acetophenone is brominated in ice-cold chloroform solution, no hydrogen bromide is liberated, neither does the brownish-red solution contain free bromine until at least 1 mol. of bromine for each mol. of ketone has been added. Only on warming or shaking with water is hydrogen bromide liberated, and the solution becomes lighter in colour; it then contains ω-bromoacetophenone. If bromination is performed in a solution of sodium acetate in acetic acid, bromine is not fixed, even at the temperature of the water-bath, so long as no enol is present. On the addition of concentrated hydrochloric acid a trace of enol is formed and a violent reaction sets in, the solution being immediately decolorised. E. F. A.

Chemical Action of Light. XX. GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1911, **44**, 1554—1558. Compare *ibid.*, 1901, **34**, 1541).—By the action of light on a mixture of acetone (1 vol.) and ethyl ether (2 vols.) there are formed *iso*propyl alcohol, an additive product of acetone and ether, $C_7H_{16}O_2$, b. p. 138—141°, probably the *monoethyl ether* of *β-methylbutylene βγ-glycol*, and a product, $C_{11}H_{22}O_3$ or $C_{11}H_{24}O_3$, b. p. 109—112°/20 mm.

Acetophenone and ethyl ether after seven months' exposure to light yield an additive product, $C_{12}H_{18}O_2$, b. p. 247°, together with a further condensation product.

Benzophenone and ethyl ether form benzopinacone and an additive product, $C_{17}H_{20}O_2$, crystallising in colourless prisms, m. p. 51°, and stable towards permanganate; it has probably the composition $OH\cdot CPh_2\cdot CHMe\cdot OEt$. A more complicated condensation product is also obtained. E. F. A.

Ketens. XIX. Formation and Preparation of Diphenylketen. HERMANN STAUDINGER (*Ber.*, 1911, **44**, 1619—1623).—Diphenylketen is formed in almost quantitative yield by the interaction of equal molecular quantities of diphenylacetyl chloride and tripropylamine in ethereal solution. It is also obtained, together with ω-chlorodiphenylmethane and tetraphenylethylene, when diphenylacetyl chloride is distilled in a current of carbon monoxide under ordinary pressure. It is, however, best prepared by allowing a benzene solution of azibenzil to flow slowly into a flask heated at 100°, and distilling the resulting diphenylketen under diminished pressure (compare Schroeter, Abstr., 1909, i, 617).

The residue from the distillation separates from glacial acetic acid in yellow crystals of the composition $C_{28}H_{20}O_2N_2$, m. p. 201°, and consists of an *additive* compound of diphenylketen with azibenzil. F. B.

Beckmann Transformation. FERDINAND HENRICH (*Ber.*, 1911, **44**, 1533—1536. Compare Schroeter, this vol., i, 505).—When ethereal solutions of the *syn*-modifications of dypnoneoxime (Abstr., 1904, i, 431) and of benzylideneacetophenoneoxime (Abstr., 1907, i, 324) are subjected to the Beckmann transformation by phosphorus pentachloride, white substances are first precipitated, which are then converted by the further addition of phosphorus pentachloride into the yellow products, from which the anilides are finally obtained by the action of water. Similar behaviour is exhibited by pivalophenoneoxime (Schroeter, *loc. cit.*) and by benzophenoneoxime. These white substances are shown to be the *hydrochlorides* of the oximes, since they are produced by passing hydrogen chloride into ethereal solutions of the *syn*-oximes, and regenerate the oximes by treatment with cold aqueous sodium carbonate. It seems, therefore, that an oxime undergoes the Beckmann transformation only when it has basic (unsaturated) properties. The *anti*-oximes of the preceding substances, which do not undergo the Beckmann transformation, likewise do not have pronounced basic (unsaturated) properties. C. S.

Isomerism and Isomorphism of the Yellow and the Red Fluorenones. Hans Stobbe (*Ber.*, 1911, **44**, 1481—1488).—Kerp's statement that the red and the yellow modifications of fluorenone (diphenylene ketone) are true isomerides (Abstr., 1896, i, 238) is confirmed by the author, who shows that the two substances differ, not only in the solid, but also in the liquid state and in solution.

The yellow ketone has m. p. 83—84°, and melts again at this temperature after resolidifying. The red ketone has m. p. 82—83°, but after resolidifying has m. p. 83—84°. Mixtures of the two ketones in any proportions have m. p. 83—84°. The fused mixture is orange, and solidifies in orange crystals. The red and the yellow, crystalline forms and also the orange mixed crystals are all isomorphous, crystallising in rhombic plates, more rarely in flattened needles. The red ketone crystallises from light petroleum in the dark, at first in blood-red, short crystals, but after repeated crystallisation in orange crystals which get paler in colour and more elongated, indicating a gradual conversion of the red into the yellow form. The conversion is readily accomplished by cold concentrated sulphuric acid.

The absorption spectra of the two modifications in alcohol, both in the visible and in the ultra-violet regions, have been measured. The latter are identical, the former, of course, are different. The optical behaviour leads the author to the opinion that Kerp's constitutions for the two ketones (*loc. cit.*) are untenable, and that the two substances furnish yet another instance of a pair of isomerides, the constitutions of which cannot be represented by present-day structural or stereochemical theories (compare Schaum, Abstr., 1910, i, 391). C. S.

$\beta\zeta$-Dibenzoyl-$\beta\zeta$-dimethylheptane and $\alpha\alpha\epsilon\epsilon$-Tetramethylpimelic Acid. Albin Haller and Édouard Bauer (*Compt. rend.*, 1911, **152**, 1638—1642).—The general method for preparing trialkyl derivatives of acetic acid (Abstr., 1909, i, 131) has been applied to the synthesis of dibasic acids.

The sodium derivative of phenyl *iso*propyl ketone, prepared by means of sodamide, reacts with αγ-dibromopropane, giving a small quantity of an unstable liquid, b. p. 171—173°/13 mm., probably of the constitution $COPh\cdot CMe_2\cdot [CH_2]_2\cdot CH_2Br$; the principal portion of the product, however, consists of *βζ-dibenzoyl-βζ-dimethylheptane*,

$$COPh\cdot CMe_2\cdot [CH_2]_3\cdot CMe_2\cdot COPh,$$

silky needles, m. p. 48—49°, b. p. 250—255°/15 mm. This diketone forms a *dioxime*, m. p. 223—224°, and undergoes the usual scission when treated with sodamide, giving rise to *ααεε-tetramethylpimelamide*, needles, m. p. 191—192°. *ααεε-Tetramethylpimelic acid*,

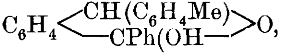
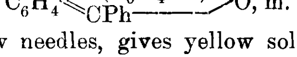
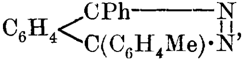
$$CO_2H\cdot CMe_2\cdot [CH_2]_3\cdot CMe_2\cdot CO_2H,$$

forms hard crystals, m. p. 168—169°.

The reaction follows the same course when α-chloro-γ-bromopropane is used instead of the dibromo-derivative. *ε-Chloro-β-benzoyl-β-methylpentane*, $COPh\cdot CMe_2\cdot CH_2\cdot CH_2\cdot CH_2Cl$, has b. p. 165°/11 mm.

W. O. W.

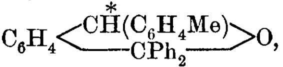
o-Dibenzoylbenzene and its Homologues. ALFRED GUYOT and F. VALLETTE (*Ann. Chim. Phys.*, 1911, [viii], **23**, 363—397).—Guyot and Catel (Abstr., 1905, i, 226, 516, 540; 1906, i, 761; 1907, i, 76) have drawn attention to the analogy which exists between the reactions of *o*-dibenzoylbenzene and those of diphenylphthalide and phenyloxanthranol, and Haller, Guyot, and Pignet have shown that under certain conditions the phthaleins are capable of being isomerised into *o*-dibenzoylbenzene derivatives (Abstr., 1910, i, 285). The authors have therefore generalised the work of Guyot and Catel, and prepared a number of dibenzoylbenzene homologues.

When magnesium phenyl bromide in ether reacts with excess of tolylphthalide, *2-hydroxy-2-phenyl-1-tolyl-1:2-dihydro*iso*benzofuran*,  $C_6H_4<\begin{matrix}CH(C_6H_4Me)\\CPh(OH)\end{matrix}>O$, is formed. It is a colourless, crystalline powder, is very soluble in most organic solvents, and undergoes dehydration slowly at atmospheric temperature, but immediately and quantitatively on adding hydrochloric acid to its solution in alcohol, forming *2-phenyl-1-tolyl*iso*benzofuran*,  $C_6H_4<\begin{matrix}C(C_6H_4Me)\\CPh\end{matrix}>O$, m. p. 83°, which crystallises in slender, yellow needles, gives yellow solutions showing a green fluorescence, of which the colour gradually disappears by the oxidation of the substance in air to *o-toluoylbenzoylbenzene*, m. p. 139°. This crystallises from a hot mixture of alcohol and benzene in small, brilliant prisms, dissolves in sulphuric acid with an intense magenta colour, and is recovered unchanged on addition of water. With hydrazine hydrate, it furnishes *phenyltolylphthalazine*,  $C_6H_4<\begin{matrix}CPh{=\!=}N\\C(C_6H_4Me)\cdot N\end{matrix}$, m. p. 117°, crystallising in small, colourless spangles. *o-Benzhydryltolhydrylbenzene*,

$$OH\cdot CHPh\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4Me,$$

m. p. 104°, is obtained by the reduction of either hydroxyphenyltolyldihydro*iso*benzofuran or benzoyltoluoylbenzene with sodium amalgam in alcohol. It crystallises in thin, colourless spangles. Under similar conditions, phenyltolyl*iso*benzofuran furnishes the *1:2-dihydride*, m. p. 104°, which crystallises in brilliant, colourless needles.

When, on the contrary, excess of magnesium phenyl bromide in ether is added to tolylphthalide, the condensation goes a stage further, and *o-tolhydryltriphenylcarbinol*, $HO\cdot CPh_2\cdot C_6H_4\cdot CH(OH)\cdot C_6H_4Me$, m. p. 182°, small crystals, is formed. This, on treatment with warm sulphuric acid, loses 2 mols. of water and gives *10-phenyl-9-tolylanthracene*, m. p. 192°, which crystallises in feebly yellow, bulky prisms, and fluoresces violet on solution in benzene. On oxidation with sodium dichromate, it yields *9:10-dihydroxy-10-phenyl-9-tolyldihydroanthracene*, m. p. 212° (anhydrous), which crystallises with some alcohol in transparent needles, gives an indigo-blue coloration with sulphuric acid, and liberates iodine from potassium iodide. Its constitution is established by its synthesis from the ethyl ether of phenyloxanthranol by the action of magnesium tolyl bromide (compare Guyot and Staehling, Abstr., 1905, i, 885). In acetic acid solution, *o*-tolhydryltriphenylcarbinol is dehydrated by hydrochloric acid, forming *2:2-diphenyl-1-tolyldihydroisobenzofuran*,



$$C_6H_4<\begin{matrix}C\overset{*}{H}(C_6H_4Me)\\CPh_2\end{matrix}>O,$$

m. p. 123°, which crystallises in small, colourless needles from alcohol, and on oxidation with sodium dichromate in acetic acid exchanges the $\overset{*}{H}$ atom for a hydroxyl group; this *hydroxy*-compound has m. p. 130°, and crystallises from alcohol, ether, or benzene. Its constitution was established by its synthesis from diphenylphthalide by the action of magnesium tolyl bromide.

The action of magnesium *p*-tolyl bromide on tolylphthalide is analogous to that of magnesium phenyl bromide on this substance, and the following products were obtained by methods strictly analogous to those employed for the lower homologues described above.

2-Hydroxy-1:2-ditolyl-1:2-dihydroisobenzofuran forms small crystals, and on heating loses 1 mol. of water, forming *1:2-ditolylisobenzofuran*, m. p. 125°, crystallising in long, yellow needles. Ditoluoylbenzene, m. p. 184°, forms colourless crystals, and gives an intense magenta colour with sulphuric acid (compare Bauer, Abstr., 1905, i, 210). Its *monophenylhydrazone*, m. p. 171°, forms small, brilliant yellow prisms. Ditolylphthalazine, m. p. 221°, crystallises from alcohol in long, slender needles. *o-Ditolhydrylbenzene*, m. p. 118°, forms small, colourless spangles. *1:2-Ditolyl-1:2-dihydroisobenzofuran*, m. p. 89°, separates from methyl alcohol in slender, colourless needles.

Ditolyl-o-tolhydrylphenylcarbinol,

$$C_6H_4Me\cdot CH(OH)\cdot C_6H_4\cdot C(C_6H_4Me)_2\cdot OH,$$

m. p. 138°, forms small, brilliant prisms, and in contact with sulphuric acid loses 2 mols. of water, giving *9:10-p-ditolyl-2-methylanthracene*, which crystallises in yellow prisms and fluoresces violet in benzene and its homologues. On oxidation it gives *9:10-dihydroxy-9:10-ditolyl-2-methyldihydroanthracene*, m. p. 207° (anhydrous), which crystallises with some alcohol in brilliant prisms, gives an indigo-blue coloration with sulphuric acid, and liberates iodine from potassium iodide.

Magnesium *a*-naphthyl bromide in ether reacts with phenyl-phthalide, forming *2-hydroxy-1-phenyl-2-naphthyl-1 : 2-dihydroisobenzofuran*. This was obtained as an oil, which, on oxidation, gave *o-benzoylnaphthoylbenzene*, m. p. 104°, in small, colourless crystals. *o-Toluoylnaphthoylbenzene*, m. p. 144°, crystallising in small, colourless prisms, was obtained similarly from the condensation product of magnesium α-naphthyl bromide and tolylphthalide. T. A. H.

Quinhydrones. WILHELM SIEGMUNDS (*J. pr. Chem.*, 1911, [ii], **83**, 553—555).—By the addition of a warm ethereal solution of the phenol to a warm solution of *p*-benzoquinone in petroleum, the following *quinhydrones* have been obtained: $3C_6H_4O_2,4C_6H_3(OH)_3$, m. p. 78°, black needles, from *p*-benzoquinone (2 mols.) and pyrogallol (1 mol.); $3C_6H_4O_2,4C_6H_3(OH)_3$, m. p. 164°, green needles, from *p*-benzoquinone (1 mol.) and hydroxyquinol (1 mol.);

$$3C_6H_4O_2,2C_6H_3(OH)_3,$$

m. p. 103°, red crystals, from *p*-benzoquinone (4 mols.) and phloroglucinol (1 mol.); $C_6H_4O_2,C_{10}H_6(OH)_2$, from *p*-benzoquinone (1 mol.) and 2 : 3-dihydroxynaphthalene (1 mol.), separates initially in pale red leaflets, finally in garnet-red needles, both forms having m. p. 78—80° (compare Abstr., 1909, i, 109). C. S.

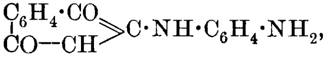
Constitution of Quinhydrone-like Substances. ANGELO KNORR (*Ber.*, 1911, **44**, 1503—1506)—Richter's conception of quinhydrones as oxonium compounds (this vol., i, 136) is inapplicable to the quinhydrones obtained by Haakh from quinones and hydrocarbons (Abstr., 1910, i, 48). The author selects several of Richter's examples and shows that the constitutions ascribed to them are at variance with their properties. A true *imonium* compound,

$$NO_2\cdot C_6H_4\cdot O\cdot NH_2{:}C_6H_4{:}NH_2\cdot O\cdot C_6H_4\cdot NO_2,$$

m. p. 59° (decomp.), has been prepared from quinonedi-imine and *p*-nitrophenol in ether. It forms yellow crystals and lacks, therefore, the chief criterion of a quinhydrone, namely, an intense colour in comparison with those of its components. C. S.

Vat Dyes from α-Naphthaquinone. RUDOLF PUMMERER and KURT BRASS (*Ber.*, 1911, **44**, 1647—1656).—A number of substituted 2-amino-α-naphthaquinones have been prepared by the condensation of amino-compounds with α-naphthaquinone. On reduction with alkaline hyposulphite, the majority of these compounds yield vats which dye cotton without a mordant. The dyes are, however, of no technical importance, partly on account of their lack of vivid shades, and partly because of their insufficient fastness to chlorine and light.

From experiments on the behaviour of several leuco-compounds of vat-dyes towards vegetable fibres, the authors draw the conclusion that the production of fast colours is determined by the following two factors: (1) the affinity of the leuco-compounds for the fibre, and (2) the firmness with which the dye is mechanically fixed on the fibre when the leuco-compound is oxidised.

2-p-Aminoanilino-α-naphthaquinone, 

$$\begin{array}{l}C_6H_4\cdot CO\\ |\\ CO{-}CH\end{array}\!\!>C\cdot NH\cdot C_6H_4\cdot NH_2,$$

obtained by reducing 2-*p*-nitroanilino-α-naphthaquinone with alkaline hyposulphite and oxidising the resulting solution with a current of air, crystallises in dark violet prisms, m. p. 214° (not sharp); with strong sulphuric acid it gives a safranine-red solution, from which a yellowish-red *sulphate* is precipitated by water.

N-N′-*Di-2-a-naphthaquinonyl*-p-*phenylenediamine*,

$$C_6H_4(NH\cdot C_{10}H_5O_2)_2,$$

is prepared by heating *a*-naphthaquinone with *p*-phenylenediamine in glacial acetic acid solution; it forms a brownish-violet, crystalline powder, m. p. 250° (not sharp), and gives with alkaline hyposulphite a light yellow vat, in which cotton is dyed brownish-violet. It is oxidised with lead peroxide in xylene solution, yielding probably p-*benzoquinonedi-2-a-naphthaquinonyldi-imine.*

2-(4′)-*Diphenylylamino-a-naphthaquinone*, $C_{10}H_5O_2\cdot NH\cdot C_6H_4Ph$, obtained by heating *a*-naphthaquinone and 4-aminodiphenyl in alcoholic solution, crystallises in red needles, m. p. 215°.

2-*Benzidino-a-naphthaquinone*, $C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot C_6H_4\cdot NH_2$, prepared from benzidine and *a*-naphthaquinone, crystallises in brown needles, m. p. 259°, and gives scarlet-red salts; the *acetyl* derivative forms violet crystals, m. p. 329° (decomp.).

2-o-*Tolidino-a-naphthaquinone* is a dark violet powder; the *acetyl* derivative, $C_{26}H_{22}O_3N_2$, crystallises in spindle-shaped prisms, m. p. 233°.

2-o : o′-*Dichlorobenzidino-a-naphthaquinone*, $C_{22}H_{14}O_2N_2Cl_2$, has m. p. 237° with previous sintering; the *acetyl* and *benzoyl* derivatives crystallise in plates having a coppery lustre, m. p. 264° and 302° respectively.

N-p-*Aminophenyl*-N′-p-2-*a-naphthaquinonylaminophenylcarbamide*, $C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot NH_2$, prepared from *p* : *p*′-diaminodiphenylcarbamide and *a*-naphthaquinone in glacial acetic acid solution, has m. p. 348°.

4-*Amino*-4′-(2)-*a-naphthaquinonylaminobenzophenone*,

$$C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot NH_2,$$

prepared from 4 : 4′-diaminobenzophenone, crystallises in flat, brick-red prisms.

4-*Amino*-4′-(2)-*a-naphthaquinonylaminodiphenylmethane*,

$$C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot NH_2,$$

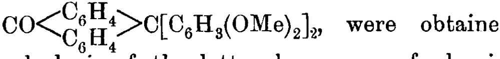
prepared from 4 : 4′-diaminodiphenylmethane, has m. p. 182°. F. B.

Preparation of 2:2′-Dianthraquinonylcarbamide. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 232739).—The preparation of arylanthraquinonylcarbamides has previously been described (this vol., i, 469); it is now found that the action of carbonyl chloride at 170° on a nitrobenzene solution of 2-aminoanthraquinone forms initially 2-anthraquinonylcarbamide chloride, which then combines with another molecule of the base, yielding 2 : 2′-*dianthraquinonylcarbamide*, which separates in small, orange crystals. F. M. G. M.

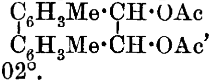
Condensation of Anthraquinone with Phenols. WASSILI W. SCHARWIN [with K. A. KUSNEZOFF, W. A. NAUMOFF, A. L. GANDURIN, N. I. BJENKOFF, and S. A. DMITRIEFF] (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 562—574).—Most of this work has been already published (Abstr., 1903, i, 640; 1904, i, 1032), the new matter being as follows.

Tetrabromophenolanthrone (*tetrabromophenolanthraquinone*), $C_{26}H_{14}O_3Br_4$, forms colourless needles, m. p. 290°.

Dinitrophenolanthrone, $C_{26}H_{16}O_7N_2$, forms shining, yellow plates with a faint green tint, m. p. 236°; in alkaline solution it gives a pure, bright yellow coloration, which, as with other nitrophenols (compare Scharwin, Abstr., 1910, ii, 396), increases in intensity on dilution. *Tetranitrophenolanthrone*, $C_{26}H_{14}O_{11}N_4$, forms lemon-yellow needles, m. p. 278°, and, in an acid-bath, dyes wool and silk bright yellow. *Hexanitrophenolanthrone*, $C_{26}H_{12}O_{15}N_6$, was also prepared.

Dinitroresorcinolanthrone, $C_{26}H_{14}O_8N_2$, and *tetramethoxydiphenylanthrone*,  $CO<\begin{matrix}C_6H_4\\C_6H_4\end{matrix}>C[C_6H_3(OMe)_2]_2$, were obtained as yellow powders; hydrolysis of the latter by means of aluminium chloride yields resorcinolanthrone. T. H. P.

Synthesis of Orthoquinones. CARL LIEBERMANN (*Ber.*, 1911, **44**, 1453—1455. Compare Liebermann and Zsuffa, this vol., i, 202, 387).—*p*-Ditolyl condenses with oxalyl chloride and aluminium chloride, yielding 2 : 7-dimethylphenanthraquinone together with 4 : 4′-dimethyldiphenic acid.

2 : 7-*Dimethylphenanthraquinone*, $C_{16}H_{12}O_2$, crystallises from alcohol in glistening, orange-red plates, m. p. 224°, and gives a green solution in concentrated sulphuric acid. The corresponding quinol is unstable, but yields a stable *diacetyl* derivative,  $\begin{matrix}C_6H_3Me\cdot CH\cdot OAc\\|\qquad\quad\ |\\C_6H_3Me\cdot CH\cdot OAc\end{matrix}$, in the form of colourless, glistening plates, m. p. 202°.

4 : 4′-*Dimethyldiphenic acid*, $CO_2H\cdot C_6H_3Me\cdot C_6H_3Me\cdot CO_2H$, has m. p. 324°. The calcium salt crystallises in transparent prisms containing $2H_2O$. J. J. S.

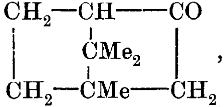
Colloidal Chemical Observations on the Pyranthrone Vat Dyes. ROLAND SCHOLL (*Ber.*, 1911, **44**, 1448—1452).—Pyranthrone yields a purple-red vat dye when reduced with a hot alkaline solution of sodium hyposulphite (Abstr., 1910, i, 271) and a yellow cherry-red vat when reduced at the ordinary temperature. Both products react with *p*-bromobenzoyl chloride, yielding di-*p*-bromobenzoyltetrahydropyranthrones, which differ somewhat in appearance, but when the compound from the cherry-red vat is crystallised several times from nitrobenzene, it has the same appearance as the product from the purple-red vat. The conclusion drawn is that the cold vat consists essentially of the same tetrahydropyranthrone as the hot vat, and that its cherry-red colour is due to a small amount of impurity, namely, colloidal pyranthrone, which forms a colloidal complex with the vat.

Experiments are described which support this view.

The formation of lighter tones by immersing fabrics dyed with pyranthrone in boiling soap solution is shown to be due to a process of oxidation, and the same results can be obtained by exposing the dyed fabric to a 10% solution of sodium hydroxide containing a little potassium ferricyanide and to dilute alkali and atmospheric oxygen. The deeper tone can be restored by treatment with alkaline hyposulphite solution, slowly at the ordinary temperature and more rapidly by warming.

Tetrahydropyranthrone can be obtained by allowing the vat, obtained by using hot alkaline hyposulphite, to cool in an atmosphere of hydrogen and then precipitating with dilute acetic acid. When dry, the precipitate has a yellowish-red colour, and gives a violet-red solution in sodium hydroxide.

When kept for some hours, the precipitate becomes darker, and yields an opalescent, brown solution with sodium hydroxide, probably containing dihydropyranthrone, as it turns yellow when shaken with air, owing to the formation of pyranthrone, and violet-red when treated with hyposulphite solution. J. J. S.

β-Camphor (Bornylone) from Bornylenecarboxylic Acid. JULIUS BREDT and W. HILBING (*Chem. Zeit.*, 1911, **35**, 765).—An account of the synthesis of β-camphor, 

$$\begin{array}{lcr} CH_2\text{—}CH & \text{——} & CO \\ | & CMe_2 & | \\ CH_2\text{—}CMe & \text{——} & CH_2 \end{array}$$

, from bornylenecarboxylic acid (Bredt, Abstr., 1906, i, 680; 1909, i, 499). *Bornylenecarboxyl chloride*, $C_{10}H_{15}\cdot COCl$, b. p. 114—115°/14 mm., when treated with hydrazine hydrate, yields the corresponding *hydrazide*, $C_{10}H_{15}\cdot CO\cdot NH\cdot NH_2$, m. p. 109—110°, which is converted, according to the method of Curtius, into the *azide*, $C_{10}H_{15}\cdot CO\cdot N_3$, and then into *β-iminocamphor*. On hydrolysis with acids, this yields β-camphor, b. p. 213·1—213·4°, m. p. 184—185°, which is identical with the epicamphor (of m. p. 165°) recently described by Lankshear and Perkin (Proc., 1911, **27**, 166).

On oxidation with nitric acid, β-camphor yields camphoric acid.

The oxime has m. p. 103—104°; the semicarbazone, m. p. 237° (compare Lankshear and Perkin, *loc. cit.*).

Wagner's (*Chem. Zeit.*, 1903, **27**, 721) β-camphor consists mainly of ordinary camphor. F. B.

Hydrogenation of Limonene. GUSTAVE VAVON (*Compt. rend.*, 1911, **152**, 1675—1677).—Determination of the rate at which limonene absorbs hydrogen in presence of platinum-black shows that the hydrogenation takes place in two stages, enabling the dihydride or tetrahydride to be obtained at will. *Dihydrolimonene*, $C_{10}H_{18}$, has physical constants approaching those of Δ^1-tetrahydro-*p*-cymene (carvomenthene): b. p. 175—177°, n_D^{18} 1·4563, D_4^{18} 0·8246, $[\alpha]_{\lambda 578}$ +118°, $[\alpha]_{\lambda 436}$ +234°; the *dibromide*, $C_{10}H_{18}Br_2$, has b. p. 136—140°/16 mm., n_D^{21} 1·5236, D_4^{21} 1·459, $[\alpha]_{\lambda 578}$ +49°, $[\alpha]_{\lambda 436}$ +100°. The *nitrosochloride*, $C_{10}H_{18}ONCl$, remarkable for its high rotatory power, has m. p. 95—96°, $[\alpha]_{\lambda 578}$ +344°, $[\alpha]_{\lambda 436}$ +724°; the racemic form has been described by Wallach (this vol., i., 470). W. O. W.

Chemistry of Caoutchouc. Theory of Vulcanisation. D. SPENCE and J. H. SCOTT (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 304—312).—The properties of vulcanised caoutchouc have been examined in relation to the chemical and the absorption theories of vulcanisation. It is found that a portion of the sulphur cannot be removed either by the action of acetone or hot sodium hydroxide solution. When the vulcanised caoutchouc is treated with bromine by Budde's method, the product obtained contains sulphur and bromine in proportions which indicate that four atoms of bromine in the tetrabromide, $C_{10}H_{16}Br_4$, are in fact replaced by two atoms of sulphur. This equivalence of the "fixed" sulphur and the bromine is regarded as strong evidence in favour of the chemical combination of the "fixed" sulphur. Experiments, in which the quantities of sulphur removed by acetone in successive equal extraction periods were measured, indicate that a portion of the so-called "free" sulphur is adsorbed. The curves obtained by plotting the successive quantities of extracted sulphur against the period of extraction are in agreement with the requirements of an exponential adsorption equation.

From these results the following conclusions are drawn: (1) the "fixed" sulphur is chemically combined with the caoutchouc; (2) the "free" sulphur, that is to say, the portion which can be removed by solvents, is, in part, adsorbed, the remainder being present in the non-adsorbed condition. The amount of the non-adsorbed free sulphur is dependent on the conditions of the vulcanising process.

H. M. D.

Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and G. SANNA (*Gazzetta*, 1911, **41**, i, 395—414).—The authors have examined the yield and properties of the essential oil obtained from specimens of *Bupleurum fructicosum* in different stages of development and from different localities.

The value of D^{15} varies from 0·8257 to 0·8692; the diminution per 1° rise of temperature is about 0·0008. The specific rotation varies for plants from different places and for the essences yielded by different organs; its maximum and minimum were found to be +45·5° and +19·72° respectively. The rotation diminishes with lapse of time, whilst the density increases. The value of n_D is 1·4783—1·4862, and the b. p. varies for any sample between about 167° and 200°.

In the air and light, it readily oxidises, forming a resinous substance, and this change may also be induced by heating in absence of air for three to four hours at 210°.

The yield of essential oil increases with the development of the plant, and during the periods of advanced and complete inflorescence is greater for the flowers than for the leaves. The density, rotation, and index of refraction increase up to the beginning of flowering and then diminish. The ester content is greater in plants growing at great altitudes, and diminishes with increase of the moisture in the air of the region. The rotatory power varies inversely, and the density directly, with the ester content. The amount of free alcohol is greater in the flowers than in the leaves, and increases in relation to the combined alcohol as flowering progresses. The principal constituents of the essential oil are hydrocarbons. T. H. P.

Essential Oil of Wallflowers. KUMMERT (*Chem. Zeit.*, 1911, **73**, 667—668).—With low-boiling solvents, the blooms of *Cheiranthus Cheiri* yield a dark unctuous extract, which, when freed from fatty matter by strong alcohol and distilled with steam, gives about 0·06% of a yellow, evil-smelling oil, showing in alcoholic solution a slightly blue fluorescence. Distilled under low pressure (3 mm.), less than 1% comes over at 40°, consisting mainly of tear-producing sulphur and nitrogen compounds, resembling mustard oil, which probably unite in the seed-pods to complex molecules, producing the substance cheirolin discovered by Schneider (Abstr., 1909, i, 826; 1910, i, 658). The higher fractions contain aldehydes and ketones, which were separated by their carbazones. These, on treatment with oxalic acid, gave a distinct odour of violets (irone?) and hawthorn (anisaldehyde?). The oil, freed from aldehydes and ketones, was saponified with alcoholic potash, washed, steam-distilled, dried in vacuum, and heated in the water-bath with benzene and phthalic anhydride. The primary alcohols nerol, geraniol, and benzyl alcohol were identified. In the neutral oil, linalool was detected. From the potassium hydroxide extract were obtained phenols (*p*-cresol?) and lactones (coumarin-like substances), acetic, salicylic and anthranilic acids.

The last small fractions contained methyl anthranilate and indole, along with substances smelling like pyridine. J. D. K.

Meliatin, a New Glucoside Hydrolysable by Emulsin, obtained from the Marsh Trefoil. MARC BRIDEL (*Compt. rend.*, 1911, **152**, 1694—1696).—A new glucoside, *meliatin*, $C_{15}H_{22}O_9$, has been extracted from the marsh trefoil (*Menyanthes trifoliata*) by extraction with alcohol. The compound occurs in colourless crystals with a bitter taste, m. p. 222° (corr.), $[\alpha]_D$ $-81·96°$ in aqueous solution. It undergoes hydrolysis by emulsin with production of dextrose. W. O. W.

Preparation of Mixed Formic Acetic Esters of Aloins. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 233326).—When aloin is heated at 100° with a mixture of formic and acetic acids (or with formic acetic anhydride) in the presence of zinc chloride, mixed esters are produced.

The *ester*, containing two formyl and three acetyl residues, forms an almost tasteless, yellow powder, decomposing at 75—90°.

F. M. G. M.

Chlorophyll. XVI. The Primary Decompositions of Chlorophyll. RICHARD WILLSTÄTTER and MAX UTZINGER (*Annalen*, 1911, **382**, 129—194).—Crystalline chlorophyll (ethylchlorophyllide) (Willstätter and Benz, Abstr., 1908, i, 199; Willstätter and Stoll, this vol., i, 142) consists of two definite compounds, *a* and *b* (compare Willstätter and Isler, this vol., i, 392). The analysis of the product dried over phosphoric oxide in the vacuum of a water-pump agrees with the formula $C_{38}H_{44}O_7N_4Mg$, not $C_{38}H_{42}O_7N_4Mg$; when heated at 100—105°/0·001—0·01 mm., a further loss of about 5% occurs, probably due to water and ether, and the residue has a composition corresponding with the formula $C_{37}H_{39}O_{5·5}N_4Mg$. It is suggested that this probably consists of a mixture of the chlorophyllide-*a*, $C_{37}H_{39}O_{5·5}N_4Mg$, and chlorophyllide-*b*, $C_{37}H_{37}O_{6·5}N_4Mg$ (or $C_{37}H_{39}O_{6·5}N_4Mg$), in the ratio 2·5 : 1. The *a* compound is regarded as a mixture of practically equal parts of the lactam, $C_{37}H_{38}O_5N_4Mg$, and the lactam hydrate, $C_{37}H_{40}O_6N_4Mg$.

The ethylchlorophyllide, dried at 100—105°, yields methyl and ethyl iodides in molecular proportions when heated with hydriodic acid. It is shown that these two alkyl iodides can be recognised and separated by conversion into quaternary ammonium salts. This can be accomplished by the aid of dimethylaniline in the absence of alcohol, or by means of an alcoholic solution of trimethylamine. Dimethylaniline reacts with methyl iodide much more readily than with ethyl iodide; for example, after six hours 95% of the methyl iodide has combined, whereas only 8% of the ethyl iodide has reacted. The separation can also be accomplished by means of the different solubilities of the two quaternary ammonium iodides. Phenyltrimethylammonium iodide is very sparingly soluble in chloroform, whereas phenyldimethylethylammonium iodide, m. p. 136°, dissolves with the greatest readiness. With trimethylamine the separation is even more marked, especially with absolute alcohol as solvent. One gram of tetramethylammonium iodide dissolves in 1060 grams of absolute alcohol, whereas 1 gram of trimethylethylammonium iodide dissolves in 1·23 grams of absolute alcohol.

A slightly modified method for the isolation of ethylchlorophyllide is described; it consists in removing the colouring matter from its alcoholic solution by ether, drying with sodium sulphate, evaporating until the solution has a thick consistency, then mixing well with talc, keeping for a day, then filtering, and washing well with ether. The mixture of talc and coloured crystals, which is free from yellow pigments, is then extracted with alcohol (not absolute), mixed rapidly with ether, and the alcohol removed by washing. The ethereal solution when evaporated slowly yields crystals of ethylchlorophyllide. Two points of importance in the isolation are: (*a*) sufficient time must be allowed for the complete ethanolysis of the original chlorophyll to ethylchlorophyllide (Willstätter and Stoll, this vol., i, 141); (*b*) the alcohol must contain water; previously 96% alcohol was recommended, but 10% of water increases the rate of alcoholysis.

Different specimens of ethylchlorophyllide differ somewhat in appearance; in solution under the microscope some are bluish-green and others yellowish-green. These differences are probably due to the different amounts of the *a* and *b* compounds present. Some preparations are sparingly soluble in ether (1 gram in 2·5 litres), but the products dried at 100° under reduced pressure are extremely readily soluble in absolute ether, although when hydrolysed by alkali they give the characteristic brown phase.

Ethylchlorophyllide undergoes a change when kept for some time in absolute ethyl or methyl alcohol, and the products formed no longer give the brown phase when hydrolysed by alkalis. The altered compound dissolves readily in ether, cannot be crystallised, but is thrown down as a bluish-black powder on the addition of light petroleum to its ethereal solution. When fractionally precipitated, the first fraction is more yellowish-green and the last distinctly blue. Analyses of the product formed by the action of methyl alcohol agree with the view that half a molecule of water and half a molecule of methyl alcohol have combined with the ethylchlorophyllide.

Ethylphæophorbide, the product free from magnesium formed by the action of cold acids on ethylchlorophyllide, consists of two distinct compounds. It is obtained crystalline by the action of a saturated ethereal solution of hydrated oxalic acid on an ethereal solution of the chlorophyllide. At the end of two days, large brownish-black plates with a metallic lustre are deposited (Fraction I), and from the mother liquors, after removal of oxalic acid, long, pointed prisms are obtained (Fraction II). Both fractions can be recrystallised by solution in chloroform, mixing with a little ether, and pouring into much ether; fraction II can also be crystallised from ether. Fraction I is extremely sparingly soluble in cold alcohol or ether; its solutions in most organic solvents have a reddish-olive colour, but its solution in formic acid is bluish-green. When hydrolysed with alcoholic potash, it yields much phytorhodin-*g*, together with phytochlorin-*e*. Fraction II is more readily soluble in ether; its solutions are generally olive-green, but that in formic acid is blue. When hydrolysed with alkalis, it yields mainly phytochlorin-*e*, together with a very small amount of phytorhodin. Molecular-weight determinations of ethylchlorophyllide, ethylphæophorbide, and other products by cryoscopic and ebullioscopic methods indicate that they have not the double formulæ.

When chlorophyll-*a* in light petroleum solution is hydrolysed with 7% methyl-alcoholic potassium hydroxide, the potassium salt of chlorophyllin, $C_{34}H_{31}O_6N_4MgK_3$ (compare Willstätter and Fritzsche, Abstr., 1910, i, 126), separates as glistening, dark blue plates, which appear pure green under the microscope in transmitted light. The salt is not quite pure, and contains about 1% of methoxyl.

When decomposed with hydrochloric acid, it yields phytochlorin-*g*, which can be extracted from its ethereal solution by 11% hydrochloric acid.

When the chlorophyllin salt is heated in sealed vessels with alcoholic potassium hydroxide, it yields glaucophyllin, then rhodophyllin, and finally pyrrophyllin (Willstätter and Fritzsche, *loc. cit.*). A different chlorophyllin, iso*chlorophyllin*, is formed when chlorophyll-*a* in pyridine solution is hydrolysed with warm alcoholic potassium hydroxide. The potassium salt could not be isolated in the form of good crystals, and contained too little nitrogen and magnesium. The *calcium* salt forms a pale green, flocculent precipitate. When decomposed with hydrochloric acid, the *iso*chlorophyllin yields phytochlorin-*e*, and when heated with alcoholic potassium hydroxide at 150°, it yields a phyllin the alkaline and ethereal solutions of which are deep blue. With alcoholic potassium hydroxide at 225—230°, it yields a phyllin identical with or closely allied to phyllophyllin. The ammonium and calcium salts are soluble in ether, and the calcium salt sparingly soluble in chloroform.

Phytochlorin-*e* can be obtained by hydrolysing crude chlorophyll extract with barium hydroxide, dissolving the barium salt of *iso*-chlorophyllin in ether, and shaking with 16% hydrochloric acid.

Alcoholic potassium hydroxide can react with phæophytin and ethylphæophorbide in two different ways, according to the conditions of the experiment.

With concentrated alcoholic potassium hydroxide, either cold or hot, the products are phytochlorin-*e* and phytorhodin-*g*. By the action of alcoholic potash on an ethereal solution of alkylphæophorbides, phytochlorin-*g* is formed together with a faintly basic phytorhodin—phytorhodin-*i* or a similar compound. These two processes correspond with the hydrolysis of chlorophyll by hot and by cold potassium hydroxide solution.

The analyses of various specimens of phytochlorin-*e* do not agree, and this is shown to be due to the fact that the compounds exist in two forms, which differ in the amount of water they contain, namely, $C_{34}H_{34}O_5N_4$ and $C_{34}H_{36}O_6N_4$, termed respectively the *lactam* and *lactam-hydrate*. It is possible that the two can unite to form a definite compound, which would be a half hydrate like many other chlorophyll derivatives.

In the isolation of the hydrate, it is essential that the method of extraction and purification should not entail prolonged treatment with hydrochloric acid, as this converts the hydrate into the lactam. The hydrate forms compact, opaque, crystalline plates with a violet lustre; the lactam, small, glistening plates which appear black to the eye. They are doubly refractive, and the colours in transmitted light are pale green, olive-green, and brown. Both compounds lose in weight when heated at 105°/0·01 mm. The lactam loses some 3%, and the hydrate 0·5 to 1%. The hydrate is quite stable, and is unaltered at the end of nine months. The lactam crystals are also stable, but after drying in a desiccator they undergo decomposition when kept; at the end of nine months an appreciable amount of a rhodin, probably phytorhodin-*h*, is present, together with phytochlorin-*f*. The lactam dissolves more readily than the hydrate in most solvents. The hydrate is extremely sparingly soluble in cold alcohol, and is insoluble in chloroform. Its solution in formic acid is blue and in pyridine olive-coloured. Concentrated hydrochloric acid does not decompose phytochlorin-*e*, but concentrated sulphuric acid transforms it into an amorphous product insoluble in ether. With acetic anhydride, the phytochlorin yields glistening, bluish-black, rhombic plates, and when oxidised with chromium trioxide in sulphuric acid solution, it yields a mixture of acid and neutral products, including methylethylmaleinimide and the imide of hæmatic acid. When heated with crystallised phosphoric acid at 140°, it yields phylloporphyrin, but at 100° it yields only a small amount of phylloporphyrin, together with phytochlorin-*h*, which dissolves in dilute hydrochloric acid, giving a reddish-violet solution. It is formed from the original phytochlorin by the elimination of carbon dioxide. The following salts of phytochlorin-*e* have been prepared: $C_{34}H_{33}O_6N_4K_3$, brown, rectangular plates; $C_{34}H_{33\cdot5}O_6N_4Cs_{2\cdot5}$ and $C_{34}H_{35}O_6N_4\cdot NH_4$. The *trimethyl* ester, $C_{31}H_{33}N_4(CO_2Me)_3$, obtained from the potassium salt and methyl sulphate, separated in steel-blue, felted prisms, m. p. 188—190°. The compound is also partly esterified by methyl alcohol and hydrogen chloride.

Phytochlorin-*f* (Willstätter and Isler, this vol., i, 392; Willstätter and Hocheder, Abstr., 1907, i, 785) has not been obtained from chlorophyllin-*a*. It has the formula $C_{34}H_{34}O_5N_4$, and loses but little in weight when dried at 105° under reduced pressure, and is sparingly soluble in most solvents, with the exception of formic acid and pyridine. The solution of the ammonium salt in ether has a brilliant green colour, and the solution in hydrochloric acid (10%) has a pure blue colour. The *caesium* salt, $C_{34}H_{31\cdot5}O_5N_4Cs_{2\cdot5}$, forms glistening, steel-blue prisms; the *methyl* ester, $C_{36}H_{36}O_4N_4(?)$, forms blue, monoclinic, six-sided plates or prisms, and is less basic than the acid.

Phytochlorin-*g* is formed also when chlorophyll-*a* is kept for some time in light petroleum, and then hydrolysed with alcoholic potassium hydroxide and acidified. Its ethereal solution is olive-green, but turns brown when kept. The hydrochloric acid number is 10—11, and the solution in acid is bluish-green. When evaporated and warmed for a short time with alcohol, an unstable, brilliant red product is formed. When heated with alcoholic potassium hydroxide in silver vessels at 140—150°, phytochlorin-*g* yields a dicarboxylic product similar to glaucoporphyrin (Willstätter and Fritzsche, Abstr., 1910, i, 127); its hydrochloride is, however, less soluble, and the colours of its solutions are somewhat different. With alcoholic potassium hydroxide at 225—230°, phytochlorin-*g* yields pyrroporphyrin. Phytochlorin-*f*, when heated for seven hours at 140—150° with alcoholic potassium hydroxide, yields rhodoporphyrin, and at 200° yields pyrroporphyrin. Phytochlorin-*e* and alcoholic potassium hydroxide at 140—150° yield the monocarboxylic phylloporphyrin, the *methyl* ester of which, $C_{33}H_{38}O_2N_4$, crystallises from ether or acetone, has m. p. 224° after sintering at 220°, and acid number 1—1·25.

Phytorhodin-*g*, $C_{34}H_{34}O_7N_4$, is formed from the *b*-chlorophyll component of all plants by hydrolysing the phæophytin or phæophorbide in undiluted form with alkali. It is also formed from *iso*chlorophyllin and acid, and crystallises in compact, glistening, black, six-sided prisms, and appears to be a tribasic acid. A hydrated form also exists, $C_{34}H_{36}O_8N_4$. It is a strongly acid compound, and is removed from its ethereal solution by 0·001% ammonia. Its solution in dilute alcoholic potassium hydroxide has a deep red colour, but in concentrated, a green colour. The *potassium* salt,

$$C_{34}H_{31}O_7N_4K_3,$$

blackish-brown plates, *caesium* salt, $C_{34}H_{31}O_7N_4Cs_3$, rhombic plates, and *methyl* ester, $C_{37}H_{40}O_7N_4$, glistening, black, rectangular plates and prisms, m. p. 207—210°, have been prepared.

Phytorhodin-*i*, $C_{34}H_{32}O_6N_4$, the feebly basic phytorhodin previously described (this vol., i, 392), crystallises in brown or black, microscopic plates; its ethereal solution is brownish-red, and its solution in hydrochloric acid green. Its *potassium* salt is sparingly soluble in water. With alcoholic potassium hydroxide at 150°, it yields a dibasic porphyrin similar to rhodoporphyrin, and at 200° the monobasic pyrroporphyrin.

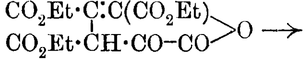
The relationships of many of the compounds are discussed.

J. J. S.

Dibasic Ketonic Acids. III. EDMOND E. BLAISE and HENRI GAULT (*Bull. Soc. chim.*, 1911, [iv], 9, 588—592).—This paper gives in greater detail, with some modifications, the results described already (Abstr., 1908, i, 713; 1909, i, 134).

Ethyl dioxalylsuccinate on hydrolysis by hydrochloric acid in the cold furnishes 3-hydroxy-2-pyrone-6-carboxylic acid, m. p. 87° (approx.), which crystallises in colourless needles, gives a violet coloration with ferric chloride, a green coloration with pine wood moistened with hydrochloric acid, and reduces ammoniacal silver nitrate slowly in the cold and immediately on warming. When heated at 150°, it furnishes *iso*pyromucic acid (3-hydroxy-2-pyrone), m. p. 87°, by loss of carbon dioxide (*loc. cit.*, Chavanne, Abstr., 1904, i, 82). In view of these results the authors suggest that the lactone and its derivatives obtained by Wislicenus and Boeckler (Abstr., 1895, i, 506) by the action of alkalis on ethyl dioxalylsuccinate should be represented by the following formulæ:

$CO_2Et\cdot C(OH)\colon C(CO_2Et)\cdot CH(CO_2Et)\cdot CO\cdot CO_2Et \longrightarrow$



$$\begin{array}{l} CO_2Et\cdot C\colon C(CO_2Et) \\ \qquad\quad | \\ CO_2Et\cdot CH\cdot CO{-}CO \end{array} \!\!> O \longrightarrow$$

$CO_2H\cdot C(OH)\colon C(CO_2Et)\cdot CH(CO_2Et)\cdot CO\cdot CO_2H.$

T. A. H.

Migration of Phenyl in the Synthesis of Phenylated Coumarones. Phosphorus Tribromide as a Reducing Agent. III. RICHARD STOERMER (*Ber.*, 1911, 44, 1853—1865. Compare Abstr., 1904, i, 181; 1907, i, 446).—Aromatic γ-lactones, such as the lactone of phenyl-*p*-hydroxytolylacetic acid, when heated with phosphorus tribromide under ordinary pressure at a high temperature form 2-phenylated coumarones, whereas above 200° under pressure 1-phenylated compounds are also formed. It is supposed that an intermediate unsaturated compound is formed and not a brominated phenylcoumarone, which, when prepared in another manner, is not altered on heating with phosphorus tribromide. Similarly, 2-phenylcoumarone is unaltered by heating with phosphorus tribromide.

The lactone of dibromohydroxydiphenylacetic acid could not be converted into bromophenylcoumarone in this manner.

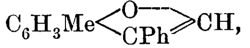
The tendency of the phenyl group to wander to position (1) is but small, and it is destroyed by the introduction of substituents.

The synthesis of 1-phenylcoumarone has been effected from homosalicylaldehyde and chlorophenylacetic acid in order to establish its constitution. Characteristic of this is the yellow coloration with concentrated sulphuric acid, which soon turns green.

1-Bromo-2-phenylcoumarone interacts very readily with nitrous fumes, forming 1-nitro-2-phenylcoumarone. This is still more conveniently prepared by dissolving the brominated coumarone in acetic acid, adding a little nitric acid and sodium nitrite, and warming until the bromine vapour has all been given off. On pouring into water, the nitro-compound is now obtained pure. Presumably an additive product with nitrogen trioxide is first formed, from which nitrosyl bromide is subsequently eliminated.

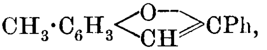
With phosphoryl chloride under pressure, 1-chloro-2-phenylcoumarone is obtained, and no migration of phenyl takes place. This product cannot be reduced to the chlorine-free compound.

[With Claus Decker.]—2-*Phenyl*-4-*methylcoumarone*,



$$C_6H_3Me\left<\begin{matrix}O\\CPh\end{matrix}\right>CH,$$

has b. p. 193°/20 mm., does not solidify on cooling, and gives an intense red coloration with concentrated sulphuric acid. It forms 2-phenyl-4-methylcoumarone on reduction.

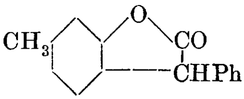
1-*Phenyl*-4-*methylcoumarone*,  $CH_3 \cdot C_6H_3\left<\begin{matrix}O\\CH\end{matrix}\right>CPh$, forms colourless, matted needles, m. p. 129°.

1-*Bromo*-2-*phenyl*-4-*methylcoumarone* crystallises in stellar aggregates of needles, m. p. 65°, which show a faint red coloration with concentrated sulphuric acid.

1-*Nitro*-2-*phenyl*-4-*methylcoumarone* forms radially-grouped, yellow needles, m. p. 115—116°.

1-*Bromo*-2-*phenylcoumarone* is an oil of sweet odour, b. p. 195°/20 mm. 1-*Nitro*-2-*phenylcoumarone* separates in long, yellow needles, m. p. 105°. The *bromo*-derivative of 1-phenylcoumarone has b. p. 203°/23 mm., crystallising in lustrous, silvery platelets, m. p. 81°. Nitrous acid is without action on it.

The lactone of phenyl-*m*-hydroxytolylacetic acid (annexed formula) when heated with phosphoryl chloride at 130° forms 1-*chloro*-2-*phenyl*-5-*methylcoumarone*, b. p. 175°/10 mm., crystallising in needles of silvery lustre, m. p. 85·5°. On reduction of this chloride, or of the corresponding bromide, 2-*phenyl*-5-*methylcoumarone* is obtained in small, colourless needles, m. p. 45°, b. p. 170°/14 mm. This, when brominated in acetic acid, is converted into 4(?)-*bromo*-5-*methyl*-2-*phenylcoumarone*, which crystallises in short, pointed needles, m. p. 125°.



Phenylmethylcoumarone when heated with alkali hydroxide at 200° under pressure yields *phenyl*-m-*hydroxytolylethylene*,

$$OH \cdot C_6H_3Me \cdot CPh{:}CH_2,$$

a colourless oil, b. p. 205°/20 mm., soluble in alkali, and becoming intense red with concentrated sulphuric acid.

2-*Phenyl*-5-*methylcoumarone*, obtained by the action of phosphorus tribromide on the lactone of phenyl-*m*-hydroxytolylacetic acid, forms short needles, m. p. 31°, b. p. 168°/18 mm., and gives an intense orange coloration with concentrated sulphuric acid.

The isomeric 1-*phenyl*-5-*methylcoumarone*, obtained on more strongly heating, crystallises in silvery needles, m. p. 135·5°, and gives a yellow coloration with sulphuric acid, changing to dark green. This compound is identical with that obtained on condensing phenylchloroacetic acid with *m*-homosalicylaldehyde. Accordingly, the formula of the lactone of phenyl-*m*-hydroxytolylacetic acid is established as that given above.

1-*Bromo*-2-*phenyl*-5-*methylcoumarone* has m. p. 95°; the corresponding 1-*nitro*-derivative forms small, yellow crystals, m. p. 119—120°.

The *lactone* of o-*hydroxyphenylanisylacetic acid*, prepared from anisaldehyde cyanohydrin, phenol, and sulphuric acid, forms colourless needles, m. p. 178°. The corresponding anisylcoumarone could not be obtained.

p-*Hydroxytolylanisylacetic acid lactone* forms colourless plates, m. p. 135°. On heating with phosphorus tribromide, 2-*anisyl*-4-*methylcoumarone* is obtained in matted needles, m. p. 73·5°; this shows a strong eosin coloration with strong sulphuric acid.

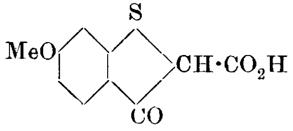
[With Karl Hildebrandt.]—The *lactone* of p-*chloro*-o-*hydroxydiphenylacetic acid* forms colourless needles, m. p. 125°; the corresponding *bromo*-compound is very similar, m. p. 123°. On heating with phosphoryl chloride, 1-*chloro*-2-p-*chlorophenylcoumarone* is obtained in long, silvery needles, m. p. 122°.

2-p-*Chlorophenylcoumarone*, m. p. 34°, gives an orange coloration with sulphuric acid; the isomeric 1-phenyl derivative could not be obtained.

1-*Chloro*-2-p-*bromophenylcoumarone* forms long, lustrous needles, m. p. 119°.

2-p-*Bromophenylcoumarone* crystallises in long, matted needles, m. p. 38°, giving an orange-red coloration with sulphuric acid. The 1-phenyl compound could not be detected. E. F. A.

Preparation of Alkyloxy- and Alkylthio-derivatives of 3-Hydroxy-(1)-thionaphthen-2-carboxylic Acid. Kalle & Co. (D.R.-P. 232377. Compare Abstr., 1908, i, 451, 797).—The preparation of 3-hydroxy-(1)-thionaphthen-2-carboxylic acid from phenyl-*o*-carboxymethylthiolbenzoic acid has been recorded previously, and the preparation of its alkyloxy- and alkylthio-derivatives containing the substituted group in the benzene ring is now described. 3-*Keto*-6-*methoxy*-(1)-*thionaphthen*-2-*carboxylic acid* (annexed formula), yielding a yellow *nitroso*-derivative and converted by boiling dilute hydrochloric acid into 3-*keto*-6-*methoxy*-(1)-*thionaphthen* (needles, m.p. 118—119°), was prepared by the following series of operations.



o-Amino-*p*-cresol was acetylated, and subsequently methylated with methyl sulphate in alkaline solution, yielding o-*acetylamino*-p-*tolyl methyl ether*, needles, m. p. 96°; this was oxidised to 2-*acetylamino*-4-*methoxybenzoic acid*, colourless needles, m. p. 197—199°, which by successive hydrolysis, diazotisation, xanthogenation, and treatment with chloroacetic acid, yielded 6-*methoxyphenylthioglycol*-o-*carboxylic acid*, needles, m. p. 224—225°; this acid when fused at 180—200° with sodium hydroxide yielded the foregoing 6-methoxy-3-oxy-(1)-thionaphthen-2-carboxylic acid.

4-*Acetylaminophenol*-3-*carboxylic acid*, m. p. 224—226°, by similar treatment yielded 2-*carboxymethylthiol*-5-*methoxybenzoic acid*, yellow prisms, m. p. 197—199°, which was subsequently converted by fusion with alkali into 3-*keto*-5-*methoxy*-(1)-*thionaphthen*-2-*carboxylic acid*; this acid forms a *nitroso*-derivative (yellow needles, m. p. 208—209°), and is converted by boiling dilute hydrochloric acid into 3-*keto*-5-*methoxy*-(1)-*thionaphthen*, yellow needles, m. p. 102—104°.

3-*Keto*-6-*ethylthiol*-(1)-*thionaphthen*, yellow needles, m. p. 84—85°, yielded a *nitroso*-derivative, and the following intermediate compounds were obtained in its preparation. 4-*Acetylaminoanthranilic acid*, m. p. 193—194°. 2-*Carboxymethylthiol*-4-*acetylaminobenzoic acid*, colourless needles, m. p. 249° (decomp.), which on hydrolysis, diazotisation, and xanthogenation yielded 2-*carboxymethylthiol*-4-*ethylxanthatobenzoic acid*,

$$EtO\cdot CS_2\cdot C_6H_3(S\cdot CH_2\cdot CO_2H)\cdot CO_2H,$$

a yellowish-red powder, which was converted into 2-*carboxymethylthiol*-4-*ethylthiolbenzoic acid*, yellow needles, m. p. 188°. 3-*Keto*-6-*ethylthiol*-(1)-*thionaphthen*-2-*carboxylic acid*, $SEt\cdot C_6H_3{<}\substack{S\\ CO}{>}CH\cdot CO_2H$, a colourless powder, yielded a *nitroso*-derivative, glistening, reddish-yellow needles, m. p. 176°.

3-*Keto*-5-*methylthiol*-(1)-*thionaphthen*, yellow needles, m. p. 81—82°, yielded a *nitroso*-derivative, m. p. 178°, and was prepared through the following compounds: 2-*carboxymethylthiol*-5-*acetylaminobenzoic acid* (obtained from 5-acetylaminoanthranilic acid), colourless needles, m. p. 249—250°; 2-*carboxymethylthiol*-5-*ethylxanthatobenzoic acid*, yellow crystals; 2-*carboxymethylthiol*-5-*methylthiolbenzoic acid*, yellow needles, m. p. 195°; and 3-*keto*-5-*methylthiol*-(1)-*thionaphthen*-2-*carboxylic acid*, which has no characteristic melting point. F. M. G. M

[Preparation of Thionaphthen Derivatives.] KALLE & Co. (D.R.-P. 232995).—*Bistolylthioglycollic acid*, glistening leaflets, m. p. 167—168°, prepared by methods previously described (Abstr., 1880, 476), is converted by treatment with chlorosulphonic acid into *bisketotolylthionaphthen*, and *bisketophenylthionaphthen* is obtained in a similar manner from bisphenylthioglycollic acid. These oxythionaphthen derivatives furnish blue dyes on oxidation, and condense with compounds containing the groups CO–, CS–, C:NR, C:N·NHR, and CX_2– (where R is alkyl and X a halogen). F. M. G. M.

Salts of Arginine. FRITZ WEISS (*Zeitsch. physiol. Chem.*, 1911, 72, 490—493).—dl-*Arginine aurichloride*,

$$C_6H_{14}O_2N_4,2HCl,AuCl_3,\tfrac{1}{2}H_2O,$$

separates from water in brownish-red, nodular masses, m. p. 105—115°. d-*Arginine aurichloride*, $C_6H_{14}O_2N_4,2HAuCl_4,1\tfrac{1}{2}H_2O$, is somewhat more soluble in water than the *dl*-salt; it sinters at 140°, and has m. p. 160°. The *acid sulphate*, $C_6H_{14}O_2N_4,H_2SO_4,H_2O$, forms hard, crystalline crusts from dilute alcohol with no definite m. p. The corresponding *d*-salt forms a deliquescent, crystalline powder.

J. J. S.

Nitroclupeine. ALBRECHT KOSSEL and E. L. KENNAWAY (*Zeitsch. physiol. Chem.*, 1911, 72, 486—489).—By the addition of well cooled fuming nitric acid (1 c.c.) to a well stirred mixture of clupeine sulphate (2 grams), concentrated sulphuric acid (4 c.c.), and fuming sulphuric acid (2 c.c. of 10% SO_3) cooled to 0°, and, after five to ten minutes, pouring the mass on to ice, it has been found possible to obtain a *nitroclupeine*, which dissolves in dilute sodium hydroxide solution and can be precipitated by the addition of dilute acid.

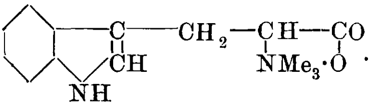
When hydrolysed with 30% sulphuric acid, the nitro-compound yields *nitroarginine*, $C_6H_{13}O_4N_5$, which crystallises from water, has m. p. 227—228°, and is dextrorotatory. It dissolves in dilute hydrochloric or nitric acid, and also in dilute ammonia.

A similar compound can be obtained by the action of nitric acid on *d*-arginine nitrate. J. J. S.

Hypaphorine and the Relation of this Substance to Tryptophan. PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1177—1180).—The alkaloid hypaphorine, found by Greshoff (Abstr., 1891, i, 335) in the seeds of *Erythrina Hypaphorus* (the "dadap minjak" of Eastern Java), crystallises as a hydrate, efflorescing in a desiccator, m. p. 255°, $[\alpha]_D$ + 91—93°. It yields a sparingly soluble nitrate.

Analysis of the anhydrous base agrees with the formula $C_{14}H_{18}O_2N_2$. When heated with strong aqueous potassium hydroxide, trimethylamine and indole are produced.

Tryptophan, treated with methyl iodide and sodium hydroxide in methyl alcohol, yields a substance, the nitrate of which closely resembles that of hypaphorine, and gives on heating with aqueous potassium hydroxide the odour of amine and indole. It is considered that hypaphorine is most probably α-trimethyl- β-indolepropiobetaine (annexed formula) (Ellinger, Abstr., 1907, i, 737). The investigation is being continued in conjunction with Barger, who has quite recently methylated tryptophan by the method of Engeland (Abstr., 1910, i, 843), with like results. J. D. K.



Preparation of Formyl Derivatives of Morphine Alkaloids. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R-P. 233325).—The preparation of formyl derivatives of morphine alkaloids has been described previously (Abstr., 1910, i, 765); it is now found that the reaction proceeds quantitatively and at the ordinary temperature if the anhydride of another paraffinoid acid (such as acetic) is employed in conjunction with the formic acid. Details of the preparation of formylcodeine and of formyl-β-methylmorphimethine are given.

F. M. G. M.

Dihydromorphine. L. OLDENBERG (*Ber.*, 1911, **44**, 1829—1831).—Hitherto hydrogenised derivatives of morphine and codeine have not been obtained. By shaking aqueous morphine hydrochloride,

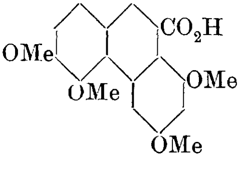
$$C_{17}H_{19}O_3N,HCl,3H_2O$$

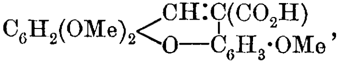
(10 grams in 250 c.c. of water), with aqueous colloidal palladium (0·1 gram in 10 c.c.) saturated with hydrogen, the author has obtained *dihydromorphine*, $C_{17}H_{21}O_3N,H_2O$, in colourless needles, m. p. 155—157°. The base has the same bitter after-taste and physiological action as morphine, reacts with ferric chloride in a similar manner, and instantly reduces silver nitrate; the *hydrochloride* and the *sulphate* are described. C. S.

Constitution of Morphothebaine. II. Synthesis of the Tetramethoxyphenanthrene Derived from Morphothebaine.

Robert Pschorr and Georg Knöffler (*Annalen*, 1911, **382**, 50—61. Compare Freund and Holthof, Abstr., 1899, i, 308; Pschorr, Abstr., 1904, i, 767; Knorr and Pschorr, 1905, i, 814).—The structural formula previously suggested (Abstr., 1910, i, 423) for morphothebaine has been confirmed by synthesising 3 : 4 : 6 : 8-tetramethoxyphenanthrene and proving that it is identical with the product formed from morphothebaine.

3 : 4-Dimethoxybenzaldehyde, hippuric acid, anhydrous sodium acetate, and acetic anhydride yield the *anhydride* of *benzoylaminodimethoxycinnamic acid*, $C_{18}H_{15}O_4N$, which crystallises from dilute alcohol in colourless needles, m. p. 182° (corr.), and on hydrolysis with 10% sodium hydroxide solution yields dimethoxyphenylpyruvic acid and benzoic acid. The mixture of the two acids is oxidised with hydrogen peroxide in alkaline solution and then acidified and extracted with ether, when 50% of the 2 : 4-*dimethoxyphenylacetic acid* crystallises out on cooling to 0°. The remainder can be separated from benzoic acid by fractionation of the mixture of their ethyl esters. The acid, $C_6H_3(OMe)_2\cdot CH_2\cdot CO_2H$, crystallises in colourless needles, m. p. 113° (corr.), and its anhydrous sodium salt condenses with *o*-nitrovanillin methyl ether in the presence of acetic anhydride at 105—110°, yielding α-2′ : 4′-*dimethoxyphenyl*-2-*nitro*-3 : 4-*dimethoxycinnamic acid*, $NO_2\cdot C_6H_2(OMe)_2\cdot CH{:}C(CO_2H)\cdot C_6H_3(OMe)_2$. The acid is purified by means of its sparingly soluble ammonium salt, and crystallises in yellow plates, m. p. 232° (corr.). When reduced with ferrous sulphate in the presence of ammonium hydroxide, the nitro-acid yields the corresponding *amino-acid*, $C_{19}H_{21}O_6N$, which crystallises from methyl alcohol in yellow cubes, m. p. 207—208°. When dissolved in methyl alcohol and dilute sulphuric acid, diazotised by the addition of *N*-sodium nitrite solution, and the resulting solution heated on the water-bath, a 30% yield of 3 : 4 : 6 : 8-*tetramethoxyphenanthrene*-9-*carboxylic acid* (annexed formula) is obtained. It crystallises from methyl alcohol in plates, m. p. 226° (corr.). By-products formed at the same time are: 3 : 4 : 4′-*trimethoxy*-2 : 2′-*oxidostilbene*-α′-*carboxylic acid*,

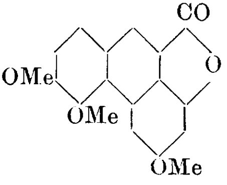




$$C_6H_2(OMe)_2{<}\begin{matrix}CH{:}C(CO_2H)\\ |\\ O\text{—}C_6H_3\cdot OMe\end{matrix},$$

well-developed prisms, m. p. 253°, and a product insoluble in ammonia.

The tetramethoxy-acid when heated with glacial acetic acid at 240° for twenty hours yields 3 : 4 : 6 : 8-tetramethoxyphenanthrene (10% yield), together with the *lactone* of 3 : 4 : 6-trimethoxy-8-hydroxyphenanthrene-9-carboxylic acid (annexed formula), m. p. 202—203°. On hydrolysis the lactone yields the corresponding acid, which crystallises from methyl alcohol in yellow prisms, m. p. 195°. With methyl sulphate, the acid yields *methyl* 3 : 4 : 6 : 8-*tetramethoxyphenanthrene*-9-*carboxylate*, m. p. 136—137°, which on hydrolysis gives the corresponding acid. J. J. S.



Preparation of Compounds from the Interaction of Cotarnine on Amides, Imides, or Ureides. KNOLL & Co. (D.R.-P. 232785).—The combination of cotarnine with amides, imides, or ureides yields a new class of compounds having therapeutic value.

Two *cotarnine-a-bromoisovalerylcarbamides* have been prepared; one is obtained by mixing molecular proportions of cotarnine and α-bromo*iso*valerylcarbamide in alcoholic solution and allowing the mixture to remain until the product separates; it forms flat prisms, m. p. 125—127°, and is decomposed by dilute mineral acids into its generators. The second compound has m. p. 105—110°, and is prepared by employing two molecules of α-bromo*iso*valerylcarbamide in aqueous solution. The preparation of the following molecular compounds of cotarnine is also recorded: *cotarnineacetamide*, m. p. 135° (about); *cotarninecarbamide*, m. p. 180°; *cotarnineurethane*, m. p. 110°; and *cotarninephthalimide*, m. p. 130°. F. M. G. M.

Solanine Extracted from Solanum sodomaeum. IV. GIUSEPPE ODDO and MARCELLO CESARIS (*Gazzetta*, 1911, **41**, i, 490—534. Compare Abstr., 1905, i, 455; 1906, i, 527, 980).—Since solanine from *Solanum sodomaeum* differs in composition from that extracted from *Solanum tuberosum*, the authors term it solanine-*s*.

On analysis, after being dried in a vacuum over potassium hydroxide and paraffin, solanine-*s* gives the formula $(C_{27}H_{46}O_9N)_2,H_2O$, which is confirmed by the analysis of various normal and basic salts and other derivatives, and also by investigation of its hydrolytic products.

Carefully purified solanidine (see succeeding abstract) has the formula $C_{18}H_{31}ON$, and a study of the sugars also formed on hydrolysis of solanine shows that this change is represented thus: $(C_{27}H_{46}O_9N)_2,H_2O + H_2O + H_2 = 2C_{18}H_{31}ON + C_6H_{12}O_6$ (galactose) + $C_6H_{12}O_6$ (? dextrose) + $C_6H_{12}O_5$ (? rhamnose). In estimating the methylpentose (? rhamnose) by conversion into methylfurfuraldehyde, and weighing this in the form of its phloroglucinol derivative, higher results than were expected were obtained, and, on investigation, it was found that the presence of certain sugars, such as galactose, dimimishes, whilst that of others, namely, dextrose, increases markedly the yield of methylfurfuraldehyde.

The action of acetic anhydride on solanine-*s* yields a deca-acetyl-derivative, $C_{54}H_{82}O_{18}N_2Ac_{10}$, which yields solanine again on hydrolysis, whilst in the total products of hydrolysis of solanine, 16 atoms of hydrogen are replaceable by acetyl groups.

The action of nitrous acids on solanine-*s* (*loc. cit.*) gives a compound of the formula $C_{54}H_{86}O_{18}N_2,HNO_2,3H_2O$, which does not behave as a salt, since treatment with alkali does not yield a basic compound. When heated gently with dilute acetic acid, this compound loses all its nitrogen (it is therefore named azosolanine), yielding a compound which has not been obtained crystalline, but has the formula $C_{54}H_{86}O_{21},2H_2O$ (*oxysolanol*). Treatment of solanine with a nitrite in hot aqueous acetic acid solution results in the formation of another nitrogen-free compound, $C_{54}H_{88}O_{20},2H_2O$, which crystallises well, and is termed solanol. When heated with a dilute mineral acid, both these non-nitrogenous compounds undergo hydrolysis, yielding sugars and other substances, which can also be obtained from solanidine; these substances are being investigated.

The following salts of solanine have been prepared: (1) Normal salts: the *hydrochloride*, $C_{54}H_{92}O_{18}N_2,2HCl$; the *sulphate*,
$C_{54}H_{92}O_{18}N_2,H_2SO_4$;
the o-*nitrobenzoate*, $C_{54}H_{92}O_{18}N_2,2NO_2{\cdot}C_6H_4{\cdot}CO_2H,8H_2O$; and the *picrate*, $C_{54}H_{92}O_{18}N_2,2OH{\cdot}C_6H_2(NO_2)_3$. (2) Basic salts: the *hydrochloride*, $C_{54}H_{92}O_{18}N_2,HCl$; the *hydrobromide*, $C_{54}H_{92}O_{18}N_2,HBr$; and the *sulphate*, $(C_{54}H_{92}O_{18}N_2)_2H_2SO_4$.

As has been indicated above, during hydrolysis solanine undergoes reduction, this being effected by the sugars formed. In fact, when heated with dextrose, solanine gives rise to a *dihydrosolanine*, $C_{54}H_{94}O_{18}N_2,H_2O$, which forms prismatic crystals, and may be the original product from which solanidine is formed.

Deca-acetylsolanine was not obtained crystalline, and may possibly be a mixture of deca- and undeca-acetyl derivatives.

Azosolanine forms tufts of faintly green, silky needles, and in the anhydrous condition has the normal molecular weight in boiling *iso*amyl alcohol. It is a neutral compound, and gives neither the nitroso-reaction with phenol and sulphuric acid nor the *iso*nitroso-reaction with a sulphuric acid solution of diphenylamine. When heated in a capillary tube it turns yellow, and contracts at 230°, blackens at 275°, and begins to melt at 280° without, however, completely fusing.

Solanol forms tufts of slender needles, which turn yellow at 210° and decompose at 240—245°. T. H. P.

Solanidine sodomaeum. V. GIUSEPPE ODDO (*Gazzetta*, 1911, **41**, i, 534—552. Compare preceding abstract).—The author describes a new method of purifying solanidine. Thus obtained it has the formula $C_{18}H_{31}ON$ when dried at 105° or $3C_{18}H_{31}ON,2H_2O$ when dried under reduced pressure at the ordinary temperature. This new formula is confirmed by analysis of the various salts prepared (see below) and by a study of the hydrolysis of solanine-*s* (*loc. cit.*).

When treated with acetic anhydride, solanidine-*s* gives a diacetyl derivative, which yields the base again on hydrolysis. The formation of this compound is best explained by supposing that the oxygen exists in the molecule in the form of hydroxyl and the nitrogen in a secondary state: $OH{\cdot}C_{18}H_{29}{:}NH$. These functions of the oxygen and nitrogen atoms have been confirmed by treating solanidine-*s* (1 mol.) with magnesium ethyl iodide (3 mols.) in ethereal solution and measuring the amount of gas evolved:

$$OH{\cdot}C_{18}H_{29}{:}NH + 2MgEtI = MgI{\cdot}O{\cdot}C_{18}H_{29}{:}N{\cdot}MgI + 2C_2H_6;$$

2 vols. of ethane were evolved, whereas if the nitrogen atom were primary, 3 vols. should be obtained, if it were tertiary only 1 vol., due to the hydroxyl, and, if the latter were also missing, no ethane would be evolved. The iodo-magnesium compound thus obtained gives solanidine again when treated with water, and with acetyl chloride, it yields a diacetyl compound identical with that given by the action of acetic anhydride on the base.

When solanidine-*s* is treated with sodium nitrite in presence of a little acid, a compound is obtained which is similar to that given by solanine-*s* (see preceding abstract), and is hence named azosolanidine. When treated with moderately concentrated acids, azosolanidine loses all its nitrogen, giving products which vary with the conditions of the action and are being investigated.

The formula given above for solanidine-*s* shows that this belongs to the series C_nH_{2n-4}. The lack of the six valencies necessary to make it a saturated compound is not due to the presence of double linkings in the molecule, since solanidine does not decolorise bromine in aqueous or chloroform solution, and only decolorises permanganate after some time. Solanidine-*s* must hence be regarded as a tricyclic compound.

[With Eugenio Ferrari.]—Solanidine-*s*, separated and purified by means of its hydrochloride, crystallises from alcohol in nacreous, white scales, m. p. 197—198°, and with concentrated sulphuric acid gives a reddish-yellow coloration, which, on addition of increasing proportions of water, becomes violet, green, and colourless.

[With Giovanni Moneta].—The following salts of solanidine-*s* were prepared: the *basic hydrochloride*, $(C_{18}H_{31}ON)_3,2HCl$, forms silky, white needles, m. p. 302—303° (decomp.); the *hydrochloride*,

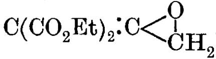
$$C_{18}H_{31}ON,HCl,$$

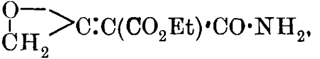
elongated prisms, turning yellow at about 250°, m. p. 291—292° (decomp.); the *hydrobromide*, $C_{18}H_{31}ON,HBr$, elongated prisms, becoming decidedly yellow at 270°, m. p. 282—283° (decomp.); the o-*nitrobenzoate*, $C_{18}H_{31}ON,NO_2\cdot C_6H_4\cdot CO_2H$, colourless, shining prisms, m. p. 222°; and the *picrate*, $C_{18}H_{31}ON,C_6H_3O_7N_3$, quadrangular, shining prisms, which become orange-yellow on heating, m. p. 144—145°.

[With Eugenio Ferrari].—*Diacetylsolanidine*-s, $OAc\cdot C_{18}H_{29}:NAc$, was obtained only in the amorphous condition. The *iodomagnesium* compound gives solanidine when treated with water.

[With Giulio Buzio].—*Azosolanidine*-s form microscopic, regular, prismatic needles or rosettes of prismatic needles with a faint green tint, m. p. 260° (decomp.); its formula and the products its yields on heating with acids are being investigated. T. H. P

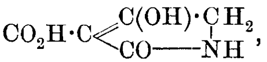
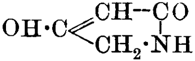
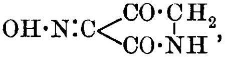
Action of Halogeno-Fatty Acid Halides on Esters of Malonic Acid. II. Synthesis of Tetramic Acid.

Erich Benary (*Ber.*, 1911, **44**, 1759—1765).—The substance, $C_9H_{12}O_5$, obtained as a by-product in the formation of ethyl tetrone-4-carboxylate from chloroacetyl chloride and ethyl sodiomalonate in warm ether (Abstr., 1907, i, 381) is now shown to have the constitution  $C(CO_2Et)_2:C<\begin{array}{l}O\\|\\CH_2\end{array}$. The amide,

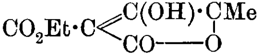


$$\begin{array}{l}O—\\|\\CH_2\end{array}>C:C(CO_2Et)\cdot CO\cdot NH_2,$$

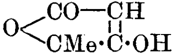
obtained from it by the action of dry ammonia, is converted by an excess of boiling, alcoholic potassium hydroxide into a *potassium* salt, $C_5H_3O_4NK_2$, from which by acidification is obtained, *tetrame-*

4-*carboxylic acid*,  $\mathrm{CO_2H\cdot C}<\begin{array}{l}\mathrm{C(OH)\cdot CH_2}\\ \mathrm{CO{-}{-}{-}NH}\end{array}$, decomp. 214°. This acid does not develop a coloration with alcoholic ferric chloride, and is easily decomposed by boiling water, yielding *tetramic acid*,  $\mathrm{OH\cdot C}<\begin{array}{l}\mathrm{CH{-}{-}CO}\\ \mathrm{CH_2\cdot NH}\end{array}$, m. p. 211° (decomp.). Tetramic acid gives a blood-red coloration with ferric chloride, has only feeble acid properties, reduces warm ammoniacal silver nitrate, and develops a violet coloration with nitrous acid, due to the *oximino*-compound,  $\mathrm{OH\cdot N{:}C}<\begin{array}{l}\mathrm{CO\cdot CH_2}\\ \mathrm{CO\cdot NH}\end{array}$, pale blue leaflets, decomp. 205°.

A by-product is not produced by the interaction of chloroacetyl chloride and methyl sodiomalonate in ether at 0°, methyl tetrone-4-carboxylate, m. p. 188—189° (decomp.), alone being produced. In a similar manner, α-bromopropionyl bromide and ethyl sodiomalonate (2 mols.) yield *ethyl* 1-*methyltetrone*-4-*carboxylate*,



$$\mathrm{CO_2Et\cdot C}<\begin{array}{l}\mathrm{C(OH)\cdot CMe}\\ \mathrm{CO{-}{-}{-}O}\end{array},$$

m. p. 89—90°, which is decomposed by dilute hydrochloric acid, forming *methyltetronic acid*,  $\mathrm{O}<\begin{array}{l}\mathrm{CO{-}CH}\\ \mathrm{CMe{\cdot}C{\cdot}OH}\end{array}$, m. p. 117—119°, which develops red and violet colorations with ferric chloride and sodium nitrite respectively. C. S.

Chromoisomerism of Pyridine, Quinoline, and Acridine Salts, and its Explanation by Valency Isomerism. Arthur Hantzsch (*Ber.*, 1911, **44**, 1783—1828).—The existence of coloured modifications of certain pyridine, quinoline, and acridine salts has been explained at different times by the ionisation of chromophores (Decker, Abstr., 1904, ii, 702), by structural isomerism (Decker, Abstr., 1909, i, 408), or by polymerism (Hantzsch and Leupold, Abstr., 1909, ii, 198; Tinkler, Trans., 1909, **95**, 921). The explanation, however, is not to be found in polymerism (compare this vol., i, 608), nor in structural isomerism in Decker's sense, but rather in the existence of chromoisomeric ammonium ions. The author quotes examples to prove that the polychromy of the salts in question, in the solid state, is independent of the nature of the anions and the cations, and in solutions is independent of the degree of association or of dissociation (in aqueous solution). The ultra-violet absorption spectra of polychromatic solutions of polychromatic salts differ greatly; even in one and the same solvent the absorption spectra vary enormously with the nature of the anion and with change of temperature or of concentration. This optical variability of polychromatic salts is in marked contrast to the optical constancy of the salts of cotarnine, the absorption spectra of which are practically identical in water, alcohol, or chloroform, and are independent of the nature of the anion. The absorption spectra show that the selective absorption of coloured ammonium salts is exclusively a property of the coloured ammonium ions, and that these organic chromophores are, in the absence of chemical change, optically constant. It follows therefore that the solutions of the polychromatic pyridine, quinoline, *iso*quinoline, and acridine salts must, in consequence of their optical variability with the nature of the solvent or of the anion or with change of temperature or of concentration, contain, as chemically changeable chromophores, isomeric ammonium ions of different selective absorptive power; in other words, such solutions contain chromoisomeric ammonium salts. Only in certain limiting cases (as, for example, in the case of the cotarnine salts) do these solutions contain individual chromoisomerides; usually two or more chromoisomerides are present in equilibrium in the solution. The equilibrium of chromoisomeric ammonium halides is disturbed, in favour of the more strongly coloured chromoisomeride, by an increase in the associating power (or, better, by a decrease in the dissociating power) of the solvent, by an increase in the atomic weight of the halogen, and by an increase in the temperature or the concentration.

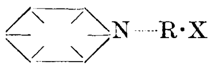
Since the solutions of a polychromatic salt (for example, 5-phenyl-10-methylacridonium sulphite) in different solvents are polychromatic, and the salt in the solid state occurs in differently coloured modifications, the polychromy is independent of a solvent and of the state of aggregation; moreover, since in solution the polychromy is referable to isomerism, the polychromy of the solid salts is also due to isomerism, not to association or polymorphism. This also follows from the genetic relation between polychromatic salt solutions and the solid salts, a relation manifested primarily by the identity of the colour of many salt solutions with that of the "solvates" (hydrates, alcoholates, chloroformates) separating therefrom. Several other phenomena are quoted to prove that the polychromy of solid pyridine, quinoline, and acridine salts is attributable to the existence of chromoisomerides.

From the foregoing, the chromotropy (change of colour) of the solid salts naturally is due to chemical causes. It is a true intramolecular change of an unstable chromoisomeride into a more stable one, brought about, occasionally apparently spontaneously, more frequently by contact with a trace of a catalyst, especially with the vapours of those solvents which dissolve the chromotropic chromoisomerides with the same change of colour. The interconversions of the brown, red, yellow, and green modifications of 5-phenyl-10-methylacridonium sulphite, spontaneously or by contact with alcohol, ether, chloroform, nitrobenzene, or acetic acid, are tabulated. With regard to the number of individual chromoisomerides, it can be stated with considerable certainty in the case of the acridonium salts that the green, yellow, and red modifications are individual; all the other modifications are solid solutions or mixed salts of two, or even of all three, of these individuals.

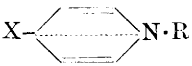
The number of chromoisomeric salts in the pyridine, quinoline, and *iso*quinoline series cannot yet be stated with any degree of certainty, because these isomerides are much more labile than those of the acridine series, and can be isolated in the solid state only under exceptional circumstances. Apparently, however, there are two chromoisomerides in each series. One has a feeble absorbing power, and is represented by the almost colourless salts in the quinoline series, and by the quite colourless salts of the pyridine series. The other chromoisomeride exhibits stronger selective absorption (the deep yellow to orange-red salts of the quinoline series, and the yellow salts of the pyridine series).

The salts of cotarnine and of neocotarnine also exhibit chromoisomerism (compare Salway, Trans., 1910, **97**, 1208). Cotarnine salts are especially interesting. Most of the salts with colourless anions (except the yellow iodide) are very faintly yellow in the solid state; in solution, all are intensely yellow and optically identical. This behaviour is explained by the existence of two chromoisomerides; one, feebly absorptive, is the predominating form in the solid salts, the other, strongly absorptive, is the only form stable in solution.

Chromoisomerides can be represented as valency isomerides in the light of Werner's theory of the constitution of ammonium salts. Of the four groups attached to the nitrogen atom one differs from the other three in being bound by a supplementary valency; the anion is attached to this unique group. The two chromoisomerides of the pyridine series (and in a similar manner those of the quinoline and *iso*quinoline series) can therefore be represented by the formulæ:

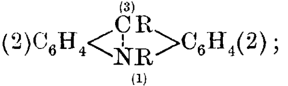


More stable, feebly absorptive
benzenoid salt.



Strongly absorptive
quinonoid salt.

In the acridine series three formulæ are possible, according as the anion is linked at positions 1, 2, or 3 in the group



$$(2)C_6H_4<\overset{(3)}{CR}\atop\underset{(1)}{NR}>C_6H_4(2);$$

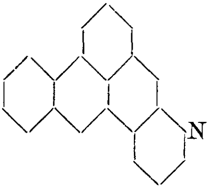
the yellow salts probably are benzenoid (anion in position 1), the green and the red salts quinonoid (anion in positions 2 and 3). The tendency to the formation of quinonoid instead of benzenoid salts is the greater the more unsaturated is the ring attached to the nitrogen atom; consequently, the quinonoid forms of chromoisomerides are rare in the pyridine series, occur somewhat frequently in the quinoline series, and are commonest in the acridine series.

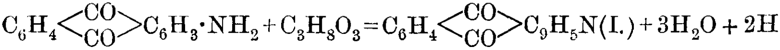
Throughout the paper numerous examples are quoted in support of the statements made. Methods are described for the preparation of yellow, green, and red modifications of the salts of the acridine series. A few new compounds, such as the yellow, orange, and green modifications of 5-*phenyl*-10-*methylacridonium thiocyanate*, are described. C. S.

Preparation of Indoxyl Derivatives. GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 232780).—The action of carbonyl chloride on indoxyls (substituted or otherwise) is capable of a wide application, and leads to the production of crystalline derivatives in quantitative yield.

The *compound*, $C_6H_4<{N(COCl)\atop CO}>CH_2$, is prepared by treating an ice-cold acid solution of indoxyl with carbonyl chloride, when the product separates out as a greyish-white, crystalline powder, m. p. 109—110°; its solution in concentrated sulphuric acid is yellow with a green fluorescence. F. M. G. M.

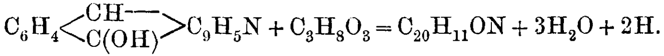
Action of Glycerol and Sulphuric Acid on Amino-compounds and on Compounds Free from Nitrogen Belonging to the Anthracene Group: Benzanthrone and Its Reduction Products. Observations on the Nomenclature of Complex Ring-Systems of the Anthracene Group. OSCAR BALLY and ROLAND SCHOLL (*Ber.*, 1911, 44, 1656—1670).—The compound, $C_{20}H_{11}ON$, obtained by Bally (Abstr., 1904, i, 237) by the action of sulphuric acid and glycerol on 1-aminoanthraquinone in the absence of an oxidising agent, is now found to be 3:4-pyridino-1:9-benzanthrone (annexed formula). With respect to the mechanism of the reaction, the authors consider that the first stage consists in the formation of β-anthraquinolinequinone (I.), which is then reduced to the anthranol derivative (II.), and finally converted by the further action of glycerol into pyridinobenzanthrone, according to the equations:





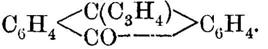
$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_3\cdot NH_2 + C_3H_8O_3 = C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_9H_5N\text{(I.)} + 3H_2O + 2H$$

(II.)



$$C_6H_4{<}\begin{smallmatrix}CH{-}{-}{-}\\C(OH)\end{smallmatrix}{>}C_9H_5N + C_3H_8O_3 = C_{20}H_{11}ON + 3H_2O + 2H.$$

This view is supported by the fact that β-anthraquinolinequinone, on treatment with sulphuric acid and glycerol, yields pyridinobenzanthrone, and also by the behaviour of anthranol, which, when subjected to the same treatment, yields benzanthrone (Bally, *loc. cit.*). It is suggested that the formation of the latter compound is preceded by the intermediate formation of allylideneanthrone,

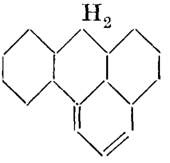


$$C_6H_4{<}\begin{smallmatrix}C(C_3H_4)\\CO{-}{-}{-}\end{smallmatrix}{>}C_6H_4.$$

Benzanthrone may also be obtained from anthracene by the action of sulphuric action and glycerol. In this case it is probable that benzanthrene is formed as an intermediate product.

When reduced with alkaline hyposulphite or with zinc and aqueous sodium hydroxide, benzanthrone yields greenish-yellow solutions, which are considered to contain *dihydrobenzanthrone*, $C_{17}H_{12}O$.

Benzanthrene (annexed formula), prepared by distilling benzanthrone over zinc dust in a stream of hydrogen, crystallises in lustrous, pale yellow leaflets, m. p. 84°. It gives a red coloration with sulphuric acid, and dissolves in organic solvents with a green fluorescence. In solution it is oxidised rapidly by the air to benzanthrone. The *picrate*, $C_{17}H_{12},C_6H_2(NO_2)_3\cdot OH$, crystallises in slender, dark red needles, m. p. 110—111°.



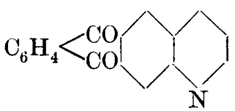
10-*Dibromobenzanthrene*, $C_{17}H_{10}Br_2$, is obtained by brominating benzanthrene in glacial acetic acid solution; it forms yellow crystals, m. p. 174°.

[With G. LENTZ.]—When reduced with hydriodic acid and phosphorus, benzanthrone yields (1) a *hydrocarbon*, $C_{34}H_{26}$ or $C_{34}H_{30}$, m. p. above 320°, and (2) *dihydrobenzanthrene*, $C_{17}H_{14}$, which crystallises in yellow needles, m. p. 81°, and gives green, fluorescent solutions (compare Liebermann and Roka, Abstr., 1908, i, 427); the *picrate*,

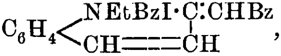
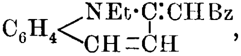
$$C_{17}H_{14},C_6H_2(NO_2)_2\cdot OH,$$

forms feather-shaped aggregates of lustrous, yellow needles, m. p. 125°. *Bromodihydrobenzanthrene*, $C_{17}H_{13}Br$, prepared by brominating dihydrobenzanthrene in glacial acetic acid solution, crystallises in lustrous, colourless needles, m. p. 123°. *Dibromodihydrobenzanthrene*, $C_{17}H_{12}Br_2$, forms almost colourless needles, m. p. 157°.

2 : 3-*Pyridinoanthraquinone* [*γ-anthraquinolinequinone*] (annexed formula) is produced in small quantity in the preparation of 3 : 4-pyridino-1 : 9-benzanthrone from anthranol; it crystallises in yellow needles, m. p. 322°.



For details of the authors' proposed nomenclature of benzanthrone derivatives and allied compounds, the original must be consulted. F. B.

Quinaldinium Bases. EDUARD VONGERICHTEN and W. ROTTA (*Ber.*, 1911, **44**, 1419—1422. Compare Vongerichten and Höfchen, Abstr., 1908, i, 914).—The quinaldinium base obtained by the action of *N*-sodium hydroxide solution on 2-ethylquinoline ethiodide reacts in the cold with alkali and benzoyl chloride, yielding a green oil, a warm dilute acetic acid solution of which reacts with potassium iodide and yields a pale yellow, crystalline *iodide*,  $C_6H_4{<}\begin{matrix}NEtBzI\cdot C{:}CHBz\\ CH{=\!=\!=}CH\end{matrix}$, with m. p. 197°. This iodide does not give a coloration with alcoholic sodium hydroxide or with quinoline methiodide and sodium ethoxide. When boiled with concentrated hydrochloric acid in a reflux apparatus, the iodide yields benzoic acid, and on the addition of ammonia a *base*,  $C_6H_4{<}\begin{matrix}NEt\cdot C{:}CHBz\\ CH{=}CH\end{matrix}$, which crystallises from alcohol in golden-yellow plates, m. p. 139°. The base dissolves in dilute acids, even acetic acid, yielding colourless solutions, but when warmed the acetic acid solution becomes deep yellow. When heated with hydrobromic acid at 200° for three hours and then made alkaline, the base yields an oil which with hydrochloric acid yields 1-ethylquinaldinium hydrochloride.

If *p*-chlorobenzoyl chloride is used instead of benzoyl chloride, the chlorinated *base*, $C_{19}H_{16}ONCl$, m. p. 187°, is obtained.

2-Methylquinoline methiodide and benzoyl chloride yield a *product*, $C_{18}H_{15}ON$, which crystallises in brilliant yellow needles, m. p. 107—108°.

The behaviour of 2-methylquinoline alkyl iodides with alkalis is thus entirely different from the reaction between quinoline alkyl iodides and alkalis, as in the latter case a rupture of the pyridine ring occurs (compare Kaufmann and Strübin, this vol., i, 321).

J. J. S.

Preparation of Thiazole Compounds of "Thioindigo-Reds" and their Derivatives. KALLE & Co. (D.R.-P. 233741).—The action of aldehydes and sulphur (or polysulphides) on the nitro- or amino-substituted 2-carboxymethylthiolbenzoic acids yields thiazole derivatives, which by oxidation and closing of the ring furnish "thiazole-thioindigo" derivatives. The *product* (a thiazole derivative of 2-carboxymethylthiolbenzoic acid) prepared from benzaldehyde and 4-nitro-2-carboxymethylthiolbenzoic acid forms yellow crystals, m. p. about 250°. F. M. G. M.

***holo-* and *meri*-Quinonoid Salts of Benzidine.** WALTER MADELUNG (*Ber.*, 1911, **44**, 1674—1676).—Mainly a reply to Piccard's criticism (this vol., i, 493) of previous work of the author (this vol., i, 323). F. B.

Action of Hydrazine Hydrate on *cyclo*Hexanone. NICOLAI M. KIJNER and S. BELOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 577—582).—cyclo*Hexylidenehydrazine hydrate*, $C_6H_{10}{:}N{\cdot}NH_2,H_2O$, formed by the action of hydrazine hydrate on *cyclo*hexanone, is a colourless liquid, b. p. 107—108°/28 mm., $D_0^{19\cdot5}$ 0·9866; on heating with dilute hydrochloric acid, it is resolved into its components, and on mixing with one or two vols. of water, it solidifies to a crystalline mass at 0°.

When reduced with absolute alcohol and sodium, the above compound yields: (1) *cyclo*hexanol; (2) cyclo*hexylhydrazine*,

$$C_6H_{11}{\cdot}NH{\cdot}NH_2,$$

m. p. 46—50°, b. p. 195·5°/758 mm., and gives a silver mirror with ammoniacal silver nitrate solution in presence of alkali; it gives the *thioureide*, $NHPh{\cdot}CS{\cdot}NH{\cdot}NH{\cdot}C_6H_{11}$, m. p. 143—143·5°, and with pyruvic acid forms the cyclo*hexylhydrazone* of the acid,

$$CO_2H{\cdot}CMe{:}N{\cdot}NH{\cdot}C_6H_{11},$$

m. p. 110—112°; on oxidation with potassium ferricyanide it yields *cyclo*hexane.

cyclo*Hexylideneazine*, $C_6H_{10}{:}N{\cdot}N{:}C_6H_{10}$, also obtained by the interaction of hydrazine nitrate and *cyclo*hexanone, forms rhombic plates, m. p. 33·5—34°, b. p. 175°/28 mm.; the liquid remains supercooled for a long time, and has D_0^2 0·9847, n_D^{20} 1·5268.

*Di*cyclo*hexylhydrazine*, $NH_2{\cdot}N(C_6H_{11})_2$, obtained by reducing the preceding compound, has b. p. 220—260°, and gives a *hydrochloride*, $C_{12}H_{25}N_2Cl$. This compound is probably formed by isomerisation of the *s*-compound, $NH{\cdot}C_6H_{11}{\cdot}NH{\cdot}C_6H_{11}$, which should be given by the reduction of the azine. T. H. P.

Relations of α-Benzaldehydephenylhydrazone to Certain Nitrogen Compounds. ROBERTO CIUSA and UGO PESTALOZZA (*Gazzetta*, 1911, **41**, i, 391—395).—The aim of the authors' experiments was to ascertain if any analogy is shown between the chemical behaviour of the more stable or α-form of benzaldehydephenylhydrazone, m. p. 156°, and that of the stable diazoaminobenzene, m. p. 96°, which may be regarded as the phenylhydrazone of nitrosobenzene.

With the latter, picric acid and picryl chloride in benzene solution give the respective intensely brown additive compounds, as is the case with phenylhydrazones of aromatic aldehydes, but these are almost always unstable. In 96% alcohol the action of picric acid (1 mol.) on diazoaminobenzene (1 mol.) yields immediately a brown, powdery precipitate (? the picrate), which, in a few minutes, undergoes transformation into diazobenzene picrate, so that picric acid here acts in the same way as hydrochloric acid:

$$\mathrm{NPh{:}N{\cdot}NHPh + 2HCl = NPh{:}N{\cdot}Cl + NH_2Ph,HCl.}$$

This action affords a convenient and rapid method of preparing diazobenzene picrate.

The actions of amyl nitrate and of mercuric oxide on diazoaminobenzene were studied to see if an oxidation product containing a chain of six nitrogen atoms, and analogous to that formed by benzaldehydephenylhydrazone, could be obtained:

$$\mathrm{2NPh{:}N{\cdot}NHPh \longrightarrow H_2 + NPh{:}N{\cdot}NPh{\cdot}NPh{\cdot}N{:}NPh.}$$

With amyl nitrate the reaction is very complex, the only product identified being diazobenzene nitrate; with mercuric oxide the latter is not reduced, the mercury salt of diazoaminobenzene being formed. This different behaviour of diazoaminobenzene from that of benzaldehydephenylhydrazone is in agreement with the acid character of the former and the feebly basic nature of the hydrazones. T. H. P.

Catalytic Decomposition of Alkylidenehydrazines as a Method of Obtaining Hydrocarbons. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 582—595).—When an alkylidenehydrazine is heated in presence of a large quantity of solid potassium hydroxide, the base decomposes as follows: $\mathrm{C_nH_{m-2}{:}N{\cdot}NH_2 = C_nH_m + N_2}$, these products being the same as are obtained by the oxidation of the primary hydrazines by means of potassium ferricyanide in an alkaline solution. The alkylidenehydrazine is probably first converted by the alkali into the tautomeric diazo-form, thus:

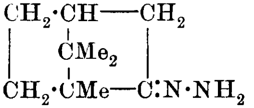
$$\mathrm{C_nH_{m-2}{:}N{\cdot}NH_2 + KOH \longrightarrow C_nH_{m-1}{\cdot}N(OK){\cdot}NH_2 \longrightarrow}$$
$$\mathrm{C_nH_{m-1}{\cdot}N{:}NH + KOH \longrightarrow C_nH_m + N_2.}$$

In this way 1-methyl*cyclo*hexylidene-3-hydrazine gives a yield of 54% of methyl*cyclo*hexane, and thujylidenehydrazine, of 70% of thujane.

Camphylidenehydrazine (annexed formula), prepared by boiling camphor and hydrazine hydrate in alcoholic solution, forms a white, crystalline mass, m. p. 53—55°, $[\alpha]_D$ −40·81° (in ether), −32·74° (90% alcohol), and yields a liquid hydrate soluble in water. Its *hydrochloride*, $\mathrm{C_{10}H_{16}{:}N{\cdot}NH_2,HCl}$, m. p. 186°, $[\alpha]_D$ −31·33° (water), was prepared. When hydrolysed with excess of hydrochloric acid, it is completely converted into camphor and hydrazine hydrochloride, but when 1 mol. of the acid is used per 1 mol. of the camphylidenehydrazine, in addition to camphor, a considerable quantity of camphanazine (compare Angeli and Castellana, *Atti R. Accad. Lincei*, 1905, [v], **14**, i, 669—677) is also obtained:

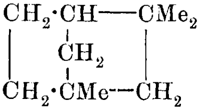
$$\mathrm{C_{10}H_{16}{:}N{\cdot}NH_2,HCl + C_{10}H_{16}O = C_{10}H_{16}{:}N{\cdot}N{:}C_{10}H_{16} + H_2O + HCl;}$$

camphanazine has the rotations, $[\alpha]_D$ = −92·33° (benzene), −90·06° (ether), −37·27° (methyl alcohol), −19·25° (ethyl alcohol), and −14·18° (propyl alcohol).



When heated with potassium hydroxide, camphylidenehydrazine (30 grams) yields camphane (10 grams).

[With A. PROSKURJAKOFF.]—*Fenchane* (annexed formula), obtained together with fenchanazine (see below) by heating fenchylidenehydrazine (from fenchone and hydrazine hydrate) with dry potassium hydroxide, is a mobile liquid with a faint camphor-like smell, b. p. 151·5°/763 mm., D_0^{20} 0·8326, n_D^{20} 1·4463, $[\alpha]_D$ −16·53°; it does not react with permanganate, bromine, boiling fuming nitric acid, or fuming hydriodic acid in a sealed tube at 210°.



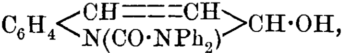
Fenchanazine, $C_{10}H_{16}:N\cdot N:C_{10}H_{16}$, forms oblique, quadrangular plates, m. p. 106°, $[\alpha]_D$ +212·9°, and is converted into fenchone and hydrazine hydrochloride on heating with concentrated hydrochloric acid.

When heated with solid potassium hydroxide, *cyclo*hexylidenehydrazine hydrate yields *cyclohexane*, $C_6H_{10}:N\cdot NH_3\cdot OH = C_6H_{12} + N_2 + H_2O$, and *cyclo*hexanol, $2C_6H_{10}:N\cdot NH_3\cdot OH = 2C_6H_{11}\cdot OH + N_2 + N_2H_4$. T. H. P.

Quaternary Ammonium Chlorides from Diphenyl Carbamide Chloride and Pyridine or Quinoline. JOHANNES HERZOG and K. BUDY (*Ber.*, 1911, **44**, 1584—1594).—Acid chlorides in presence of tertiary bases are converted into acid anhydrides by means of water or sodium carbonate. It is now found that sodium or potassium hydroxide is even more efficient at 0° in facilitating this change. The additive compound of diphenylcarbamide chloride and pyridine is thus readily converted into *diphenylcarbamic anhydride*, $(NPh_2\cdot CO)_2O$, which forms yellow crystals, m. p. 121—123°.

In addition a yellow, crystalline quaternary base, *diphenylcarbamylpyridinium hydroxide*, m. p. 189°, is obtained. This base is remarkable in being neutral, soluble in organic solvents, but insoluble in water; when hydrolysed by boiling with acetic and hydrochloric acids, diphenylcarbamide and glutaconaldehyde are formed, the latter being identified as Zincke's dianilide. Accordingly, the base has the composition : $NPh_2\cdot CO\cdot N:CH\cdot CH:CH\cdot CH:CH\cdot OH$.

Diphenylcarbamylquinolinium chloride, obtained by the interaction of the components in sunlight, forms red crystals, m. p. 135—137°. The *platinichloride* separates in yellow crystals, m. p. 232°. This reacts quite differently with sodium hydroxide; diphenylcarbamic acid is not formed, the sole product of the reaction being C-*hydroxy*-N-*diphenylcarbamyldihydroquinoline*,

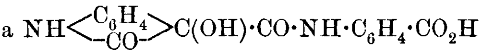


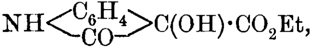
$$C_6H_4{<}\begin{matrix}CH{=\!=}CH\\N(CO\cdot NPh_2)\end{matrix}{>}CH\cdot OH,$$

a reddish-white, amorphous powder. The *ethyl ether* forms long, faintly yellow-coloured needles, m. p. 195° (quickly heated); the *methyl ether* crystallises in yellow needles, m. p. 160—162°. Both ethers on boiling with 10% hydrochloric acid are converted into diphenylcarbamylquinolinium chloride. E. F. A.

Dehydroindigotin. III. Decomposition by means of Acids and Alkalis. LUDWIG KALB (*Ber.*, 1911, **44**, 1455—1464. Compare Abstr., 1909, i, 966, 967; 1910, i, 340).—Dilute mineral acids react with dehydroindigotin in two different ways: (1) Two molecules of water react with one of dehydroindigotin, yielding equimolecular quantities of dioxindole and isatin. (2) Two molecules of water react with two of the compound, yielding one molecule of indigotin and two of isatin. The second is the chief reaction when dehydroindigotin is boiled with water (compare O'Neill, *Chem. News*, 1892, **65**, 124; Marchlewski and Radcliffe, Abstr., 1899, i, 74). The dioxindole and isatin react to form isatyde (Heller, Abstr., 1904, i, 416), a good yield of which can be obtained by shaking dehydroindigotin acetate for sixteen hours with a mixture of concentrated hydrochloric acid and water (2 : 1).

Di-isatic acid (Marchlewski and Radcliffe, *loc. cit.*), prepared by the action of sodium hydroxide solution on dehydroindigotin, is decomposed when warmed for two hours at 85° with 10% potassium hydroxide solution, yielding anthranilic acid, dioxindole, and carbon dioxide.

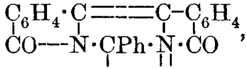
The formula  $NH<\substack{C_6H_4\\CO}>C(OH)\cdot CO\cdot NH\cdot C_6H_4\cdot CO_2H$ is suggested for di-isatic acid, and during its formation molecular rearrangement occurs. Hydrocyanoisatin when hydrolysed with alcoholic hydrochloric acid yields *ethyl hydroxyoxindole-3-carboxylate*,



$$NH<\substack{C_6H_4\\CO}>C(OH)\cdot CO_2Et,$$

which crystallises from water in hexagonal plates, m. p. 152°. The same ester is also formed by the action of $2N$-sodium carbonate solution on ethyl indoxanthinate, a reaction which involves a molecular rearrangement similar to that which occurs in the formation of di-isatic acid. The reaction between alkalis and dehydroindigotin is regarded as consisting first of all in the addition of water, yielding a dihydroxyindigo-white. This by a wandering of oxygen atoms undergoes decomposition into indigotin and 2-hydroxyindoxyl-2'-carboxyanilide-2-carboxylic acid; the greater part of the latter then passes over into di-isatic acid, whilst the smaller portion is decomposed, yielding anthranilic acid, dioxindole, and carbon dioxide. J. J. S.

Indigo-Yellow. BERTHOLD WUTH (*Chem. Zeit.*, 1911, **73**, 667).—When heated with excess of benzoyl chloride, indigotin yields dibenzoylindigotin. In the presence of condensing agents, such as metals and metallic chlorides, however, the reaction proceeds differently. Only one molecule of benzoyl chloride is used, and a hitherto unknown compound of intense yellow colour is produced, crystallising from nitrobenzene in greenish-yellow needles (m. p. 275—277°). Unlike dibenzoylindigotin, it cannot be re-converted into indigotin by saponifying agents. It follows that substitution takes place at the imino-groups, and that inner condensation occurs with the formation of a new ring, thus:



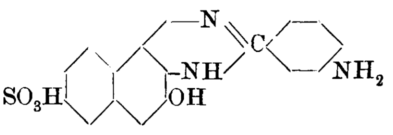
$$\begin{array}{l}C_6H_4\cdot C \equiv\!\equiv C-C_6H_4\\ \;|\qquad\;\; |\qquad\;\; |\quad\;\; |\\ CO-\!\!-N\cdot CPh\cdot N\cdot CO\end{array},$$

But whether the spare carbon valency is saturated by hydrogen or hydroxyl or by one of the indigo-nitrogens is not yet decided. Determination of the molecular weight by the boiling-point method points to the empirical formula $C_{23}H_{14}O_2N_2$.

Substitution products of indigotin, such as di-bromo-indigotin, react similarly with benzoyl chloride. Yellow condensation products are likewise obtained by replacing benzoyl chloride by its nuclear substitution products, or by benzotrichloride, benzylidene chloride, and similar substances. The compounds produced have the characteristic qualities of the vat dyes, and gives rise to greenish-yellow shades.

The above-described compound is the indigo-yellow 3G-Ciba of commerce. J. D. K.

[Preparation of 4-Hydroxy-2-*m*-aminophenyl-α-naphthiminazole-7-sulphonic Acid.] LEOPOLD CASSELLA & CO. (D.R.-P. 233939).—4-*Hydroxy*-2-m-*aminophenyl*-α-*naphthiminazole* - 7 - *sulphonic acid* (annexed formula) is prepared by the condensation of 3 : 4-diamino-β-naphthol-7-sulphonic acid with aminobenzaldehyde bisulphite; its *sodium* salt is crystalline and sparingly soluble in water. When coupled with diazotised aniline in alkaline solution, it yields a red *aminoazo*-derivative, and the properties of numerous valuable direct cotton dyes obtained when it is combined with diazo- and bisdiazo-compounds are described in the patent.



F. M. G. M.

Formation of 1-Nitroso-5-phenyl-3-pyrazolidone from Cinnamoyl Hydrazide. ERNST MUCKERMANN (*J. pr. Chem.*, 1911, [ii], **83**, 513—540).—Hydrazides of monobasic unsaturated acids have been hitherto unexamined. The present work deals with *cinnamoylhydrazide*, $CHPh:CH\cdot CO\cdot NH\cdot NH_2$, m. p. 101°, which is readily obtained by boiling ethyl cinnamate with alcohol and hydrazine hydrate. It exhibits the usual reducing properties of primary acid hydrazides, yields *dicinnamoylhydrazide*, $N_2H_2(CO\cdot CH:CHPh)_2$, m. p. 247—248°, by boiling with alcoholic iodine, and forms a *hydrochloride*, m. p. 201° (decomp.), *benzylidene* compound,

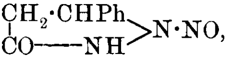
$$CHPh:CH\cdot CO\cdot NH\cdot N:CHPh,$$

m. p. 180°, *benzoyl* derivative, m. p. 158—159°, and condensation *products* with acetone, $CHPh:CH\cdot CO\cdot NH\cdot N:CMe_2$, m. p. 127°, and with ethyl acetoacetate, $CHPh:CH\cdot CO\cdot NH\cdot N:CMe\cdot CH_2\cdot CO_2Et$, m. p. 125—126°. Its hydrochloride reacts with aqueous potassium cyanate to form *cinnamoylsemicarbazide*, $CHPh:CH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 161—162°. *Cinnamoylphenylthiosemicarbazide*,

$$CHPh:CH\cdot CO\cdot NH\cdot NH\cdot CS\cdot NHPh,$$

from cinnamoylhydrazide and alcoholic phenylthiocarbimide, has m. p. 146°.

Aqueous cinnamoylhydrazide hydrochloride reacts with sodium nitrite at 0° to form, not the expected azoimide, but a yellow *substance*, $C_9H_9O_2N_3$, m. p. 127—128° (decomp.), which is a nitroso-compound, but not a hydrazide on account of its strongly acid nature and absence of reducing properties. Its acid properties indicate the presence of the group $\cdot NH\cdot CO\cdot$, and the constitution, 1-*nitroso*-5-*phenyl*-3-*pyrazolidone*,

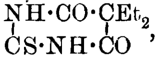

$\begin{array}{l}CH_2\cdot CHPh\\ CO\text{——}NH\end{array}\!\!>N\cdot NO$, is supported by the following evidence (compare also Knorr, Abstr., 1887, 665; von Rothenburg, *ibid.*, 1895, i, 302). Its *ammonium* salt, $C_9H_9O_2N_3,NH_3$, m. p. 147° (decomp.), obtained from the nitrosophenylpyrazolidone and 10% ammonia, is easily converted into the *silver* salt, $C_9H_8O_2N_3Ag$, m. p. 144—145°, *barium* salt, $(C_9H_8O_2N_3)_2Ba,H_2O$, greenish-blue *copper* salt,

$$(C_9H_8O_2N_3)_2Cu,2H_2O,$$

and *picrate,* $C_9H_9O_2N_3.NH_3,C_6H_2(NO_2)_3\cdot OH$, m. p. 127°; from the silver salt ethereal ethyl iodide produces 1-*nitroso*-5-*phenyl*-2-*ethyl*-3-*pyrazolidone*, m. p. 98°. The nitrosophenylpyrazolidone yields with bromine and glacial acetic acid at 0° von Rothenburg's 4:4-dibromo-3-phenyl-5-pyrazolone (Abstr., 1895, i, 686). 1-Nitroso-5-phenyl-3-pyrazolidone is converted by boiling concentrated hydrochloric acid into cinnamic acid, by cold concentrated hydrochloric acid into β-chlorodihydrocinnamic acid (?), and by boiling dilute sulphuric acid, D 1·06, into von Rothenburg's 4-oximino-3-phenyl-5-pyrazolone (*loc. cit.*).

C. S.

Preparation of 5:5-Dialkylthiobarbituric Acids. EMANUEL MERCK (D.R.-P. 234012).—The preparation of 5:5-dialkylbarbituric acids by means of carbamide has previously been described (Abstr., 1904, i, 380), and the results obtained by substituting thiocarbamide in the reaction are now recorded

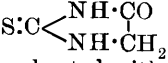
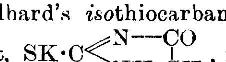
Diethylthiobarbituric acid,

$\begin{array}{l}NH\cdot CO\cdot CEt_2\\ CS\cdot NH\cdot CO\end{array}$, yellow tablets or needles, m. p. 180°, is prepared by heating ethyl diethylmalonate with thiocarbamide in alcoholic sodium ethoxide solution at 105° with continual stirring.

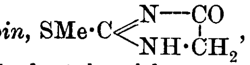
Dipropylthiobarbituric acid, glistening leaflets, m. p. 154°, can be converted by removal of sulphur into *dipropylbarbituric acid,* m. p. 145°.

F. M. G. M.

Synthesis of Thiohydantoin. SHIGERU KOMATSU (*Mem. Coll. Sci. Eng.*, 1911, 3, 1—12).—The author has succeeded in preparing the previously unknown thiocarbamide form of thiohydantoin from glycine and potassium thiocyanate at 100°, using acetic anhydride as a catalyst. Thiohydantoic acid is first formed, and this loses H_2O on beating with hydrochloric acid on the water-bath, leaving the compound referred to. Similarly, *r*-alanine yields *r*-5-methylthiohydantoin.

Thiohydantoic acid, $NH_2\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, forms colourless needles, m. p. 170—171° (decomp.).

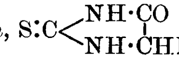
Thiohydantoin,

$S:C\!<\!\begin{array}{l}NH\cdot CO\\ NH\cdot CH_2\end{array}$, forms colourless needles, decomposing on heating. When heated with hydrochloric acid in sealed tubes at 160°, it is decomposed into glycine, carbon dioxide, hydrogen sulphide, and ammonium chloride. It is not hydrolysed to thioglycollate like Volhard's *iso*thiocarbamide form of this hydantoin. The *potassium* salt,

$SK\cdot C\!\ll\!\begin{array}{l}N\text{——}CO\\ NH\cdot CH_2\end{array}$, forms a colourless, crystalline precipitate.

2-*Methylthiohydantoin*,  $\mathrm{SMe{\cdot}C}\Big<\begin{matrix}\mathrm{N{-}CO}\\ \mathrm{NH{\cdot}CH_2}\end{matrix}$, prepared by heating the potassium salt of thiohydantoin with excess of methyl iodide on the water-bath, forms colourless needles, soon darkening when kept. When fused with potassium hydroxide and acidified, it gives the odour of mercaptan.

r-α-*Methylthiohydantoic acid*, $NH_2{\cdot}CS{\cdot}NH{\cdot}CHMe{\cdot}CO_2H$, forms colourless needles, m. p. 164—165°. The *barium* salt,

$$Ba(C_4H_7O_2N_2S)_2,H_2O,$$

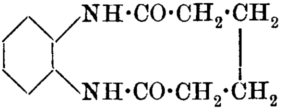
is very hygroscopic, m. p. about 100°.

r-5-*Methylthiohydantoin*,  $\mathrm{S{:}C}\Big<\begin{matrix}\mathrm{NH{\cdot}CO}\\ \mathrm{NH{\cdot}CHMe}\end{matrix}$, prepared from *r*-α-methylthiohydantoic acid, forms pearly scales, m. p. 158°. By treating the hot aqueous solution of *r*-5-methylthiohydantoin with mercuric oxide, *r*-5-methylhydantoin (Urech, Abstr., 1873, 380) is obtained.

J. D. K.

A Group of Synthetic Organic Colloids. Edgar Wedekind (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 303—304).

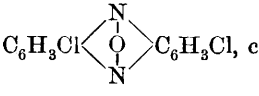
—By the action of adipyl chloride on *o*-diamines of the benzene series, amorphous substances are obtained which contain a ring of ten atoms (annexed formula). These substances are typical colloids, are insoluble in most solvents except acetic acid, and cannot be obtained in crystalline form. Colloidal solutions can be prepared by pouring acetic acid solutions into water or by triturating with potassium hydroxide solution, and afterwards treating with successive quantities of distilled water. Opalescent, milky liquids are thus obtained, which can be purified by dialysis, and exhibit all the properties of colloidal solutions. The solutions are coagulated by electrolytes, and much less readily by freezing. The possibility of obtaining these substances in colloidal form by the trituration method is supposed to be connected with their acid amide character.



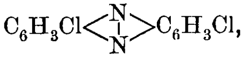
H. M. D.

Behaviour of Certain Para-substituted Nitrosobenzenes towards Sulphuric Acid. Eugen Bamberger and W. Ham (*Annalen*, 1911, **382**, 82—128. Compare Bamberger, Büsdorf, and Sand, Abstr., 1898, i, 521).

—By allowing a glacial acetic acid solution of *p*-chloronitrosobenzene to drop slowly into well stirred concentrated sulphuric acid kept at 20—24°, the chief products are 2 : 7-dichlorophenazine-5 : 10-oxide, which is insoluble in dilute alkalis and in alcohol, 4′-chloro-4-nitrosodiphenylhydroxylamine, which is soluble in dilute alkalis, unaltered *p*-chloronitrosobenzene, and 4 : 4′-dichloroazoxybenzene.

2 : 7-*Dichlorophenazine* 5 : 10-*oxide*,  $\mathrm{C_6H_3Cl}\Big<\begin{matrix}\mathrm{N}\\ \mathrm{O}\\ \mathrm{N}\end{matrix}\Big>\mathrm{C_6H_3Cl}$, crystallises

from glacial acetic acid in pale golden-yellow, lustrous needles, m. p. 237·5—238° (decomp.), when rapidly heated. As a rule, it has an orange-brown colour, but this is changed to the characteristic golden-yellow after being twice treated with fuming nitric acid at the ordinary temperature. Its solution in concentrated sulphuric acid has a blood-red colour, and when reduced with stannous chloride and hydrochloric acid, it yields 2 : 7-*dichlorophenazine*,



$$C_6H_3Cl{<}\overset{N}{\underset{N}{|}}{>}C_6H_3Cl,$$

which crystallises from glacial acetic acid or xylene in glistening, lemon-yellow needles, m. p. 265·5°. Its solution in concentrated sulphuric acid is red; when moistened with concentrated hydrochloric acid it turns red, but with more acid it dissolves, yielding a yellow solution. Its alcoholic solution reacts with an alcoholic solution of silver nitrate, yielding slender, moss-green needles with a bronzy lustre. 2 : 7-Dichlorophenazine-5 : 10-oxide can be synthesised by heating *p*-chloroaniline, *p*-chloronitrobenzene, and dry sodium hydroxide for five hours at 110—120° (compare Wohl and Aue, Abstr., 1901, i, 612), but an appreciable amount of 4 : 4′-dichloroazobenzene is formed at the same time.

4′-*Chloro*-4-*nitrosodiphenylhydroxylamine*, $C_6H_4Cl·N(OH)·C_6H_4·NO$, crystallises from acetone in greenish-yellow plates with a pronounced bronzy lustre, and has m. p. 143° (decomp.); it dissolves in alkalis and also in concentrated sulphuric acid, yielding red solutions, and when reduced with zinc dust and boiling 2*N*-ammonium chloride solution yields 4′-*chlorophenyl*-p-*phenylenediamine*,

$$C_6H_4Cl·NH·C_6H_4·NH_2,$$

which crystallises from light petroleum in glistening, flat needles, m. p. 66·5—67°, only sparingly volatile in steam. The *hydrochloride* forms colourless, glistening crystals, and the *sulphate* is sparingly soluble. When the hydroxylamine derivative is reduced with zinc dust and hot 2*N*-hydrochloric acid, *p*-chloroaniline is also formed.

The formation of chloronitrosodiphenylhydroxylamine from *p*-chloronitrosobenzene and concentrated sulphuric acid is accompanied by the elimination of an atom of chlorine in the form of hydrogen chloride.

Under specific conditions it is possible to obtain appreciable amounts of *p*-chloronitrobenzene by the action of concentrated sulphuric acid on the corresponding nitroso-compound.

p-Bromonitrosobenzene reacts with concentrated sulphuric acid in much the same manner as its chlorinated analogue. 2 : 7-*Dibromophenazine* 5 : 10-*oxide*, $C_{12}H_6ON_2Br_2$, crystallises from glacial acetic acid or xylene in glistening, red needles, or after treatment with fuming nitric acid in golden-yellow needles, m. p. 240°, and on reduction with stannous chloride and hydrochloric acid yields 2 : 7-*dibromophenazine*, $C_{12}H_6N_2Br_2$, which crystallises from glacial acetic acid in orange-yellow or golden-yellow needles, m. p. 244·5—245°. 4′-*Bromo*-4-*nitrosodiphenylhydroxylamine*,

$$C_6H_4Br·N(OH)·C_6H_4·NO,$$

is formed together with a dibromo-derivative, and after repeated fractional solution in ammonium hydroxide, fractional precipitation with dilute hydrochloric acid, and crystallisation from a mixture of acetone and light petroleum, is obtained as a yellow powder with m. p. 155°. On reduction with zinc and ammonium chloride solution it yields *4′-bromophenyl-*p*-phenylenediamine*, $C_6H_4Br\cdot NH\cdot C_6H_4\cdot NH_2$, which crystallises from light petroleum in glistening, pale yellow needles, m. p. 75·5—76°. The *sulphate*, $2C_{12}H_{11}N_2Br,H_2SO_4$, is very sparingly soluble, and has m. p. 229°.

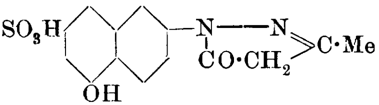
Dibromonitrosodiphenylhydroxylamine, $C_6H_4Br\cdot N(OH)\cdot C_6H_3Br\cdot NO$, has m. p. 130°. The amounts of the various products obtained from 42 grams of *p*-bromonitrosobenzene were: dibromophenazine oxide, 8·2; dibromophenazine, 0·3; bromonitrosodiphenylhydroxylamine, 5·0; dibromonitrosodiphenylhydroxylamine, 1·4; and red crystals, $C_6H_4Br\cdot NO$?, 1·5 grams.

p-Iodonitrosobenzene forms glistening, grass-green needles, m. p. 103·5—104·5° (compare *Ber.*, 1895, **28**, 249), and is accompanied by 4 : 4′-di-iodoazobenzene. *p*-Iodophenylhydroxylamine begins to sinter at 70°, but is not completely molten at 145°, and by-products obtained in its formation are 4 : 4′-di-iodoazoxybenzene, m. p. 207—208° (Gabriel, this Journ., 1877, i, 307, gives 199—199·5°), and a substance with m. p. 214—215°, which is probably an isomorphous mixture of di-iodoazobenzene and di-iodoazoxybenzene. 2 : 7-*Di-iodophenazine* 5 : 10-*oxide*, $C_{12}H_6ON_2I_2$, crystallises from xylene in glistening, brownish-yellow needles, m. p. 241° (decomp.), and when reduced yields 2 : 7-*di-iodophenazine*, $C_{12}H_6N_2I_2$, which crystallises in glistening, yellow needles, m. p. 235°. 4′-*Iodo*-4-*nitrosodiphenylhydroxylamine*, $C_6H_4I\cdot N(OH)\cdot C_6H_4\cdot NO$, crystallises from acetone in glistening, greenish-yellow plates, m. p. 150—150·5° (decomp.), and is very sparingly soluble in ammonium hydroxide solution. *Di-iodonitrosodiphenylhydroxylamine*, $C_6H_4I\cdot N(OH)\cdot C_6H_3I\cdot NO$, crystallises from acetone in brownish-yellow nodules, m. p. 157° (decomp.), and is soluble in alkalis and ammonium hydroxide solution. Small amounts of lustrous, bright red plates, m. p. 188·5°, and of glistening, orange-red or yellow crystals, m. p. 240°, are also obtained by the action of concentrated sulphuric acid on *p*-iodonitrosobenzene. The amounts of products from 45 grams of *p*-iodonitrosobenzene were: *p*-iodonitrobenzene, 0·07; di-iodophenazine oxide, 7·1; iodonitrosodiphenylhydroxylamine, 2·5; di-iodonitrosodiphenylhydroxylamine, 0·4; red plates, m. p. 188·5°, 0·4; and product, m. p. 240°, 0·05 grams.

Twenty grams of *p*-nitrosotoluene when treated with concentrated sulphuric acid in the presence of glacial acetic acid gave: dimethylphenazine oxide, 4; dimethylphenazine, 0·95; *p*-azoxytoluene, 0·55; *p*-azotoluene, 0·05; mixture of azo- and azoxy-compounds, 0·5; an amorphous, dark brown powder, 6·5, and pale red powder, 2·1 grams.

2 : 7-*Dimethylphenazine* 5 : 10-*oxide*, $C_{14}H_{12}ON_2$, crystallises in glistening, pale golden-yellow needles, m. p. 204—205°. The *hydrochloride* and *sulphate* form orange-yellow, glistening needles, which are hydrolysed by water. 2 : 7-*Dimethylphenazine*, $C_{14}H_{12}N_2$, crystallises from alcohol in pale yellow, glistening needles, m. p. 162·5—163°, and yields a *sulphate* in the form of golden-yellow needles. J. J. S.

Preparation of Hydroxy-β-naphthylpyrazolonemonosulphonic Acids. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 233068).—When the β-naphthylpyrazolonedisulphonic acids (prepared from β-naphthylhydrazinedisulphonic acids and ethyl acetoacetate) are fused with potassium hydroxide at 160—180°, they yield the corresponding hydroxynaphthylpyrazolonemonosulphonic acids.

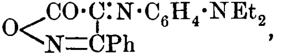


5′-Hydroxy-β-naphthyl-3-methyl-5-pyrazolone-7′-sulphonic acid (annexed formula), a colourless, crystalline powder, was thus prepared from 1-β-naphthyl-5′:7′-disulphonyl-3-methyl-5-pyrazolone; it furnishes a yellow *nitroso*-derivative.

F. M. G. M.

Azomethines derived from Phenyl*iso*oxazolone. ANDRÉ MEYER (*Compt. rend.*, 1911, **152**, 1677—1680. Compare Abstr., 1908, i, 368).—A description of new compounds analogous to that previously obtained by the condensation of phenyl*iso*oxazolone with nitrosodimethylaniline. The substances all melt with decomposition, are decomposed by alkalis, and develop a violet coloration with sulphuric acid.

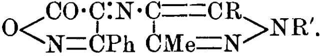
4-*Diethylaminophenylimino-3-phenyl*iso*oxazolone*,



$$\mathrm{O}\Big\langle\begin{matrix}\mathrm{CO\cdot C{:}N\cdot C_6H_4\cdot NEt_2}\\ \mathrm{N{=}CPh}\end{matrix},$$

steel-grey prisms, m. p. 117°; the *methylethylamino*-compound forms violet needles, m. p. 143°; the *anilino*-derivative, $C_{21}H_{15}O_2N_3$, has m. p. 141—142°.

Phenyl*iso*oxazolone also condenses with nitrosopyrazoles, giving red or brown compounds of the type

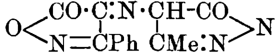


$$\mathrm{O}\Big\langle\begin{matrix}\mathrm{CO\cdot C{:}N\cdot C{\equiv\!\equiv}CR}\\ \mathrm{N{=}CPh\;\;CMe{=}N}\end{matrix}\Big\rangle\mathrm{NR'}.$$

Their solutions in acetic acid or alcohol are violet, but become colourless through hydrolysis.

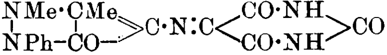
3 : 5-*Dimethylpyrazoleimino-3′-phenyl*iso*oxazolone*, $C_{14}H_{12}O_2N_4$, m. p. 140°. 1-*Phenyl-3 : 5-dimethylpyrazoleimino-3′-phenyl-*iso*oxazolone*, $C_{19}H_{14}O_2N_4$, m. p. 99°. 1 : 5-*Diphenyl-3-methylpyrazoleimino-3′-phenyl*iso*oxazolone*, $C_{25}H_{18}O_2N_4$, m. p. 143—144°.

Nitrosoantipyrine condenses with phenyl*iso*oxazolone, giving the compound



$$\mathrm{O}\Big\langle\begin{matrix}\mathrm{CO\cdot C{:}N\cdot CH{-}CO}\\ \mathrm{N{=}CPh\;\;CMe{:}N}\end{matrix}\Big\rangle\mathrm{NPh},$$

m. p. 147—148°. The corresponding *tolyl* derivative has m. p. 152°. The two foregoing substances are somewhat analogous to purpuric acid, if the latter has the constitution ascribed to it by Slimmer and Stieglitz (Abstr., 1904, i, 634). For the purpose of comparison, alloxan was condensed with aminoantipyrine. The product having the formula



$$\begin{matrix}\mathrm{NMe\cdot CMe}\\ \mathrm{NPh{-}CO{-}}\end{matrix}\Big\rangle\mathrm{C\cdot N{:}C}\Big\langle\begin{matrix}\mathrm{CO\cdot NH}\\ \mathrm{CO\cdot NH}\end{matrix}\Big\rangle\mathrm{CO}$$

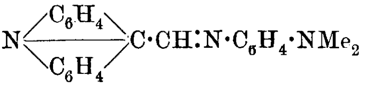
resembles murexide in appearance and solubility, and in the ease with which it undergoes hydrolysis.

W. O. W.

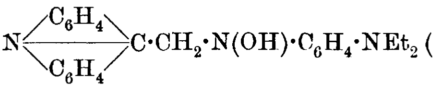
Preparation of Schiff's Bases from Nitroso-compounds. A. E. Porai-Koschitz, Y. I. Auschkap, and N. K. Amsler (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 518—525).—In order to test the general applicability of the empirical rule laid down by Sachs (Abstr., 1900, i, 362; 1901, i, 272; 1902, i, 118, 119) to the effect that the methylene group is capable of reacting with the nitroso-group only when it is accompanied by strongly acidic groups, such as CN, NO_2, $CO\cdot NH_2$, CHO, C:C, CO_2H, etc., the authors have investigated the reactions occurring between nitroso-derivatives and 2-methylquinoline, 2 : 6-dimethylquinoline and 5-methylacridine, which are distinguished by the great mobility of the hydrogen atoms of their methyl groups, and condense, for example, with aldehydes with much greater ease than does 2 : 4-dinitrotoluene. With 2-methylquinoline and 2 : 6-dimethylquinoline no reaction occurs under the conditions employed by Sachs, and at a higher temperature or pressure the nitroso-amines are converted into nitroso-phenols, no reaction being observed with either the methyl- or dimethyl-quinoline.

But on boiling a mixture of 5-methylacridine with *p*-nitrosodimethylaniline in alcoholic solution with a small proportion of soda, condensation occurs in a manner analogous to that observed by Sachs. The product possesses all the properties of the azomethines, and, on decomposition with hydrochloric acid, gives 5-aldehydoacridine pure and in good yield.

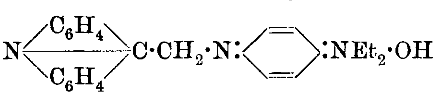
When *p*-nitrosodiethylaniline is used in place of *p*-nitrosodimethylaniline, 5-methylacridine yields two products: (1) the azomethine compound (annexed formula): (2) a compound, $C_{24}H_{25}ON_3$, forming orange-yellow needles, m. p. 210°. Assuming that this compound is formed by condensation of 5-methylacridine and *p*-nitrosodiethylaniline without separation of water, that is, in the same manner as 5-methylacridine condenses with an aldehyde, it would have the structure (I); or, if the nitroso-compounds of amines and phenols be regarded as quinoneoximes and substituted quinoneimides, it would be represented by (II).



$N\begin{matrix}C_6H_4\\C_6H_4\end{matrix}C\cdot CH{:}N\cdot C_6H_4\cdot NMe_2$



$N\begin{matrix}C_6H_4\\C_6H_4\end{matrix}C\cdot CH_2\cdot N(OH)\cdot C_6H_4\cdot NEt_2$ (I.)

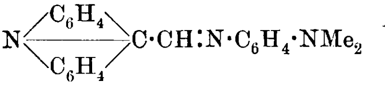


$N\begin{matrix}C_6H_4\\C_6H_4\end{matrix}C\cdot CH_2\cdot N{:}C_6H_4{:}NEt_2\cdot OH$ (II.)

The orange-yellow colour of the compound agrees better with the quinonoid formula (II) than with that (I) containing no chromophore-group, since the acridine series yields coloured compounds only on the introduction of auxochrome groups in the *p*-position to the central carbon atom. Attempts to remove the elements of water from this compound by means of various dehydrating agents were unsuccessful.

The conclusion is drawn that 5-methylacridine forms an exception to Sachs' rule.

4-*Dimethylaminophenylazomethine*-5-*acridine* (annexed formula), obtained from 5-methylacridine and *p*-nitrosodimethylaniline, forms dark red crystals, m. p. 231—232°.



4-*Diethylaminophenylazomethine*-5-*acridine*, $C_{24}H_{23}N_3$, forms dark red, almost black plates, m. p. 184°, and has the normal molecular weight in boiling benzene.

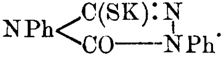
5-Aldehydoacridine (compare Bernthsen and Muhlert, Abstr., 1887, 849) crystallises in shining yellow needles, m. p. 145—146°. The hydrochloride, greenish-brown prisms, and the sulphate,

$$(C_{14}H_9ON)_2,H_2SO_4,$$

small, yellowish-green needles, were prepared. T. H. P.

Carbamide Derivatives of Phenylhydrazine. MAX BUSCH and OTTO LIMPACH (*Ber*, 1911, 44, 1573—1583. Compare this vol. i, 334).—Monothiodicarbamides of type (I) $NHR{\cdot}CS{\cdot}NR{\cdot}NH{\cdot}CO{\cdot}NHR$ are readily obtained from *a*-thiosemicarbazides, $NHR{\cdot}CS{\cdot}NR{\cdot}NH_2$, and carbimides, whilst the isomerides of type

$$\text{(II) } NHR{\cdot}CO{\cdot}NR{\cdot}NH{\cdot}CS{\cdot}NHR$$

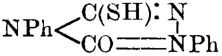
are prepared from *a*-semicarbazides and *iso*thiocarbamides, or, less easily, from *β*-thiosemicarbazides and carbimides. The two isomerides differ especially in that the thiocarbamyl residue is only very loosely bound to the *a*-nitrogen atom of the hydrazine (type I), and is eliminated on fusion or on boiling with alcohol, whereas the *β*-thiocarbamide (type II) is completely stable. Phenylated derivatives of type (I) are not affected by boiling with alcoholic potassium hydroxide, but those of type (II) lose aniline and undergo a ring condensation to 1 : 4-diphenyltriazolone-3-thiol, 

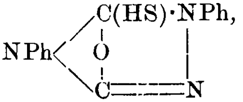
Attempts to introduce a second thiocarbimide residue into *a*-diphenylthiosemicarbazide gave *β*-diphenylthiosemicarbazide as the chief product. Addition of thiocarbimide to the *β*-nitrogen first takes place, but at the same time the group attached to the *a*-nitrogen is eliminated.

At higher temperatures phenylthiocarbimide reacts with *a*- or *β*-diphenylthiosemicarbazides, liberating hydrogen sulphide, and forming phenylanilinothiodiazolone anil.

By the action of ethyl chlorocarboxylate on *a*-diphenylthiosemicarbazide, *a-ethyl thiosemicarbazidecarboxylate* (III),

$$NHPh{\cdot}CS{\cdot}NPh{\cdot}NH{\cdot}CO_2Et,$$

is obtained, together with the isomeride (IV), $CO_2Et{\cdot}NPh{\cdot}NH{\cdot}CS{\cdot}NPh$, which is also formed in quantity from *β*-diphenylthiosemicarbazide and ethyl chlorocarboxylate. Both esters are condensed by alcoholic potassium hydroxide to triazole derivatives. The former yields 5-thiol 1 : 4-diphenyl*endo*oxydihydrotriazole (V) (annexed formula) (compare Busch and Grohmann, Abstr., 1901, i, 616); the latter gives rise to 3-thiol-1:4-diphenyltriazolone,  (VI).



This triazole (V) is readily obtained directly from ethyl phenylcarbazinate and phenylthiocarbimide in alcoholic potash. It is remarkable that some proportion of ethyl β-thiosemicarbazidecarboxylate (IV) is formed at the same time, and it is considered that in this reaction the carbethoxy-group wanders from the β- to the α-nitrogen atom of the hydrazine. Such change could not be observed in ethyl α-thiosemicarbazidecarboxylate under the influence of alcoholic potassium hydroxide.

α-Thiocarbanilido-β-carbanilidophenylhydrazine,

$$NHPh\cdot CS\cdot NPh\cdot NH\cdot CO\cdot NHPh,$$

crystallises in colourless needles, m. p. 164°. As directly prepared it contains traces of a sulphur-free substance separating in slender, colourless needles, m. p. 214—215°, and also some 3-thiol-1 : 4-diphenyltriazolone, m. p. 135°, derived from the isomeric dicarbamide.

α-Carbanilido-β-thiocarbanilidophenylhydrazine,

$$NHPh\cdot CO\cdot NPh\cdot NH\cdot CS\cdot NHPh,$$

crystallises in slender, matted needles, m. p. 178—179.

α-Thiocarbanilido-β-carbanilido-o-*tolylhydrazine* crystallises in colourless needles, m. p. 181°; the corresponding p-*tolylhydrazine* compound has m. p. 174°. Neither substance contains any quantity of the β-isomeride.

Ethyl βδ-diphenylthiosemicarbazide-α-carboxylate,

$$NHPh\cdot CS\cdot NPh\cdot NH\cdot CO_2Et,$$

from α-diphenylthiosemicarbazide, has m. p. 146° (compare Busch and Grohmann, *loc. cit.*). The isomeric *ethyl αδ-diphenylthiosemicarbazide-α-carboxylate* from the β-isomeride separates in short leaflets, m. p. 175—176°. E. F. A.

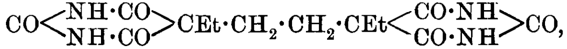
Preparation of Dialkylethylenedibarbituric Acids. ALBERT WOLFF (D.R.-P. 233968).—It is found that ethyl dialkylbutanetetracarboxylates of the general formula $CR(CO_2Et)_2\cdot CH_2\cdot CH_2\cdot CR(CO_2Et)_2$ react under pressure with carbamide in the presence of alkali alcoholates.

The following compounds are described :

Ethyl dipropylbutanetetracarboxylate, plates, m. p. 103—104°.

Ethyl dibenzylbutanetetracarboxylate, m. p. 124—125°.

Diethylethylenedibarbituric acid,



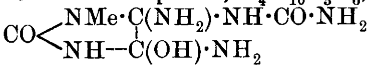
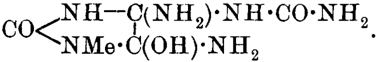
$$CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CEt\cdot CH_2\cdot CH_2\cdot CEt<\begin{matrix}CO\cdot NH\\CO\cdot NH\end{matrix}>CO,$$

colourless crystals, not melting below 300°, is prepared in 55% yield from ethyl diethylbutanetetracarboxylate, carbamide, and sodium ethoxide.

Dipropylethylenedibarbituric acid has similar properties, and is obtained in 70% yield. F. M. G. M.

Quadriurates. II. RUDOLF KOHLER (*Zeitsch. physiol. Chem.*, 1911, 72, 169—186. Compare this vol., i, 243).—A study of the solubility of uric acid in solutions of acid urates was based on the assumption that if quadriurates are formed, the solubility must be greater than in pure water, but smaller, on the other hand, if the quadriurates do not exist. Actually the solubility of uric acid decreases in presence of urates, the values agreeing with those calculated when care is taken to prevent the absorption of carbon dioxide from the air. The conclusion is drawn that quadriurates are in reality mixtures of uric acid and acid urate. E. F. A.

Oxidation of 3- and 7-Methyluric Acids in the Presence of Ammonia.

Oskar Grohmann (*Annalen*, 1911, **382**, 62—81. Compare Denicke, Abstr., 1906, i, 938).—The two methyl acids have been oxidised by potassium ferricyanide in the presence of concentrated ammonium hydroxide. By using 1 atom of oxygen for each molecule of acid, it was not found possible to isolate compounds corresponding with iminoallantoin; as a rule, a portion of the acid was unacted on, and another portion more completely oxidised. From 7-methyluric acid a small amount of β-methylallantoin was obtained, but the same product is formed in the absence of ammonia. The *compound*, $C_5H_{12}O_3N_6$, is formed from the two acids when $1\frac{1}{2}$ or 2 atoms of oxygen are used: $C_6H_6O_3N_4 + 2NH_3 + 2O = C_5H_{12}O_3N_6 + CO_2$. In addition a number of other products are formed, but these appear to be mainly decomposition products of the compound $C_5H_{12}O_3N_6$, which is presumably a methyl derivative of Denicke's compound, $C_4H_{10}O_3N_6$, and is to be represented as  $\mathrm{CO}<\begin{matrix}\mathrm{NMe\cdot C(NH_2)\cdot NH\cdot CO\cdot NH_2}\\ \mathrm{NH—C(OH)\cdot NH_2}\end{matrix}$ or  $\mathrm{CO}<\begin{matrix}\mathrm{NH—C(NH_2)\cdot NH\cdot CO\cdot NH_2}\\ \mathrm{NMe\cdot C(OH)\cdot NH_2}\end{matrix}$. It crystallises from warm water in glistening, six-sided prisms, decomposing at 185—187°. It does not give the murexide reaction, and is transformed into resinous substances by concentrated mineral acids. When boiled with water for some time, ammonia is evolved, and carbamide, an amorphous substance, and an ammonium salt, $C_5H_{13}O_5N_5$, are formed. The amorphous substance, when crystallised from water, yields ammonium oxalate. The *ammonium* salt, $C_5H_{13}O_5N_5$, crystallises from dilute alcohol in monoclinic, six-sided prisms, decomposing at 180—182°. The corresponding *silver* salt crystallises from water in glistening plates, decomposing at 204° after turning dark-coloured at 190°. Treatment of the ammonium salt with hydrochloric acid yields methyloxaluric acid (Breusing, *Annalen*, 1902, **323**, 167), carbamide, and ammonium chloride:

$$C_5H_{13}O_5N_5 + HCl \longrightarrow C_4H_6O_4N_2 + CON_2H_4 + NH_4Cl,$$

and attempts to synthesise the ammonium salt from oxaluric acid, carbamide, and ammonia were unsuccessful.

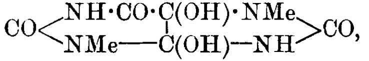
The compound $C_5H_{12}O_3N_6$, when warmed for fifteen minutes on the water-bath with 10% hydrochloric acid, yields methylparabanic acid, carbamide, and ammonium chloride: $C_5H_{12}O_3N_6 + H_2O + 2HCl \longrightarrow C_4H_4O_3N_2 + CON_2H_4 + NH_4Cl$, and when boiled with dilute potassium hydroxide solution the compound is completely decomposed into ammonia and oxalic acid. When, however, the compound is warmed with 2*N*-potassium hydroxide solution until dissolved, and then cooled and neutralised with 10% sulphuric acid, a *compound*, $C_5H_{10}O_5N_4$, decomposing at 185—190°, is obtained in the form of slender, felted needles.

In one experiment on the oxidation of the 7-methyl acid, a sparingly soluble *sodium* salt, $C_5H_6O_6N_2Na_2$, was obtained from the mother liquor on the addition of sodium hydroxide.

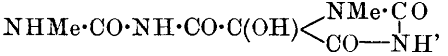
The 3-methyl acid yields a stiff jelly with ammonium hydroxide solution, and its oxidation is most readily effected by adding a suspension of the acid in potassium ferrocyanide solution to concentrated ammonium hydroxide kept at 0°. J. J. S.

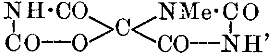
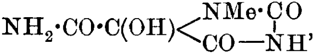
Caffolide Degradation of 3:7-Dimethyluric Acid and of Theobromine.

HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1911, 44, 1524—1532).—By the oxidation of theobromine by potassium chlorate and dilute hydrochloric acid at 40—50°, Clemm obtained "hydroxy-3:7-dimethyluric acid," which is converted into a more soluble isomeride by warm water (Abstr., 1898, i, 539). The former is now shown to be 3:7-dimethyluric acid 4:5-diglycol,



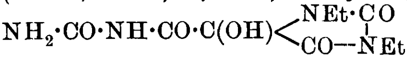
$$\mathrm{CO}<\begin{array}{l}\mathrm{NH\cdot CO\cdot C(OH)\cdot NMe}\\ \mathrm{NMe\text{——}C(OH)\text{—}NH}\end{array}>\mathrm{CO},$$

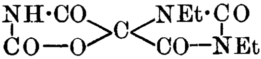
and the more soluble isomeride to be 5-hydroxy-1:9-dimethylhydantoylcarbamide,  $\mathrm{NHMe\cdot CO\cdot NH\cdot CO\cdot C(OH)}<\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{CO\text{—}NH}\end{array}$, by their degradation successively into 1-methylcaffolide and 5-hydroxy-1-methylhydantoylamide. Since 3:7-dimethyluric acid 4:5-diglycol can be obtained from 8-chlorotheobromine, which itself is prepared by the chlorination of 3:7-dimethyluric acid, the preceding degradation is the third example of the complete caffolide degradation of a uric acid (compare Abstr., 1910, i, 521; following abstract).

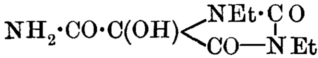
3:7-Dimethyluric acid 4:5-diglycol is obtained in 50—70% yield (as against Clemm's 10%) by passing a very rapid current of chlorine through a mixture of theobromine (not more than 10 grams) and glacial acetic acid containing rather more than the theoretical amount of water, the temperature being kept at about 40°. 8-Chlorotheobromine, which is conveniently obtained by rapidly chlorinating a suspension of theobromine in chloroform at the ordinary temperature, is also converted by the same treatment into 3:7-dimethyluric acid 4:5-diglycol, 8-chlorotheobromine 4:5-dichloride probably being formed as an intermediate product. The conversion of 3:7-dimethyluric acid 4:5-diglycol into 5-hydroxy-1:9-dimethylhydantoylcarbamide is simply effected by evaporating its aqueous solution on the water-bath. A mixture of the carbamide and ethyl acetate is saturated with hydrogen chloride at 0°, whereby methylamine hydrochloride and 1-*methylcaffolide*,  $\begin{array}{l}\mathrm{NH\cdot CO}\\ \mathrm{CO\text{—}O}\end{array}>\mathrm{C}<\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{CO\text{—}NH}\end{array}$, m. p. 218—219° (decomp.), are obtained. The latter, which can be converted through its *silver* derivatives into *allo*caffeine (1:3:7-trimethylcaffolide, Abstr., 1910, i, 522), is decomposed by boiling water into carbon dioxide and 5-*hydroxy*-1-*methylhydantoylamide*,  $\mathrm{NH_2\cdot CO\cdot C(OH)}<\begin{array}{l}\mathrm{NMe\cdot CO}\\ \mathrm{CO\text{—}NH}\end{array}$, m. p. 203—205° (decomp.), which is oxidised by potassium dichromate and boiling dilute sulphuric acid to methylparabanic acid. C. S.

Caffolide Degradation of 7 : 9-Diethyluric Acid 4 : 5-Diglycol.

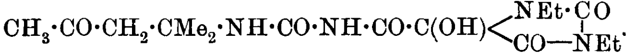
HEINRICH BILTZ and ERNST TOPP (*Ber.*, 1911, **44**, 1511—1523).—7 : 9-Diethyluric acid 4 : 5-diglycol has been converted successively into the following substances by reactions similar in the main to those recorded in the case of 7 : 9-dimethyluric acid 4 : 5-diglycol (Abstr., 1910, i, 521): 5-*hydroxy*-1 : 3-*diethylhydantoylcarbamide*,


$NH_2\cdot CO\cdot NH\cdot CO\cdot C(OH)<\begin{matrix}NEt\cdot CO\\ CO—NEt\end{matrix}$, m. p. 144—146° (decomp.); 1 : 3-*diethylcaffolide*,


$\begin{matrix}NH\cdot CO\\ CO—O\end{matrix}>C<\begin{matrix}NEt\cdot CO\\ CO—NEt\end{matrix}$, m. p. 123—124°; 5-*hydroxy*-1 : 3-*diethylhydantoylamide*,

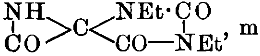

$NH_2\cdot CO\cdot C(OH)<\begin{matrix}NEt\cdot CO\\ CO—NEt\end{matrix}$, m. p. 180—182°. The last compound forms an O-*acetyl* derivative, m. p. 157—159°, an O-*ethyl ether*, m. p. 128—129° (which is obtained better from 5-hydroxy-1 : 3-diethylhydantoylcarbamide and alcoholic hydrogen chloride), and an O-*methyl ether*, m. p. 115—117°, and is hydrolysed by aqueous barium hydroxide on the water-bath, yielding ammonia, mesoxalic acid, and *s*-diethylcarbamide; it is remarkably stable to oxidising agents, being unattacked by potassium dichromate and sulphuric acid, except after heating on the water-bath for five hours, whereby diethylparabanic acid is produced. Hydroxydiethylhydantoylamide is also unchanged by 3% or 10% hydrogen peroxide and aqueous ammonia, but, after being kept for four weeks with 30% hydrogen peroxide and a little ammonia, is converted into diethyloxamide.

5-Hydroxy-1 : 3-diethylhydantoylcarbamide reacts with warm acetone to form a *substance*, $(C_{15}H_{24}O_6N_4)_2$, m. p. 127—128° (decomp.), which yields an odour of diacetoneamine with sodium hydroxide, does not lose ammonia by treatment with hydrogen chloride, and is oxidised by potassium dichromate and sulphuric acid to 5-hydroxy-1 : 3-diethylhydantoylamide; probably it has the constitution:


$$CH_3\cdot CO\cdot CH_2\cdot CMe_2\cdot NH\cdot CO\cdot NH\cdot CO\cdot C(OH)<\begin{matrix}NEt\cdot CO\\ CO—NEt\end{matrix}.$$

The *silver* derivative of 1 : 3-diethylcaffolide is converted by ethyl iodide into 1 : 3 : 7-*triethylcaffolide*, $C_{11}H_{15}O_5N_3$, b. p. 155°/15 mm., which has not been obtained pure.

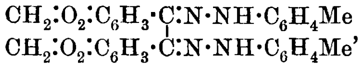
At 200° 1 : 3-diethylcaffolide loses carbon dioxide (1 mol.), and is converted into the *lactamide* of 5-hydroxy-1 : 3-diethylhydantoin-5-carboxylic acid,

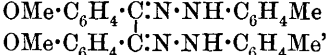

$\begin{matrix}NH\\ CO\end{matrix}>C<\begin{matrix}NEt\cdot CO\\ CO—NEt\end{matrix}$, m. p. 280—290° (decomp.); the lactamide from 1 : 3-dimethylcaffolide (*loc. cit.*) is constituted similarly.

C. S.

Preparation and Phototropy of Certain Osazones. II.

MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 675—680. Compare Abstr., 1910, i, 779).—β-*Benzil*-m-*tolylosazone*, $C_2Ph_2(:N\cdot NH\cdot C_6H_4Me)_2$, forms canary-yellow needles, m. p. 163°, and is feebly phototropic.

β-Piperil-m-*tolylosazone*,  $\begin{array}{l} CH_2{:}O_2{:}C_6H_3{\cdot}C{:}N{\cdot}NH{\cdot}C_6H_4Me \\ CH_2{:}O_2{:}C_6H_3{\cdot}C{:}N{\cdot}NH{\cdot}C_6H_4Me \end{array}$, forms dark yellow needles, m. p. 187°, and is phototropic.

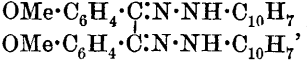
β-Anisil-m-*tolylosazone*,  $\begin{array}{l} OMe{\cdot}C_6H_4{\cdot}C{:}N{\cdot}NH{\cdot}C_6H_4Me \\ OMe{\cdot}C_6H_4{\cdot}C{:}N{\cdot}NH{\cdot}C_6H_4Me \end{array}$, crystallises in pale yellow scales, m. p. 150·5°, and is phototropic.

β-Piperil-β-naphthylhydrazone,

$$CH_2{:}O_2{:}C_6H_3{\cdot}CO{\cdot}C({\cdot}C_6H_3{:}O_2{:}CH_2){:}N{\cdot}NH{\cdot}C_{10}H_7,$$

forms a yellow, crystalline powder, m. p. 162°, and becomes darker on exposure to sunlight, but it cannot be stated with certainty that this is a phototropic change, since there is no apparent retrocession in the dark.

β-Piperil-β-naphthylosazone (*loc. cit.*) forms an *additive* compound with chloroform, $C_{36}H_{26}O_4N_4,CHCl_3$, which is obtained in yellow crystals, m. p. 80° (decomp.), and is non-phototropic.

β-Anisil-β-naphthylosazone,  $\begin{array}{l} OMe{\cdot}C_6H_4{\cdot}C{:}N{\cdot}NH{\cdot}C_{10}H_7 \\ OMe{\cdot}C_6H_4{\cdot}C{:}N{\cdot}NH{\cdot}C_{10}H_7 \end{array}$, forms stellar aggregates of pale yellow needles, m. p. 165—169°, and exhibits phototropy. It forms a non-phototropic *additive* compound with benzene (1 mol.), in white needles, m. p. 155—158°.

β-Anisil-o-*tolylosazone* forms non-phototropic, dark orange-yellow crystals, m. p. 168°.

β-Anisil-p-*tolylosazone* forms a pale yellow, phototropic powder, m. p. 153°, and gives a non-phototropic *additive* compound with benzene (1 mol.), m. p. 166°. T. H. P.

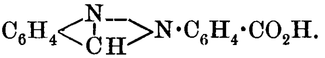
o-o′-**Azoxybenzaldehyde.** EUGEN BAMBERGER (*Ber.*, 1911, **44**, 1966—1979).—The *diethyl acetal* of *o-o′*-azoxybenzaldehyde,

$$ON_2[C_6H_4{\cdot}CH(OEt)_2]_2,$$

prepared by the reduction of *o*-nitrobenzaldehydediethylacetal (*p*-nitro-ωω-diethoxytoluene) with methyl alcoholic sodium methoxide, crystallises in colourless prisms, m. p. 76·5°. On hydrolysis with dilute hydrochloric acid in acetic acid solution, it yields *o-o′*-azoxybenzaldehyde.

o-o′-*Azoxybenzaldehydedimethylacetal*, $C_{18}H_{22}O_5N_2$, prepared in a similar manner to the ethyl derivative, crystallises in colourless plates, m. p. 58·5—59·5°.

When heated with aqueous sodium hydroxide, *o-o′*-azoxybenzaldehyde yields 3-hydroxy-*o*-indazylbenzoic acid. Owing to the transformation into the lactone, this has a variable m. p., depending on the method of heating. When immersed in a bath at 270°, it partly melts, then solidifies, and finally melts again at 299—300° (compare Carré, Abstr., 1906, i, 705). It yields a crystalline *hydrochloride*, which is readily hydrolysed by water. When distilled over hot zinc dust and calcium carbonate, it gives aniline and phenazine. When oxidised with chromium trioxide in glacial acetic acid solution, it yields *o-o′*-azobenzoic acid, and, when warmed with glacial acetic acid or mineral acids, it is converted into the corresponding lactone.

o-o′-Azoxybenzaldehyde, on treatment with warm glacial acetic acid, yields 3-hydroxy-*o*-indazylbenzoic acid and its lactone, together with *o-indazylbenzoic acid*,  $C_6H_4{<}\overset{N}{\underset{CH}{|}}{>}N\cdot C_6H_4\cdot CO_2H$. The latter compound, which has also been prepared by reducing Pawlewski's *N*-*o*-nitrobenzylanthranilic acid (Abstr., 1904, i, 316) with hydrochloric acid and tin in boiling alcoholic solution, crystallises in lustrous, colourless leaves, m. p. 207·5—208·5°.

The transformation of *o*-*o'*-azoxybenzaldehyde into 3-hydroxy-*o*-indazylbenzoic acid and its lactone is also effected by exposure to light.

F. B.

Diazonium Sulphinates. MAX CLAASZ (*Ber.*, 1911, 44, 1415—1419).

—Previous attempts to prepare diazonium sulphinates by von Pechmann and Hantzsch have proved unsuccessful, but it is shown that such compounds can be prepared if the sulphinic acid contains negative substituents.

o-*Nitrobenzenediazonium* o-*nitrobenzenesulphinate*,

$$NO_2\cdot C_6H_4\cdot N(\vdots N)\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

prepared by adding a diazotised solution of *o*-nitroaniline to an aqueous solution of sodium *o*-nitrobenzenesulphinate (this vol., i, 437), forms yellow crystals, and has most of the properties characteristic of diazonium salts. It explodes at about 100°, and when boiled with water yields *di*-o-*nitrobenzenesulphone*, $SO_2(C_6H_4\cdot NO_2)_2$, m. p. 164°. In alcoholic solution the sulphinate has $\mu_{1000}^{18°} = 1\cdot538$.

Sulphur dioxide reacts with a diazotised solution of *o*-nitroaniline, yielding *di*-o-*nitrophenylsulphohydrazide*,

$$NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

which crystallises from ethyl alcohol in glistening, brown plates, decomposing at 153—155°. Its solutions in alkalis have a blood-red colour, and it reduces hot Fehling's solution. The same product can be obtained by condensing *o*-nitrophenylhydrazine with *o*-nitrobenzenesulphonyl chloride in alcoholic solution. When alkali is used, the products are potassium *o*-nitrobenzenesulphonate and azimidole. When oxidised with lead peroxide in the presence of acetone, the hydrazide yields *di*-o-*nitrobenzenediazosulphone*,

$$NO_2\cdot C_6H_4\cdot N\colon N\cdot SO_2\cdot C_6H_4\cdot NO_2,$$

a compound isomeric with the diazonium sulphinate. It crystallises from glacial acetic acid in yellow, flocculent masses, decomposing at 145°, is not explosive, and does not couple with β-naphthol.

J. J. S.

Theory of the Action of Inorganic Salts on Proteins in Solution. T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1911, 9, 303—326).

—The author discusses the general questions of the precipitation and coagulation of proteins. The latter term is used when a large quantity of precipitating agent is required, and it takes place even when the protein is in the non-ionic state. The precipitating agent may or may not undergo decomposition during the process.

It is suggested that the high acid and alkali combining capacities of the proteins are not to be attributed to terminal amino- and carboxylic groups, but rather to the $-CO\cdot NH-$ or $-C(OH)\colon N-$ groups present. In the latter form the group can react with acid in the following manner:

$-C(OH){:}N- + H^{\cdot} + Cl' = -C(OH)^{\cdot\cdot} + {\genfrac{}{}{0pt}{}{H}{Cl}}{>}N''-$, and with alkali as follows: $-C(OH){:}N- + Na^{\cdot} + OH' = -C(ONa)^{\cdot\cdot} + {\genfrac{}{}{0pt}{}{H}{HO}}{>}N''-$, and in each case only protein ions are formed. The following arguments are brought forward. (1) The compounds of proteins with acids and alkalis are excellent conductors in aqueous solution, and yet do not yield the ordinary ionic reactions, for example, a compound with hydrochloric acid does not yield chloride ions, and the equivalent conductivities at infinite dilution point to the presence of bulky organic ions. (2) Edestin is capable of displacing sodium hydroxide from its combination with hydrochloric acid, and casein can displace carbonic acid from its combination with calcium hydroxide, and yet edestin is not a strong base. The compounds do not undergo hydrolysis when diluted, and this is attributed to the fact that water does not enter into the equations given above (compare also Abstr., 1910, ii, 679). (3) Each equivalent of a mono-acid base neutralised by casein or serum-globulin yields two equivalents of protein salt, whereas if the neutralisation were effected by means of a carboxyl group each equivalent of the base would produce an equivalent of salt. (4) The osmotic pressure and depression of freezing point of casein increase in geometrical and not in arithmetical proportion on the addition of one, two, and three equivalents of a base. (5) According to Vernon (Abstr., 1904, ii, 626) the non-hydrolysed protein has nearly the same combining capacity for acid or alkali as the sum of its hydrolytic products.

It is suggested that the action of salts on the compounds of proteins with acids and alkalis is a dehydrating process, and various experiments in support of this suggestion are cited. The process of precipitation (as distinguished from coagulation) is represented by means of equations of the types:

$$-C(OK)^{\cdot\cdot} + OH{\cdot}NH''- + KCl = -C(OK){\cdot}\underset{|}{N}{<}{\genfrac{}{}{0pt}{}{K}{Cl}} + H_2O \text{ and}$$

$$-C(OH)^{\cdot\cdot} + Cl{\cdot}NH''- + 2KCl = -C(OK){\cdot}\underset{|}{N}KCl + 2HCl;$$

the product $-C(OK){\cdot}\underset{|}{N}KCl$ tends to undergo hydrolysis in the presence of water, yielding $-C(OK){\cdot}\underset{|}{N}HCl$, which is very sparingly soluble, and the formation of this results in precipitation. In the presence of a greater concentration of salt or of some other dehydrating agent, the hydrolysis is stopped, and hence no precipitation occurs. In the presence of still further amounts of dehydrating agents or on heating, the terminal amino- and carboxyl groups of the protein molecules react, yielding water and anhydrides which are usually insoluble, and thus coagulation is brought about. J. J. S.

Sulphur in Proteins. Thiopolypeptides. TREAT B. JOHNSON and GERALD BURNHAM (*J. Biol. Chem.*, 1911, 9, 331—332).—It is suggested that the sulphur present in proteins may be present in groups similar to those in which the oxygen is usually found, namely, $-SH$ and $-CS-NH-$. Cystein represents a compound containing the thiol group, but hitherto compounds with the $-CS{\cdot}NH-$ group have not been isolated. Several compounds of this type and their derivatives have been prepared, and are being investigated. J. J. S.

The Isoelectric Point of Genuine and Denaturated Serum-Albumin. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, **33**, 456—473).—The authors employed with small modifications the methods already described, and found that the coagulation optimum point for denaturated albumin was $0{\cdot}4 \times 10^{-5}$. The same isoelectric point was found by the method of electro-cataphoresis. The isoelectric point for genuine albumin found by the latter method was 2×10^{-5}. The electrolyte content of the mixture (which varied between $N/10$- and $N/50$-sodium acetate) had no appreciable influence. From these results it was found that the relative acidity, k_a/k_b, of albumin falls during denaturation from $7{\cdot}10^4$ to $3{\cdot}10^3$. S. B. S.

Hydrolysis of Sodium "Iodeigon." ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **72**, 374—379. Compare Mosse and Neuberg, Abstr., 1903, ii, 496).—When sodium "iodeigon" is boiled with barium hydroxide solution, 96·5% of the iodine is eliminated as hydriodic acid within the first 4·5 hours. Non-crystallisable resins are also obtained, but no indication of di-iodotyrosine and no *o*-iodobenzoic acid. The behaviour of "iodeigon" towards hydrolysing agents is thus different from that of iodo-albacid (this vol., i, 203) and iodo-glidin (*ibid.*, 372). J. J. S.

Analysis of the Products of Hydrolysis of Wheat Gliadin. THOMAS B. OSBORNE and H. H. GUEST (*J. Biol. Chem.*, 1911, **9**, 425—438).—Owing to improved methods, it appeared desirable to undertake a fresh investigation of gliadin, a protein much used in nutrition experiments. Analytical results are given in full, in reference to the partition of nitrogen, the yield of amino-acids, and these results are compared with those in other proteins. The total yield of amino-acids amounted to 83·54% of the original protein, and the deficit is probably due to losses incurred in estimating those amino-acids which are obtained from their esters. W. D. H.

A New Decomposition Product of Keratin which gives Millon's Reaction. ROSS A. GORTNER (*J. Biol. Chem.*, 1911, **9**, 355—357).—A positive reaction with Millon's reagent in a protein is generally taken as evidence of the presence of tyrosine. It is, however, shown that in a melano-protein prepared from black wool after hydrolysis yielded, not only tyrosine, but there was in the mother liquor a substance which still gave Millon's reaction with great intensity. This substance is evidently an aromatic phenolic material, but it has not yet been identified. W. D. H.

The Laws of Enzyme Action. P. VON GRÜTZNER [with W. WALDSCHMIDT] (*Pflüger's Archiv*, 1911, **141**, 63—117).—Experiments showed that, under similar conditions, the amount of protein or gelatin digested is in direct linear proportion to the quantity of enzyme present. This applies to experiments with pepsin, trypsin, and ptyalin when the time occupied is short; if prolonged, this law no longer holds, but the rate of change conforms to Schütz' law, and this finally ceases to apply. The retardation of change is greater in the case of high concentration of enzyme.

When equal amounts of change are allowed to take place, the velocity of change is in direct proportion to the amount of enzyme. If the substrate be increased, there ensues in the case of pepsin (less in the case of ptyalin) a reduction in the rate of change. On the other hand, under similar conditions, the higher concentrations of trypsin digest at a proportionately greater rate than the lower concentrations.

The view is expressed that no single law can be applied to the whole course of enzymic change. H. B. H.

The Digestibility of White of Egg as Influenced by the Temperature at which it is Coagulated. PHILIP FRANK (*J. Biol. Chem.*, 1911, **9**, 463—470).—The Mett tube method is regarded as untrustworthy, owing to the inclusion of air bubbles, the setting of the albumin in the tubes in uneven layers, and to the fact that the digestibility of the egg-white varies according to the temperature used in producing coagulation. The last factor is regarded as very important and is treated at length. W. D. H.

The Identity of Pepsin and Rennet. AGNES ELLEN PORTER (*J. Physiol.*, 1911, **42**, 389—401).—Several commercial preparations of rennet were found to be milk curdling, but non-peptic, or were antipeptic. The antipeptic material is indifferent to rennet, and can be removed by dialysis. A rennet zymoid occurred spontaneously, which was indifferent to pepsin. The results are in favour of the view that the two enzymes are not identical. W. D. H.

Nucleases. II. PHŒBUS A. LEVENE and FLORENTIN MEDIGRECEANU (*J. Biol. Chem.*, 1911, **9**, 389—402).—That the final oxidation, etc., of purine bases is due to the graded action of specific enzymes has been established by Walter Jones and Schittenhelm, and is confirmed by the present experiments. The so-called nucleases really include three groups of enzymes. These may be designated: (1) *Nucleinases*, which resolve the molecule into mono-nucleotides; such an enzyme occurs in all organs, and in pancreatic juice, but not in gastric juice. (2) *Nucleotidases*, which liberate phosphoric acid, leaving the carbohydrate base complexes (nucleosides) intact. They are present in all organs, juices, and in intestinal juice, but are absent from gastric and pancreatic juices. There are probably specific enzymes to deal with each nucleotide. (3) *Nucleosidases* are the enzymes which cleave hydrolytically the nucleosides into their components, the carbohydrate ribose, and their bases of the purine or pyrimidine groups. These are absent in all the digestive juices and in the plasma of the pancreas, but are present in the plasmata of most other organs. W. D. H.

The Inhibition of the Action of Invertase. ANSELM ERIKSSON (*Zeitsch. physiol. Chem.*, 1911, **72**, 313—338).—Invertase can be removed wholly or in part from its solutions by charcoal. The removal, and in this way the inhibition, of its action is greater if the charcoal is added before the mixing of the enzyme and substrate than if it is added after the mixture has occurred. Time and temperature are other factors. Normal serum also inhibits the activity of invertase, and the order in which it is added is a factor, although not so great a one, as in the case of charcoal. Inhibiting substances occur also in the invertase solution itself; they are not destroyed by boiling, they diffuse very slowly through a membrane, and are not to any great extent absorbed by charcoal. W. D. H.

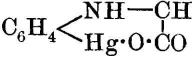
Synthesis of Mercuriated α-Anilino-fatty Acids. Walter Schoeller, Walther Schrauth, and Paul Goldacker (*Ber.*, 1911, **44**, 1300—1312). In order to determine the influence exerted by the amino-group on the introduction of mercury into the benzene nucleus, the authors have investigated the action of mercuric acetate on the ethyl esters of α-anilinoacetic acid and its homologues. It is found that the introduction of mercury proceeds more easily as the series is ascended. Whilst ethyl α-anilinoacetate forms only a mono-substitution product, the propionic ester reacts with mercuric acetate in equal molecular proportions, yielding a mixture of the mono- and di-substitution products. In the case of the butyric and *iso*valeric esters, only disubstituted products of the type

$$C_6H_3(Hg{\cdot}OAc)_2{\cdot}NH{\cdot}CHR{\cdot}CO_2Et$$

could be obtained.

Ethyl o-*acetoxymercurianilinoacetate*, $OAc{\cdot}Hg{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, prepared by the addition of aqueous mercuric acetate to a methyl alcoholic solution of ethyl anilinoacetate, forms small, tabular crystals, m. p. 132° (corr.), with previous softening at 129° (corr.). When shaken with bromine in aqueous potassium bromide, it yields *ethyl* o-*bromoanilinoacetate*, which crystallises in white needles, m. p. 82—83°; the corresponding o-*iodo*-compound forms greyish-white leaflets, m. p. 86—87°.

Ethyl o-*chloromercurianilinoacetate*, $HgCl{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2Et$, is obtained by the action of sodium chloride on the preceding acetoxymercuri-ester in aqueous alcoholic solution; it crystallises in needles or rhombic plates, m. p. 152·5° (corr.), with previous sintering at 150·5° (corr.). *Ethyl* o-*bromomercurianilinoacetate* forms rhombic plates, which sinter at 144°, and have m. p. 147·5° (corr.); the corresponding *iodo*-ester crystallises in lustrous leaflets, m. p. 139—140° (corr.), with previous sintering at 137—138° (corr.).

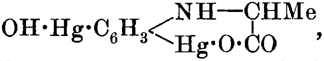
o-*Hydroxymercurianilinoacetic anhydride*, 

$C_6H_4<\begin{matrix}NH{-}CH_2\\ Hg{\cdot}O{\cdot}CO\end{matrix}$, prepared by hydrolysing the acetoxymercuri-ester with sodium hydroxide and acidifying the resulting solution, decomposes at 228° (corr.); the *copper* salt, $(HO{\cdot}Hg{\cdot}C_6H_4{\cdot}NH{\cdot}CH_2{\cdot}CO_2)_2Cu$, decomposes at 193—197° (corr.); the *lead*, *iron*, *calcium*, *silver*, *mercury*, and *platinum* salts are also mentioned.

Ethyl α-acetoxymercurianilinopropionate is obtained together with a small quantity of the diacetoxymercuri-ester by the reaction of equal molecular quantities of mercuric acetate and ethyl α-anilinopropionate, but since it could not be obtained free from the accompanying dimercuri-ester, it was converted by the action of sodium chloride into *ethyl α-chloromercurianilinopropionate*, $\mathrm{HgCl{\cdot}C_6H_4{\cdot}NH{\cdot}CHMe{\cdot}CO_2Et}$; this crystallises in microscopic needles, m. p. 165·5° (corr.).

Ethyl α-diacetoxymercurianilinopropionate,
$\mathrm{C_6H_3(Hg{\cdot}OAc)_2{\cdot}NH{\cdot}CHMe{\cdot}CO_2Et}$,
which crystallises in leaflets, m. p. 186° (corr.), is prepared by the interaction of mercuric acetate (2 mols.) and ethyl α-anilinopropionate (1 mol.) in aqueous methyl-alcoholic solution; a less soluble, apparently polymeric form is produced simultaneously. When treated with sodium chloride, it yields *ethyl α-dichloromercurianilinopropionate*, $\mathrm{C_{11}H_{13}O_2NCl_2Hg_2}$, which forms small needles, m. p. 131° (corr.), with previous softening at 128°; the corresponding *dibromomercuri*-ester crystallises in needles, m. p. 128·5° (corr.), with previous softening.

α-Dihydroxymercurianilinopropionic anhydride,

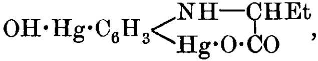


$$\mathrm{OH{\cdot}Hg{\cdot}C_6H_3}{<}\begin{array}{l}\mathrm{NH{-}CHMe}\\ \mathrm{Hg{\cdot}O{\cdot}CO}\end{array},$$

prepared from the diacetoxymercuri-ester by hydrolysis with aqueous sodium hydroxide, decomposes at 223° (corr.).

Ethyl α-diacetoxymercurianilinobutyrate,
$\mathrm{C_6H_3(Hg{\cdot}OAc)_2{\cdot}NH{\cdot}CHEt{\cdot}CO_2Et}$,
prepared from ethyl α-anilinobutyrate in the usual manner, crystallises in stout rods, sintering at 150°, m. p. 154·5° (corr.). On treatment with sodium chloride, it yields *ethyl α-dichloromercurianilinobutyrate*, $\mathrm{C_{12}H_{15}O_2NCl_2Hg_2}$, which forms slender needles, m. p. 127° (corr.), with previous softening at 125° (corr.); the corresponding *dibromo*-ester crystallises in needles, softening at 125° (corr.), m. p. 127° (corr.); the *di-iodo*-ester has m. p. 120° (corr.).

α-Dihydroxymercurianilinobutyric anhydride,



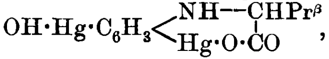
$$\mathrm{OH{\cdot}Hg{\cdot}C_6H_3}{<}\begin{array}{l}\mathrm{NH{-}CHEt}\\ \mathrm{Hg{\cdot}O{\cdot}CO}\end{array},$$

is obtained by hydrolysing the preceding diacetoxymercuri-ester; when heated, it becomes yellowish-brown at 200°, and decomposes at 209° (corr.); it readily takes up water on exposure to air, forming $\mathrm{C_{10}H_{13}O_4NHg_2}$.

*Ethyl α-diacetoxymercurianilino*iso*valerate*,
$\mathrm{C_6H_3(Hg{\cdot}OAc)_2{\cdot}NH{\cdot}CHPr^{\beta}{\cdot}CO_2Et}$,
prepare from ethyl α-anilino*iso*valerate and mercuric acetate, crystallises in tufts or stellar aggregates of needles, m. p. 126° (corr.).

*Ethyl α-dichloromercurianilino*iso*valerate*, $\mathrm{C_{13}H_{17}O_2NCl_2Hg_2}$, forms microscopic rods, m. p. 122° (corr.); the corresponding *dibromomercuri*-ester occurs in two forms: a granular, sandy, amorphous modification, which decomposes at 215° without melting, and is insoluble in ethyl acetate; and a soluble form crystallising in tufts of white needles, m. p. 135° (corr.); the *di-iodomercuri*-ester forms yellow needles, m. p. 129° (corr.).

*α-Dihydroxymercurianilino*iso*valeric anhydride*,



$$\mathrm{OH{\cdot}Hg{\cdot}C_6H_3}{<}\begin{array}{l}\mathrm{NH{-}CHPr^{\beta}}\\ \mathrm{Hg{\cdot}O{\cdot}CO}\end{array},$$

decomposes at 226° (corr.), and readily takes up water on exposure to air.

F. B.

Organic Chemistry.

The Grignard Reaction in its Application to Dihalogen Compounds. I. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, **44**, 1918—1931. Compare Abstr., 1907, i, 997; Zelinsky and Gutt, *ibid.*, 676; Grignard and Vignon, *ibid.*, 689).—The authors find that the interaction of magnesium with αδ-dibromobutane, αε-dibromopentane, αη-dibromoheptane, or ακ-di-iododecane yields only about half of the theoretical amount of the normal magnesium compound, $MgX\cdot[CH_2]_n\cdot MgX$, the remainder of the dihalogen derivative being converted into a mixture of magnesium compounds of the general formula $MgX\cdot[C_nH_{2n}]_x\cdot MgX$.

No evidence of the formation of cyclic or unsaturated hydrocarbons, or of magnesium compounds of the type $MgX\cdot[CH_2]_n\cdot Br$, was obtained.

The magnesium compound of αδ-dibromobutane reacts with carbon dioxide, yielding *cyclo*pentanone, sebacic acid, and dodecamethylenedicarboxylic acid.

When treated with water, the magnesium compound of αε-dibromopentane gave pentane, decane, pentadecane, and eicosane, together with still higher homologues.

The magnesium compound of αη-dibromoheptane, when similarly treated, yields a mixture of hydrocarbons, from which heptane and tetradecane were isolated; it reacts with carbon dioxide, yielding a mixture of acids, $CO_2H\cdot[CH_2]_{7n}\cdot CO_2H$, from which azelaic acid is separated by boiling it with water.

By decomposing the magnesium compound of ακ-di-iododecane with water, decane, eicosane and tetracontane were obtained; the action of carbon dioxide yields a mixture of the acids $CO_2H\cdot[CH_2]_{10n}\cdot CO_2H$, from which decane-ακ-dicarboxylic acid may be readily separated by extraction with hot water.

The magnesium compound of αε-dibromopentane reacts with acetone, yielding the following compounds: (1) β-methylheptan-β-ol (Muset, Abstr., 1907, i, 374), the formation of which takes place according to the scheme: $COMe_2 + MgBr\cdot[CH_2]_5\cdot MgBr \longrightarrow MgBr\cdot O\cdot CMe_2\cdot[CH_2]_5\cdot MgBr \xrightarrow{H_2O} OH\cdot CMe_2\cdot[CH_2]_5\cdot H$; (2) a *liquid*, $C_{11}H_{22}O$, b. p. 107—109°/14 mm., D_4^{20} 0·8467, n_D 1·45512, having an odour resembling citronellol, and consisting probably of a mixture of the unsaturated alcohols, $OH\cdot CMe_2\cdot[CH_2]_5\cdot CMe{:}CH_2$ and

$OH\cdot CMe_2\cdot[CH_2]_4\cdot CH{:}CMe_2$;

(3) *βι-dimethylnonan-βι-diol*, $OH\cdot CMe_2\cdot[CH_2]_5\cdot CMe_2\cdot OH$, which has b. p. 135—145°/12 mm., and readily solidifies to a white, crystalline mass, m. p. 77°.

βι-Dibromo-βι-dimethylnonane, $C_{11}H_{22}Br_2$, prepared by the action of hydrobromic acid on the preceding glycol in glacial acetic acid solution, is a viscid oil, which loses hydrogen bromide when heated with pyridine, and is converted into the unsaturated *hydrocarbon*,

$C_{11}H_{20}$, b. p. 180—185°, D_4^{20} 0·7759, n_D 1·4504; the latter compound yields an oily *tetrabromide*, and probably consists of a mixture of two or three structural isomerides.

By the interaction of trioxymethylene with the magnesium compound of αε-dibromopentane, the authors hoped to find a ready means of passing from the pentamethylene group to the heptamethylene group:

$$MgBr{\cdot}[CH_2]_5{\cdot}MgBr + 2CH_2O \longrightarrow OH{\cdot}CH_2{\cdot}[CH_2]_5{\cdot}CH_2{\cdot}OH.$$

Their hopes were, however, not realised, partly on account of the difficulty with which trioxymethylene enters into reaction, and partly because of the difficulty of isolating the easily soluble heptane-αη-glycol from the reaction product. F. B.

Attempted Preparation of Methylene Derivatives. HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1911, **44**, 2194—2197).—The authors have attempted in various ways to decompose substances such as tetrachloroethylene, tetraphenylethylene, benzyl chloride, benzylidene chloride, chlorodiphenylmethane, and ethyl orthoformate, in the hope of obtaining compounds containing a bivalent carbon atom attached to two other elements or to two carbon atoms. In every case, however, the result is negative, the methylene derivative, if formed temporarily, being converted by polymerisation into an ethylene derivative or by additive reactions into a derivative of methane. C. S.

Reduction and Oxidation by Catalysis. PAUL SABATIER (*Ber.*, 1911, **44**, 1984—2001).—A lecture before the German Chemical Society, summarising the author's experiments on the catalytic reduction of organic compounds by passing their vapours, mixed with hydrogen, through metallic tubes, especially nickel, at a temperature of about 180°. At 250° the same metals bring about a catalytic oxidation, for example, of alcohols to aldehydes or ketones. E. F. A.

Cyanopinacolin and Some Compounds Derived From It. OSKAR WIDMAN and ERIK WAHLBERG (*Ber.*, 1911, **44**, 2065—2071).—By the interaction of equivalent quantities of bromine and pinacolin, a mixture of bromo- and dibromo-pinacolin is obtained.

ω-*Bromopinacolin* is a colourless liquid, which attacks the skin and eyes, b. p. 77—78°/15 mm., 184—188°/760 mm., D^{17} 1·33.

ω-Dibromopinacolin has m. p. 75° (compare Scholl and Weil, *Chem. Zeit.*, 1899, **23**, 189).

The monobromide reacts with potassium cyanide, yielding ω-*cyanopinacolin* (tert.-*valerylacetonitrile*); this forms colourless, well-shaped crystals with many faces, and centimetre-long prisms, m. p. 68—68·5°. The *potassium* salt, $CMe_3{\cdot}C(OK){:}CH{\cdot}CN$, crystallises in colourless tablets.

The *hydrochloride* of tert.-*valerylacetimino-ether*,

$$CMe_3{\cdot}CO{\cdot}CH_2{\cdot}C(OEt){:}NH,HCl,$$

prepared by the action of hydrogen chloride on cyanopinacolin dissolved in a mixture of alcohol and ether, crystallises in large four- or six-sided prisms, m. p. 126—127° (decomp.) when quickly heated, or

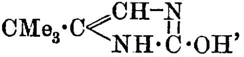
m. p. 131° (slowly heated). The *platinichloride* forms long, yellow needles, m. p. 135°.

tert.-*Valerylacetamide*, obtained on heating the imino-ether hydro chloride, crystallises in large, glistening plates, m. p. 95°.

Phthaliminopinacolin, prepared by heating bromopinacolin with potassium phthalimide in alcohol, crystallises in lustrous, stout, four-sided prisms with hemihedric faces, m. p. 102°.

Pinacolylphthalamic acid crystallises in well formed four- or six-sided plates or prisms, m. p. 132°.

Pinacolylamine, $CMe_3{\cdot}CO{\cdot}CH_2{\cdot}NH_2$, is obtained as *hydrochloride* on evaporating the phthalamic acid with hydrochloric acid; it is deliquescent. The base was characterised by warming with potassium cyanate and conversion into 2-*hydroxy*-5-tert.-*butylglyoxaline*,



$CMe_3{\cdot}C\Big<\begin{matrix}CH{-}N\\ \|\\ NH{\cdot}C{\cdot}OH\end{matrix}$, which separates in needles, m. p. 277—278°.

E. F. A.

Effect of Heating Mixed Esters of Carbonic Acid. Alfred Einhorn and Leo Rothlauf (*Annalen*, 1911, **382**, 237—265. Compare Einhorn, Abstr., 1909, i, 568).—The velocity with which mixed carbonic esters lose carbon dioxide and yield phenolic ethers depends largely on the nature of the alkyl group present. With common alkyl groups such as methyl and ethyl, the decomposition takes place slowly, but becomes more rapid when strongly basic substituents are present in the alkyl group. Attention is drawn to the fact that numerous isolated examples of this type of decomposition are recorded in chemical literature. The formation of esters of organic acids by the action of ethyl chlorocarbonate on sodium salts (R. and W. Otto, Abstr., 1888, 813; 1891, 288) is a reaction of a similar type; a mixed anhydride, $R{\cdot}CO{\cdot}O{\cdot}CO{\cdot}OEt$, is formed as an intermediate product, and decomposes into carbon dioxide and the ester. Similarly, the mixed anhydrides, formed by the action of the salts of aromatic acids on diphenylcarbamide chloride in the presence of pyridine, lose carbon dioxide and yield diphenylated acid amides (Herzog, Abstr., 1909, i, 568; Herzog and Hancu, 1908, i, 268). Acid anhydrides with catalysts yield ketones (Mailhe, Abstr., 1909, i, 692; compare Senderens, *ibid.*, 287), and by heating benzyl and *p*-nitrobenzyl esters of chlorocarbonic acid, benzyl chloride and *p*-nitrobenzyl chloride are formed (Thiele and Dent, Abstr., 1898, i, 15; compare also F. Hofmann, *Zeitsch. angew. Chem.*, 1908, **21**, 1986). Similarly, aldehydes when heated with carbonyl chloride yield carbon dioxide and the corresponding chloride.

Guaiacyl methyl carbonate, $OMe{\cdot}C_6H_4{\cdot}O{\cdot}CO_2Me$, obtained by the action of methyl chlorocarbonate on guaiacol in the presence of pyridine, has b. p. 132—134°/16 mm., and when heated at 234° and then at 218° yields guaiacol and catechol dimethyl ether, together with guaiacyl carbonate and unaltered guaiacyl methyl carbonate. Guaiacyl ethyl carbonate has b. p. 265°, and when boiled for seven days in a reflux apparatus yields guaiacol and its ethyl ether.

Resorcinyl diethyl dicarbonate, $C_6H_4(O{\cdot}CO_2Et)_2$, has b. p. 174—176°/19 mm. or 270—288° under atmospheric pressure (Wallach gives 298—302°). When boiled for twenty-eight hours it yields resorcinol mono- and di-ethyl ethers, and an insoluble product, probably a high molecular resorcinyl carbonate. *Resorcinyl ethyl carbonate*, $OH\cdot C_6H_4\cdot O\cdot CO_2Et$, when freed from resorcinol by digesting with water, crystallises from light petroleum in plates, m. p. 52—53°, b. p. 170—173°/11 mm. or 274° under atmospheric pressure, and when boiled for seven hours yields resorcinol monoethyl ether, resorcinyl carbonate, and resorcinol. By boiling β-naphthyl methyl carbonate for 46·5 hours, β-naphthol, its carbonate, and methyl ethers are obtained. Aryl-diethylaminoethyl carbonates can be prepared by the action of diethylaminoethanol on phenyl chlorocarbonates (D.R.-P. 118537) in benzene solution.

Guaiacyl chlorocarbonate (Barral and Morel, Abstr., 1899, i, 802) is best prepared by the action of a benzene solution of carbonyl chloride on guaiacol in the presence of quinoline, and with diethylaminoethanol yields guaiacyl diethylaminoethyl carbonate, the *hydrobromide* of which, $C_{14}H_{21}O_4N,HBr$, crystallises from acetone in rhombohedra, m. p. 99—100°.

Diethylaminoethylguaiacol, $OMe\cdot C_6H_4\cdot O\cdot C_2H_4\cdot NEt_2$, obtained by distilling guaiacyl diethylaminoethyl carbonate once or twice under reduced pressure, is a colourless oil, b. p. 148—150°/10 mm. The *hydrobromide* has m. p. 127—128°. *Thymyl diethylaminoethyl carbonate*, $C_6H_3MePr^{\beta}\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2$, obtained from *thymyl chlorocarbonate*, b. p. 122—124°/25 mm., is a yellow oil; the *hydrobromide* crystallises from alcohol in slender needles, m. p. 160°, and the *citrate*, $C_{23}H_{35}O_{10}N$, in microscopic crystals, m. p. 90—95°. When distilled twice under reduced pressure, the base gives a quantitative yield of *diethylaminoethylthymol*, $C_6H_3MePr^{\beta}\cdot O\cdot C_2H_4\cdot NEt_2$, as a liquid with b. p. 126°/18 mm. The *citrate*, $C_{22}H_{35}O_8N$, crystallises from alcohol in prisms, m. p. 142—143°.

β-Naphthyl chlorocarbonate, $C_{10}H_7\cdot O\cdot COCl$, has b. p. 150—152°/9 mm., and crystallises from light petroleum in slender, yellow needles, m. p. 65—66°. *β-Naphthyl diethylaminoethyl carbonate*,

$$C_{10}H_7\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

is a basic oil; its *hydrochloride*, $C_{17}H_{21}O_3N,HCl$, crystallises from acetone in colourless needles, m. p. 141°, and when the base is distilled twice under reduced pressure the *diethylaminoethyl ether* of β-naphthol, $C_{10}H_7\cdot O\cdot C_2H_4\cdot NEt_2$, is obtained as a yellow oil, b. p. 202°/18 mm.; its *hydrochloride*, $C_{16}H_{21}ON,HCl$, crystallises from a mixture of alcohol and ether in small plates, m. p. 138—139°. The *chlorocarbonate* derived from ethyl salicylate, $COCl\cdot O\cdot C_6H_4\cdot CO_2Et$, is a colourless oil, b. p. 144°/12 mm., and reacts with diethylaminoethanol, yielding the *ethyl* ester, $CO_2Et\cdot C_6H_4\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2$, as a yellow oil, the *hydrobromide* of which forms minute crystals from acetone, m. p. 106—108°. *Ethyl diethylaminoethylsalicylate*,

$$CO_2Et\cdot C_6H_4\cdot O\cdot C_2H_4\cdot NEt_2,$$

has b. p. 179—180°/10 mm., and its *hydrochloride* crystallises from ethyl acetate in needles, m. p. 112°. The *methyl* ester,

$$CO_2Me\cdot C_6H_4\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

yields a *hydrobromide*, which crystallises from a mixture of acetone and ether in needles, m. p. 127—130°.

The *chlorocarbonate* from methyl *p*-hydroxybenzoate,

$$CO_2Me\cdot C_6H_4\cdot O\cdot COCl,$$

has b. p. 144°/13 mm., and crystallises from light petroleum in yellow needles, m. p. 58°.

Methyl p-*diethylaminoethylcarbonatobenzoate*,

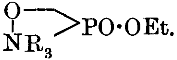
$$CO_2Me\cdot C_6H_4\cdot O\cdot CO_2\cdot C_2H_4\cdot NEt_2,$$

is a yellow oil; its *hydrochloride* crystallises from absolute alcohol in glistening needles, m. p. 133—134° (decomp.), and decomposes in the presence of water, yielding carbon dioxide, diethylaminoethanol hydrochloride, and methyl-*p*-hydroxybenzoate.

Methyl p-*diethylaminoethoxybenzoate*, $CO_2Me\cdot C_6H_4\cdot O\cdot C_2H_4\cdot NEt_2$, has b. p. 186—189°/15 mm.; its *hydrochloride* crystallises from ethyl acetate in thin, glistening plates, m. p. 147°.

Ethyl diethylaminoethyl carbonate, $OEt\cdot CO\cdot O\cdot C_2H_4\cdot NEt_2$, obtained from ethyl chlorocarbonate and diethylaminoethanol, is a colourless oil, b. p. 91—94°/10 mm.; the *citrate*, $C_{15}H_{27}O_{10}N$, crystallises from ethyl acetate in needles, m. p. 93—98°. When the base is boiled in a reflux apparatus, the temperature registered is 207°, but falls and finally remains constant at 172°, the products of decomposition being ethyl alcohol, ethyl carbonate, and diethylaminoethanol.

Menthyl diethylaminoethyl carbonate, $C_{10}H_{19}\cdot O\cdot CO\cdot O\cdot C_2H_4\cdot NEt_2$, obtained from *menthyl chlorocarbonate*, b. p. 105—106°/12 mm., and diethylaminoethanol, is a colourless liquid, b. p. 179—180°/9 mm.; its *hydrochloride*, $C_{17}H_{33}O_3N,HCl$, crystallises from ethyl acetate in prismatic needles, m. p. 142°. When the base is boiled for some hours, the temperature falls from 215° to 204°, and menthol, menthyl carbonate, m. p. 105°, diethylaminoethanol, and its carbonate are formed. J. J. S.

Esters and Amides of the Phosphoric Acids. II. Attempts to Prepare Substances Allied to the Lecithins. KURT LANGHELD (*Ber.*, 1911, **44**, 2076—2087. Compare Abstr., 1910, i, 536).—Esters of metaphosphoric acid unite with alcohols to form esters of orthophosphoric acid of the type $OR\cdot PO(OR')\cdot OH$. At the ordinary temperature the addition of alcohol takes place quantitatively in the course of four to five days, but in the case of solid alcohols, such as sugar, combination takes place very slowly. The behaviour of ethyl metaphosphate towards ammonia and its derivatives has also been studied. It is found that ammonia and primary amines yield derivatives of iminophosphoric acid, $NH[PO(OEt)\cdot OH]_2$ and $NR[PO(OEt)\cdot OH]_2$, whilst secondary amines and primary bases containing strongly acid groups in the molecule (carbamide and aminodicarboxylic acids) are converted into derivatives of ethyl aminophosphoric acid of the types $NRR'\cdot PO(OEt)\cdot OH$ and $NHR\cdot PO(OEt)\cdot OH$ respectively; tertiary bases yield salts having the constitution  $\begin{array}{l}O\text{—}\\ |\quad >PO\cdot OEt.\\ NR_3\end{array}$

When shaken with ethyl metaphosphate in chloroform solution at the ordinary temperature, aminomonocarboxylic acids give rise to readily soluble derivatives of diethyl iminopyrophosphate, whereas aminodicarboxylic acids remain unchanged. Serine unites with three molecules of ethyl metaphosphate, of which two are easily removed by boiling with water and lead carbonate. It is suggested that the separation of amino-acids might be effected by utilising these differences in their behaviour towards the ester.

Details of the preparation of ethyl metaphosphate from silver metaphosphate and ethyl iodide, and also by the interaction of phosphoric oxide and diethyl ether, are given. The ester may also be obtained by heating diethyl hydrogen orthophosphate under diminished pressure at 80°; at higher temperatures, triethyl orthophosphate is produced. Diethyl hydrogen orthophosphate is readily prepared by the interaction of ethyl metaphosphate and alcohol in molecular proportions at the ordinary temperature.

When metaphosphoric acid is heated with alcohol and the resulting solution treated with water and barium hydroxide, barium ethyl orthophosphate, $C_2H_5O_4PBa,H_2O$, and barium diethyl orthophosphate, $Ba(C_4H_{10}O_4P)_2$, are produced; the separation of these two salts is accomplished by taking advantage of the greater solubility of the latter in aqueous alcohol.

Ethyl metaphosphate reacts with water at the ordinary temperature to form *diethyl dihydrogen pyrophosphate*, which gives an amorphous *barium* salt, $C_4H_{10}O_7PBa$.

Molecular quantities of ethyl metaphosphate and ethylene chlorohydrin, when kept for three to four days at the ordinary temperature, yield *ethyl chloroethyl hydrogen orthophosphate*, which was isolated in the form of its *barium* salt, $Ba(C_4H_9O_4ClP)_2$. When ethyl metaphosphate is heated on the water-bath with excess of ethylene chlorohydrin, a mixture of diethyl hydrogen orthophosphate and ethyl chloroethyl hydrogen orthophosphate is produced.

Benzyl alcohol reacts with ethyl metaphosphate in boiling chloroform solution, yielding benzyl ethyl ether and dibenzyl ether, together with *benzyl dihydrogen phosphate* and *ethyl benzyl hydrogen phosphate*, the reaction taking place according to one or both of the following schemes:

I. $OEt\cdot PO(O\cdot C_7H_7)\cdot OH + C_7H_7\cdot OH = PO(O\cdot C_7H_7)(OH)_2 + C_7H_7\cdot OEt$.
II. (*a*) $PO_2\cdot OEt + C_7H_7\cdot OH = PO_2\cdot OH + C_7H_7\cdot OEt$.
(*b*) $PO_2\cdot OH + C_7H_7\cdot OH = PO(O\cdot C_7H_7)(OH)_2$.

The two esters were isolated in the form of their *barium* salts, $C_7H_7O_4PBa,2H_2O$ and $Ba(C_9H_{12}O_4P)_2$.

Ethyl choline phosphate is obtained as a hygroscopic, glassy mass by treating ethyl chloroethyl hydrogen orthophosphate with trimethylamine in alcoholic solution; the yellow, amorphous *platinichloride* was analysed.

Glycerolphosphoric acid is prepared by heating ethyl metaphosphate with excess of glycerol; the *barium* salt has the composition $C_3H_6O_6PBa,1\frac{1}{2}H_2O$.

When allyl iodide, diluted with chloroform, is shaken with equal molecular quantities of silver metaphosphate and ethylene chlorohydrin, allyl phosphate and *allyl chloroethyl hydrogen orthophosphate*, are produced. The *barium* salt of the last-named compound has the composition $Ba(C_5H_9O_4ClP)_2$.

The *compounds* of ethyl metaphosphate with ammonia, $C_4H_{19}O_6N_3P_2$, ethylamine, $C_{10}H_{31}O_6N_3P_2$, diethylamine, $C_{10}H_{27}O_3N_2P$, and with triethylamine, $C_{18}H_{20}O_3NP$, are all syrups, which solidify to glasses when kept in a desiccator under diminished pressure.

The *compound* with carbamide, $C_3H_9O_4N_2P$, is hydrolysed when boiled with water into carbamide and ethyl dihydrogen phosphate.

Aspartic acid and glutamic acid react slowly with ethyl metaphosphate in boiling chloroform solution, yielding glassy *substances* of the composition $C_6H_{12}O_7NP$ and $C_7H_{14}O_7NP$ respectively.

The *compounds* with alanine, $C_7H_{17}O_8NP_2$, valine, $C_9H_{21}O_8NP_2$, and leucine, $C_{10}H_{23}O_8NP_2$, were obtained in the form of glassy masses, which are decomposed when boiled with water into ethyl dihydrogen phosphate, phosphoric acid, and the corresponding amino-acid. The leucine derivative gives with diethylamine a *salt*, $C_{22}H_{56}O_8N_4P_2$, containing three molecules of diethylamine.

The *compound* of ethyl metaphosphate with serine has the composition $C_9H_{22}O_{12}NP_3$. F. B.

αβ-Dimethyl-lævulic Acid. RICHARD WILLSTÄTTER and ALESSANDRO BROSSA (*Ber.*, 1911, **44**, 2191—2194).—*αβ-Dimethyl-laevulic acid*, $COMe\cdot CHMe\cdot CHMe\cdot CO_2H$, required for comparative purposes in connexion with the degradation of phytol, has been obtained from alcoholic sodium ethoxide and equimolecular quantities of methyl α-bromopropionate and methyl methylacetoacetate, whereby mixtures of the methyl and ethyl esters of αβ-dimethylsuccinic acid and of acetyldimethylsuccinic acid are obtained. The hydrolysis of the latter by 8% barium hydroxide yields a mixture of αβ-dimethylsuccinic acid and the acid required. αβ-Dimethyl-lævulic acid has b. p. 120°/5 mm., 145°/12 mm., and D_4^0 1·112, and forms an *ethyl* ester, b. p. 90°/9 mm., D_4^0 0·999, p-*nitrophenylhydrazone*, m. p. 121—123° (decomp.), and *anhydride*, b. p. 114°/16 mm., 235—237°/727 mm., D_4^0 1·084. C. S.

Ethyl *tert.*-Valerylacetate. ERIK WAHLBERG (*Ber.*, 1911, **44**, 2071—2076).—Attempts to prepare ethyl *tert.*-valerylacetate, $CMe_3\cdot CO\cdot CH_2\cdot CO_2Et$, by the interaction of magnesium *tert.*-butyl iodide and ethyl cyanoacetate, and also by the removal of carbon monoxide from ethyl trimethylacetylpyruvate, proved fruitless. The ester is obtained in small yield by the condensation of pinacolin with ethyl carbonate by means of sodium ethoxide or sodamide. It is best prepared by heating an aqueous solution of *tert.*-valerylacetiminoether hydrochloride at 50—60° (see this vol., i, 702). It is a colourless liquid, b. p. 96—97°/15 mm., D_4^{18} 0·967, giving an intense violet coloration with ferric chloride. When hydrolysed with aqueous potassium hydroxide it yields tert.-*valerylacetic acid*,

$$CMe_3\cdot CO\cdot CH_2\cdot CO_2H,$$

which has m. p. 47—49°, and decomposes at 100° into pinacolin and carbon dioxide.

Ethyl tert.-*valerylmethylacetate* or *ethyl αγγγ-tetramethylacetoacetate*, $CMe_3\cdot CO\cdot CHMe\cdot CO_2Et$, prepared by the successive action of sodium ethoxide and methyl iodide on the above ester, is an oil, b. p. 93—94°/15 mm., D_4^{18} 0·955. The corresponding *acid*,

$$CMe_3\cdot CO\cdot CHMe\cdot CO_2H,$$

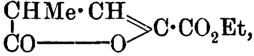
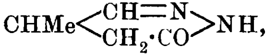
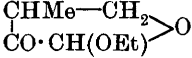
crystallises in small, lustrous plates, which have m. p. 100—101°, and simultaneously decompose into carbon dioxide and ethyl *tert.*-butyl ketone.

1-*Phenyl*-3-tert.-*butyl*-5-*pyrazolone*, $C_{13}H_{16}ON_2$, prepared by the interaction of phenylhydrazine and ethyl *tert.*-valerylacetate, crystallises from benzene in large leaves, m. p. 110·5—111·5°, and when oxidised with ferric chloride in alcoholic solution yields *bisphenyl*-tert.-*butylpyrazolone*, $C_{26}H_{30}O_2N_4$, m. p. above 290°.

1-*Phenyl*-4-*methyl*-3-tert.-*butyl*-5-*pyrazolone*, $C_{14}H_{18}ON_2$, prepared from phenylhydrazine and ethyl αγγγ-tetramethylacetoacetate, has m. p. 114·5—115·5°.

Ethyl ααγγγ-*pentamethylacetoacetate*, $CMe_3{\cdot}CO{\cdot}CMe_2{\cdot}CO_2Et$, obtained from ethyl tetramethylacetoacetate by the successive action of sodium ethoxide and methyl iodide, has b. p. 98·5—99°/15 mm., and on hydrolysis with dilute sulphuric acid yields pentamethylacetone. When heated with phenylhydrazine, it gives 1-*phenyl*-4 : 4-*dimethyl*-3-tert.-*butyl*-5-*pyrazolone* in an impure condition, m. p. 107—108°.

F. B.

Ketoglutaric Acids and the Acid-aldehydes of the Succinic Series. Edmond E. Blaise (*Compt. rend.*, 1911, **153**, 71—73).—When ethyl oxalopyrotartrate is saturated with hydrogen bromide at 0°, and allowed to remain for some weeks, crystals are obtained, together with a viscous liquid. The latter is esterified and distilled, when three fractions are obtained : (1) A liquid, b. p. 143—145°/15 mm., which consists principally of an *ester* of the above-mentioned crystalline substance; on hydrolysis it forms the *lactone*,  $\genfrac{}{}{0pt}{}{\mathrm{CHMe{\cdot}CH}}{\mathrm{CO{-}{-}{-}{-}O}}{>}\mathrm{C{\cdot}CO_2Et}$, and when treated with barium hydroxide it yields the *aldehyde*, $CO_2Et{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$, b. p. 89—90°/18 mm. The latter forms a *semicarbazone*, m. p. 110·5°, a p-*nitrophenylhydrazone*, m. p. 89°, an *oxime*, b. p. 137—138°/16 mm., and an *azine*,  $\mathrm{CHMe}{<}\genfrac{}{}{0pt}{}{\mathrm{CH{=}N}}{\mathrm{CH_2{\cdot}CO}}{>}\mathrm{NH}$, m. p. 66°, b. p. 134—136°/18 mm. (2) The foregoing aldehyde. (3) An *ethoxylactone*,  $\genfrac{}{}{0pt}{}{\mathrm{CHMe{-}CH_2}}{\mathrm{CO{\cdot}CH(OEt)}}{>}\mathrm{O}$, having b. p. 101°/18 mm.

The *acid-aldehyde*, $CO_2H{\cdot}CHMe{\cdot}CH_2{\cdot}CHO$, has b. p. 139—140°/12·5 mm.; the *semicarbazone*, m. p. 195°; the *oxime*, m. p. 77°; the p-*nitrophenylhydrazone* has m. p. 198°; the *phenylhydrazone*, m. p. 71—72°, and on distillation forms an *azine*, m. p. 42°, b. p. 183—185°/12 mm.

W. O. W.

Action of Organo-magnesium Compounds on Methyl Acetylpyrotartrate. Philippe Barbier and Réné Locquin (*Bull. Soc. chim.*, 1911, [iv], **9**, 717—722).—An attempt was made to prepare acids of the type $OH{\cdot}CRR'{\cdot}CH(CO_2H){\cdot}CH_2{\cdot}CO_2H$ by the action of magnesium alkyl bromides on methyl acetylpyrotartrate,

$$CO_2Me{\cdot}CH_2{\cdot}CMeAc{\cdot}CO_2Me.$$

The esters alone could be obtained, however, the only products on saponification being pyrotartaric acid and the corresponding ketone, $R{\cdot}COMe$.

The authors tried magnesium *iso*butyl bromide and magnesium phenyl bromide, and obtained from these respectively the compounds $CHMe_2\cdot CH_2\cdot CMe(OH)\cdot CMe(CO_2Me)\cdot CH_2\cdot CO_2Me$, an oily liquid, b. p. 157—158°/14 mm., and

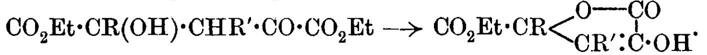
$$OH\cdot CMePh\cdot CMe(CO_2Me)\cdot CH_2\cdot CO_2Me,$$

a light-coloured, odourless oil, which decomposed on distillation even under reduced pressure.

The experiments furnish a new method of preparing ketones containing the group COMe. W. G.

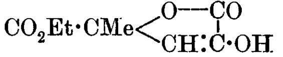
A New Method of Obtaining Glycuronic Acid. ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, **34**, 242—247 *).—The acid was obtained by the oxidation of 2% dextrose solution by hydrogen peroxide. After destruction of the excess of the latter by platinum-black, the acid was precipitated by basic lead acetate. It was identified by the isolation of the *p*-bromophenylhydrazine derivative, and by oxidation to saccharic acid. S. B. S.

Lactonisation of α-Ketonic Esters. HENRI GAULT (*Compt. rend.*, 1911, **153**, 107—110).—α-Ketonic esters of mono- and of di-carboxylic acids under the influence of amines, sulphuric acid, or, best of all, sodium ethoxide undergo condensation in accordance with the scheme: $R\cdot CO\cdot CO_2Et + CH_2R'\cdot CO\cdot CO_2Et \longrightarrow$



$$CO_2Et\cdot CR(OH)\cdot CHR'\cdot CO\cdot CO_2Et \longrightarrow CO_2Et\cdot CR\left\langle\begin{array}{l}O\text{—}CO\\ CR'{:}C\cdot OH\end{array}\right..$$

The products are viscous liquids, which cannot be distilled without decomposition, dissolve in alkali carbonates or hydrogen carbonates, develop violet-red colorations with ferric chloride, and form acyl derivatives; with the exception of the substance obtained from ethyl pyruvate, they do not react in the ketonic forms; thus ethyl pyruvate yields *ethyl α-keto-γ-valerolactone-γ-carboxylate,*



$$CO_2Et\cdot CMe\left\langle\begin{array}{l}O\text{—}CO\\ CH{:}C\cdot OH\end{array}\right.$$

(*phenylhydrazone*, m. p. 120—121°; *semicarbazone*, m. p. 220°), whilst ethyl α-ketosuccinate, α-ketoglutarate, and α-ketoadipate respectively yield substances in which R is $CH_2\cdot CO_2Et$, $CH_2\cdot CH_2\cdot CO_2Et$, and $CH_2\cdot CH_2\cdot CH_2\cdot CO_2Et$ respectively, and R′ is CO_2Et, $CH_2\cdot CO_2Et$, and $CH_2\cdot CH_2\cdot CO_2Et$ respectively. C. S.

Chemical Action of Light. II. G. INGHILLERI (*Zeitsch. physiol. Chem.*, 1911, **73**, 144—151).—The formation of a sugar, m. p. 98°, by the action of light on a mixture of 40% formaldehyde solution and crystallised oxalic acid in sealed tubes has been confirmed (compare this vol., i, 354). Formaldehyde itself (40% solution) when similarly exposed yields a yellow, syrupy liquid, but when mixed with water and then exposed to sunlight a yellow syrup, methyl alcohol, and formic acid are formed, the two latter probably by the action of the alkali of the glass on the formaldehyde. A mixture of methyl alcohol and formaldehyde (40%) under similar conditions yields methyl formate. Tubes containing glycerol, oxalic acid, and a little water gave a yellow oil containing glyceryl monobutyrate, together with a liquid containing butyric acid. J. J. S.

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* and *Monatsh.*, 1911, **33**, 623—629.

Viscose from Cellulose and from Starch. HERMANN OST, F. WESTHOFF, and L. GESSNER (*Annalen*, 1911, **382**, 340—360).—Starch yields a viscose similar to that obtained from cellulose, but it is more stable, and allows the process of "ripening" to be studied more readily. To obtain the viscose, 10 grams of potato starch are suspended in 20—25 c.c. of carbon disulphide in a stoppered bottle, the mixture is shaken, and at least 2 mols. of sodium hydroxide are added at once in the form of 10—20% aqueous solution. After some hours, a yellow jelly is obtained, which can be drawn out in the form of slender threads. This xanthate dissolves in water to a viscous liquid, from which alcohol or saturated saline solutions precipitate the xanthate as a leather-like mass. Mineral acids and concentrated acetic acid yield starch, carbon disulphide, and hydrogen sulphide. When kept, the viscose becomes thinner, it "ripens," but, even after months, coagulation is not observable. Very dilute alkali and an excess of very concentrated (50%) alkali do not yield a viscose.

The products, after purification by repeated solution in water and precipitation by alcohol, were analysed, the sodium was estimated as sodium sulphate, the sulphur estimated by oxidation by Carius' method, as Cross's method of oxidation with hypochlorite gave low results, and the starch estimated by decomposing with acid, hydrolysing to dextrose, and estimating this by means of Fehling's solution.

The composition of different samples varied appreciably, mainly owing to hydrolysis, which takes place during solution and precipitation. In most cases for 1 mol. of starch, 1·35—1·25 atoms of S and 1·3—1·2 atoms of Na were found. The formula suggested for the xanthate is $(ONa{\cdot}C_6H_8O_3{\cdot}O{\cdot}CS{\cdot}SNa)_n$, but owing to hydrolysis, which can take place according to the two equations:
(1) $(ONa{\cdot}C_6H_8O_3{\cdot}OCS_2Na)_n + nH_2O = (C_6H_9O_4{\cdot}OS_2Na)_n + nNaOH$, and (2) $(C_6H_9O_4{\cdot}OCS_2Na)_n + n/2\text{-}H_2O = (C_{12}H_{19}O_9{\cdot}OCS_2Na)_{n/2} + n/2\text{-}CS_2 + n/2\text{-}NaOH$, the percentages of sulphur and sodium are low.

During the process of ripening, the viscose becomes less and less viscous; for example, a specimen purified by three precipitations with alcohol, when dissolved in water and examined in an Engler's viscometer at 20°, had a viscosity of 130, but this fell within twenty-five days to 9. The ripening is accompanied by hydrolysis similar to that which occurs during purification, but to a greater extent. After keeping crude viscose for twelve days and then purifying by three precipitations with alcohol, the number of atoms of sulphur and sodium compared with 1 mol. of starch had fallen to 0·34 and 0·29 respectively, whereas the numbers for the fresh viscose were 1·77 and 1·82. The diminution in the viscosity is not due to this hydrolysis, but to the action of the alkali on the starch, that is, to a diminution of the value *n*. This is supported by the fact that soluble starch and dextrins of high molecular weight yield comparatively mobile xanthates.

Viscose from cellulose also undergoes hydrolysis during purification and ripening. During the latter process its viscosity first diminishes and then increases again, the final increase being due to the colloidal separation of free cellulose.

The cellulose deposited from an old specimen of viscose by means of hydrochloric acid is apparently identical with the cellulose obtained from alkali cellulose, and its composition is practically that of cellulose, provided the specimens are thoroughly dehydrated at 120—125°.

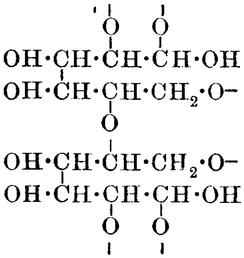
An erythrodextrin obtained by the action of malt extract on starch paste at 70° has practically no reducing properties, and differs but little from starch in composition. J. J. S.

Acid Hydrolysis of Starch Granules. CHESTER B. DURYEA (*J. Soc. Chem. Ind.*, 1911, **30**, 789—790).—It has been demonstrated experimentally that maltose is formed quite early in the hydrolysis of maize starch granules by hydrochloric acid; in fact, it is not improbable that it is an initial product of the hydrolysis of starch. It would also appear that the production of maltose is accompanied by a general simplification of the molecular condition of the carbohydrates composing the granules; in other words, the production of each successive molecule of maltose leads to the formation of a simpler dextrin. W. H. G.

Observations on Cotton and Nitrated Cotton. HENRY DE MOSENTHAL (*J. Soc. Chem. Ind.*, 1911, **30**, 782—786).—Attempts to dialyse solutions of nitrocellulose in acetone, making use of the bladder of the sturgeon and also parchment paper, have led to the conclusion that, contrary to the author's earlier statements (*ibid.*, 1904, **23**, 292; 1907, **26**, 443), nitrocellulose does not dialyse. Further, solutions of nitrated cotton in acetone do not give any indication of a pressure in a Pfeffer osmometer with various septa.

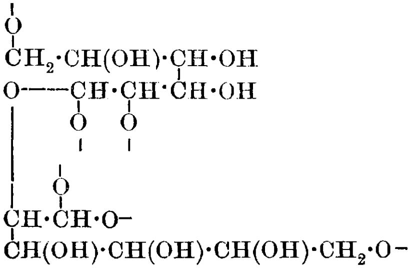
The absorption spectra of a number of solutions of cellulose nitrates and acetates were investigated; in all cases a continuous spectrum was observed, which showed a shortening in the ultra-violet progressing with the concentration; it may be assumed therefore that the cellulose group absorbs ultra-violet light.

The author inclines to the view that the dextro-cellulose of cotton is an aliphatic compound of a polysaccharide character, most suitably represented by open formulæ derived from the ring formulæ of Green and of Vignon, such as:



$$\begin{array}{l} \quad\;\; | \quad\; | \\ \quad\;\; O \quad O \\ OH\cdot CH\cdot CH\cdot CH\cdot OH \\ OH\cdot CH\cdot CH\cdot CH_2\cdot O- \\ \qquad\;\; O \\ OH\cdot CH\cdot CH\cdot CH_2\cdot O- \\ OH\cdot CH\cdot CH\cdot CH\cdot OH \\ \qquad\;\; O \quad O \\ \qquad\;\; | \quad\; | \end{array}$$

and



$$\begin{array}{l} | \\ O \\ CH_2\cdot CH(OH)\cdot CH\cdot OH \\ O—CH\cdot CH\cdot CH\cdot OH \\ |\qquad O \quad O \\ |\qquad | \quad\; | \\ |\quad | \\ |\quad O \\ CH\cdot CH\cdot O- \\ CH(OH)\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot O- \end{array}$$

The latter formula seems preferable, since the monose groups are connected by acetal linkings only, which would account for the ease with which cellulose is hydrolysed and also the formation of a large number of celluloses and hydrocelluloses by the addition of water.

W. H. G.

Acetylation of Cotton Cellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, **24**, 1256—1260).—It has been shown previously (compare Abstr., 1910, i, 224) that the cellulose acetates obtained by the processes of Bayer (D.R.-P. 159524) and of Lederer (D.R.-P. 163316) are acetates of hydrocelluloses. The present communication contains the results of experiments performed with the object of ascertaining at which stage of the process the hydrolysis of the cellulose occurs. It is found that the first product of the interaction of cotton cellulose with acetic anhydride and acetic acid in the presence of sulphuric acid is an acetate of a cellulose derivative capable of reducing Fehling's solution (hydrocellulose). As the reaction proceeds, however, cellulose acetates are formed, which, when hydrolysed, yield cellulose derivatives incapable of reducing boiling alkaline copper solutions; in agreement with this, it is found that the product first formed in the Lederer process (acetylation of hydrocellulose) consists of acetates of a cellulose derivative which does not reduce Fehling's solution. Towards the end of the reaction, acetates of hydrocelluloses again appear, and, as already stated, the final product consists almost solely of acetates of a hydrocellulose.

Evidence is also brought forward to show that the acetylation of the hydrocellulose initially produced proceeds at a far greater rate than the formation of the hydrocellulose itself from the cotton cellulose.

It is evident from the results now recorded that the hydrolysis which takes place during acetylation cannot be regarded as a tertiary process, as stated by Jentgen (compare this vol., i, 115).

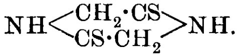
W. H. G.

Cellulose. Hydrocellulose. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1911, **24**, 1260—1262. Compare this vol., i, 115).—Polemical. A reply to Jentgen (this vol., i, 355). W. H. G.

Cellulose Acetate. HERMANN OST (*Zeitsch. angew. Chem.*, 1911, **24**, 1304—1306, 1307).—Historical. The author claims to have been the first to show that the cellulose acetate obtained by the processes of Bayer and of Lederer is a cellulose triacetate.

W. H. G.

Cellulose Acetate. ARTHUR EICHENGRÜN (*Zeitsch. angew. Chem.*, 1911, **24**, 1306—1307).—Polemical. A reply to Ost (compare preceding abstract). W. H. G.

Thioamides: Formation of Thiopolypeptide Derivatives by the Action of Hydrogen Sulphide on Aminoacetonitrile. TREAT B. JOHNSON and GERALD BURNHAM (*J. Biol. Chem.*, 1911, **9**, 449—462).—Aminoacetonitrile reacts normally with hydrogen sulphide at the ordinary temperature, giving the unknown thioamide of glycine, which, however, was not isolated. It is very unstable, and decomposes spontaneously in alcoholic solution to the thiopolypeptide derivative, *thioglycylglycinethioamide*, $NH_2{\cdot}CH_2{\cdot}CS{\cdot}NH{\cdot}CH_2{\cdot}CS{\cdot}NH_2$. In part this thioamide undergoes an inner condensation with loss of ammonia, forming a *dithiopiperazine*,  $NH<\begin{matrix}CH_2{\cdot}CS\\CS{\cdot}CH_2\end{matrix}>NH$. This cyclic derivative is the chief product of the reaction; it dissolves in cold alkali hydroxide and has no basic properties. Hydrochloric acid hydrolyses it to glycine hydrochloride and hydrogen sulphide.

2 : 5-*Dithiopiperazine* turns brown at about 160°, and black at 270—280°; the *lead* and *mercury* salts are light brown; the *silver* salt separates in a gelatinous condition, and begins to decompose at once with the formation of black silver sulphide.

Thioglycylglycinethioamide is a dark brown powder, m. p. 89—95° (decomp.). E. F. A.

The Rules of Substitution in the Benzene Nucleus. ARNOLD H. HOLLEMAN (*Bull. Soc. chim.*, 1911, [iv], **9**, i—xlv).—A lecture delivered before the French Chemical Society. W. G.

The Study of Isomorphous Sulphonic Derivatives of Benzene. HENRY A. MIERS, HENRY E. ARMSTRONG, WILLIAM J. POPE, and WILLIAM P. WYNNE (*Brit. Assoc. Reports*, 1910, 100).—This report refers to the results obtained by the examination of twenty-nine derivatives of the 1 : 4 series (Barlow and Pope, Trans., 1910, **97**, 2308), and which are found to be in accordance with Barlow and Pope's theory correlating molecular structure with crystalline form. T. S. P.

Benzylindene. RUDOLF WEISSGERBER (*Ber.*, 1911, **44**, 2216).—Benzylindene was described in 1906 by Thiele, who showed that Marckwald's so-called benzylindene was really dibenzylindene accompanied by a little viscous oil. The author has succeeded in solidifying this oil, and shows that it is identical with his benzylindene, m. p. 33—34°. C. S.

The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. FREDERIC S. KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc. Reports*, 1910, 85—99).—This report [with William J. Jones] deals with the chlorination of anilides and the transformation of acylchloroaminobenzenes, and with the bromination of anilides and the conversion of bromoamines. T. S. P.

Two New Forms of 2-Nitro-6-hydroxylaminotoluene. KURT BRAND (*Ber.*, 1911, **44**, 2045—2047).—When crude nitrohydroxylaminotoluene prepared by electrolysis (compare Brand and Zöller, Abstr., 1907, i, 755) is dissolved in boiling benzene, it first crystallises in slender, yellow needles, changing to a stable, almost colourless form, which differs from the stable, short, yellow crystals previously described. Three forms, two stable and one unstable, of nitrohydroxylaminotoluene therefore exist. The unstable form has not yet been separated pure from benzene. It is converted into either of the stable forms on inoculation. Further, solutions of either of the stable forms in hot benzene, inoculated with a crystal of the other form and allowed to cool slowly, yield the other form, or in some cases a mixture of the two stable forms. The stable yellow form has m. p. 117—117·5°; the colourless form becomes yellow at 105° and melts at 115° or 117—117·5°, the former figure applying to an incompletely converted sample. E. F. A.

Condensation of a Substituted Formamide to a Derivative of Aminomalonamide. HERMANN DECKER and PAUL BECKER (*Annalen*, 1911, **382**, 369—377).—The formyl derivative of phenylethylamine (Bischler and Napieralski, Abstr., 1893, i, 608) reacts with phosphoric oxide or zinc chloride, yielding a product identical with that obtained by Decker and Kropp (Abstr., 1909, i, 513) by the action of phosphorus pentachloride and aluminium chloride. The product is a phosphate of the base $C_{27}H_{31}O_2N_3$, and has been obtained in a crystalline form. As the base is mono-acid and on hydrolysis loses two molecules of β-phenylethylamine and one of carbon dioxide, yielding β-phenylethylglycine, which can be synthesised from chloroacetic acid and β-phenylethylamine, the conclusion is drawn that it is β-phenylethylaminomalondiphenylethylamide. A strong odour of β-phenylethylcarbylamine is noticed during the condensation, and it is possible that the carbylamine is an intermediate product in the formation of the base.

β-Phenylethylaminomalon-β-phenylethylamide,

$$CH_2Ph\cdot CH_2\cdot NH\cdot CH(CO\cdot NH\cdot CH_2\cdot CH_2Ph)_2,$$

yields a *phosphate*, which crystallises from 95% alcohol in slender, colourless needles, m. p. 176—178°. The *picrate*, $C_{33}H_{34}O_9N_6$, separates from alcohol in well-developed crystals, m. p. 192°. The *hydrochloride*, $C_{27}H_{31}O_2N_3,HCl$, crystallises from 80% alcohol containing hydrogen chloride in colourless plates, m. p. 184—186°, and the *platinichloride*, $2C_{27}H_{31}O_2N_3,H_2PtCl_6$, crystallises from alcohol in yellowish-red, glistening plates, m. p. 254—255°. The free base, obtained by the action of ammonia on the picrate, crystallises from 80% alcohol in slender needles, m. p. 85°. Both the base and its salts have an extremely bitter taste. When the base is hydrolysed with 15% hydrochloric acid and alcohol, *β-phenylethylglycine hydrochloride*, $CH_2Ph\cdot CH_2\cdot NH\cdot CH_2\cdot CO_2H,HCl$, is formed. It crystallises from dilute acid in colourless plates, m. p. 243—244° (decomp.) when rapidly heated. *β-Phenylethylglycine*, $CH_2Ph\cdot CH_2\cdot NH\cdot CH_2\cdot CO_2H$, crystallises from 80% alcohol in slender, colourless needles, m. p. 274—276°, and dissolves readily in acids and alkalis.

Alcoholic potassium hydroxide solution also hydrolyses the base in a similar manner. J. J. S.

Doubly Linked Carbon Atoms and the Carbon–Nitrogen Linking. VIII. Reduction of *N*-Alkylated Amino-ketones. HERMANN EMDE and ERNST RUNNE (*Arch. Pharm.*, 1911, **249**, 354—370. Compare this vol., i, 281).—*a-Phenylacetonyltrimethylammonium bromide*,

$COMe\cdot CHPh\cdot NMe_3Br$, an oil obtained from α-bromo-α-phenylacetone and 33% alcoholic trimethylamine in a freezing mixture, has been converted into the *aurichloride*, m. p. 158—159°, and the *platinichloride*, m. p. 207—208° (decomp.). The corresponding chloride is not attacked by zinc and dilute sulphuric acid, and is decomposed by sodium amalgam and dilute hydrochloric acid at 0°, yielding trimethylamine and phenylacetone (a portion of which is reduced to the carbinol). *α-Phenylacetonyldimethylamine hydrochloride*,

$$COMe\cdot CHPh\cdot NMe_2,HCl,$$

m. p. 193—195°, ultimately obtained from α-bromo-α-phenylacetone and dimethylamine in cold benzene, is converted into α-phenylacetone and dimethylamine by sodium amalgam in faintly acid solution. *α-Phenylacetonylmethylamine hydrochloride*,

$$COMe\cdot CHPh\cdot NHMe,HCl,$$

m. p. 210—211° (decomp.), obtained in a similar manner by means of methylamine, is only decomposed to a small extent by sodium amalgam in acid solution, the chief product being *α-methylamino-α-phenyl*iso*propyl alcohol*, $NHMe\cdot CHPh\cdot CHMe\cdot OH$, a yellow oil which forms a *hydrochloride*, m. p. 191—193°, and a *platinichloride*, m. p. 193—194° (decomp.). Betaine hydrochloride is scarcely attacked by sodium amalgam.

From these and from numerous other examples quoted from the literature, the authors state that the carbonyl group (carbon–oxygen double linking), except when present in a carboxyl group, diminishes, even to a greater extent than does the carbon double linking under otherwise the same conditions, the stability of a neighbouring single carbon–nitrogen linking during reduction. In a substance,

$$R\cdot CH_2(NH_2)\cdot COR',$$

three factors exert an influence in weakening the carbon–nitrogen linking, namely, carbon double linkings in R, the carbonyl group, and the loading of the amino-group with methyl groups; the influence of the last factor is very slight for primary and secondary amino-groups (Abstr., 1909, i, 708, 709). C. S.

Contradiction of E. Biilmann's Interpretation of Homochromoisomerism as Polymorphism. ARTHUR HANTZSCH (*Ber.*, 1911, **44**, 2001—2009).—Polemical (compare Hantzsch, Abstr., 1910, i, 474; Biilmann, this vol., i, 367). The author upholds his contention that the two phenylmethylpicramides are isomeric and not polymorphic. E. F. A.

o- and m-Iodo-p-tolyl Methyl Ether and Derivatives with Multivalent Iodine. CARL WILLGERODT and RUDOLPH SCHLOSS (*Ber.*, 1911, **44**, 1708—1711).—A mixture of *m*- and *o*-iodo-*p*-tolyl methyl ethers is obtained by boiling a glacial acetic acid solution of *p*-tolyl methyl ether with iodine chloride until hydrogen chloride ceases to be evolved, then pouring into water, and shaking with sulphurous acid. The *o*-iodo-compound has b. p. 237—238° (compare Schall and Dralle, Abstr., 1885, 146), and the *meta*-compound, $C_6H_3IMe\cdot OMe$, crystallises from dilute alcohol in colourless, rhombic plates, m. p. 75°. p-*Tolyl methyl ether* o-*iododichloride*, $OMe\cdot C_6H_3Me\cdot ICl_2$, separates from light petroleum in yellow needles, which decompose rapidly on exposure to the air, regenerating the original iodo-compound.

Phenyl-p-*methoxy*-o-*tolyliodonium iodide*, $OMe{\cdot}C_6H_3Me{\cdot}IPhI$, obtained from the iodo-dichloride and mercury diphenyl in the presence of a few drops of water, and subsequent treatment with potassium iodide, crystallises from alcohol in pale yellow needles, m. p. 181°.

p-*Tolyl methyl ether* m-*iododichloride*, $OMe{\cdot}C_6H_3Me{\cdot}ICl_2$, forms orange-yellow, felted needles, decomposing at 58—60°. The corresponding *iodoso*-compound, $OMe{\cdot}C_6H_3Me{\cdot}IO$, forms a pale yellow, amorphous powder, which decomposes at 176°. It does not yield the corresponding iodoxy-compound when warmed with water or treated with sodium hypochlorite solution. The *iodosoacetate*,

$$OMe{\cdot}C_6H_3Me{\cdot}I(OAc)_2,$$

forms long, glistening crystals, m. p. 120—122°, and *phenyl*-p-*methoxy*-m-*tolyliodonium iodide*, $C_{14}H_{14}OI_2$, crystallises from alcohol, and has m. p. 166°. J. J. S.

Products of the Action of Nitric Acid on Dihydroanethole.

Hermann Thoms and W. Drauzburg (*Ber.*, 1911, 44, 2125—2133).—When heated with 45% nitric acid, dihydroanethole (*p*-methoxypropylbenzene) yielded the following products: (1) Anisic acid. (2) Anisaldehyde. (3) 3-*Nitro*-4-*methoxypropylbenzene*, $OMe{\cdot}C_6H_3Pr^a{\cdot}NO_2$, which is an almost colourless liquid, b. p. 164—169°/9 mm., solidifying at $-6°$; it is oxidised by potassium permanganate and dilute sulphuric acid to 3-nitroanisic acid. (4) 2 : 6-*Dinitro*-4-*propylphenol*,

$$OH{\cdot}C_6H_2Pr^a(NO_2)_2,$$

which crystallises from ether in yellow, prismatic columns, m. p. 46°; the *sodium* salt forms dark reddish-green needles, which sinter at 264° and decompose explosively; the *potassium* and *silver* salts are also mentioned. The *acetyl* derivative crystallises in greenish-yellow needles, m. p. 89°; the *benzoyl* derivative has m. p. 86·5—87°. When heated with diphenylcarbamyl chloride and pyridine, the dinitrophenol yields a *diphenylurethane*, $NPh_2{\cdot}CO{\cdot}O{\cdot}C_6H_2Pr^a(NO_2)_2$, crystallising in cubes, m. p. 136·5°.

4-*Methylcarbonato*-3 : 5-*dinitro*-1-*propylbenzene*,

$$CO_2Me{\cdot}O{\cdot}C_6H_2Pr^a(NO_2)_2,$$

prepared by the action of methyl chlorocarbonate on the sodium salt, crystallises in almost white needles, m. p. 85·5—86·5°.

The dinitrophenol is reduced by tin and hydrochloric acid to 2 : 6-*diamino*-4-*propylphenol*, which is unstable in the free condition, and is, therefore, best isolated in the form of the *hydrochloride*, $OH{\cdot}C_6H_2Pr^a(NH_2)_2,2HCl$; the *benzoyl* derivative forms rosettes of slender needles, m. p. 198°. 2 : 6-*Diacetylamino*-4-*propylphenol*, $OH{\cdot}C_6H_2Pr^a(NHAc)_2$, prepared by the gradual addition of acetic anhydride to a solution of the diamine hydrochloride in the presence of a slight excess of sodium acetate and acetic acid, crystallises in needles, m. p. 161·5—162°. The action of nitrous acid on the diaminophenol results in the formation of a brown *dye*.

Since 2 : 6-dinitro-4-propylphenol is also obtained by nitrating 3-nitro-4-methoxypropylbenzene, it is probable that the latter compound is formed as an intermediate product in the preparation of the dinitrophenol from dihydroanethole by the action of nitric acid.

The above-mentioned transformations of dihydroanethole and its nitro-derivative into dinitropropylphenol constitute the first recorded examples of the oxidation of the methoxy-group to hydroxyl by means of nitric acid. F. B.

The Elimination of Methoxy-groups from Phenolic Ethers by means of Nascent Hydrogen. HERMANN THOMS and W. SIEBELING (*Ber.*, 1911, **44**, 2134—2136).—The action of sodium on pyrogallol trimethyl ether in alcoholic solution leads to the formation of resorcinol dimethyl ether, the methoxy-group in position 2 being readily replaced by hydrogen. *iso*Eugenyl methyl ether, when subjected to the same treatment, yields a small quantity of a phenol, whilst in the case of anethole, *m*-methoxypropylbenzene, and asarone no replacement of the methoxy-group was observed.

From these results the authors draw the conclusion that the ready elimination of a methoxy-group from pyrogallol trimethyl ether is due to the accumulation of methoxy-groups in adjacent positions, and not to the presence of a substituent in the para-position (compare Semmler, Abstr., 1908, i, 557, 734; Kostanecki and Lampe, *ibid.*, 442). F. B.

Stereoisomeric β-Nitro-α-methoxy-αβ-diphenylethanes prepared by the Addition of Alkali Methoxide to 7-Nitrostilbene. FRIEDRICH HEIM (*Ber.*, 1911, **44**, 2013—2016. Compare Meisenheimer and Heim, Abstr., 1907, i, 858).—By the interaction of 7-nitrostilbene and sodium methoxide, two stereoisomeric β-nitro-α-methoxy-αβ-diphenylethanes, $OMe\cdot CHPh\cdot CHPh\cdot NO_2$, are formed, distinguished as α, m. p. 130—131°, and β, m. p. 97—98°, modifications (Meisenheimer and Heim, *loc. cit.*). It is now shown that both modifications are formed simultaneously, and that by varying the conditions, one or other is obtained in larger quantity, although the less fusible form always preponderates. The isomerides are separated by crystallisation from light petroleum and mechanical sorting, the α-form yielding slender, colourless needles, and the β-isomeride stumpy, transparent crystals. The isomerides are precipitated from the reaction mixture either by means of carbon dioxide, which favours the formation of the β-isomeride, or by ammonium chloride and air, a process most favourable to the α-modification.

On heating above the melting point, the β-isomeride is the more stable, being nearly all recovered after heating at 170°. The α-isomeride at this temperature becomes dark brown, and liberates fumes with the odour of a nitrile. In neither instance did heating bring about conversion into the other isomeride. E. F. A.

Condensation of ω-Nitrotoluene with Benzaldehyde. *cis*- and *trans*-7-Nitrostilbene. FRIEDRICH HEIM (*Ber.*, 1911, **44**, 2016—2022).—On condensing benzaldehyde with ω-nitrotoluene, in addition to the 7-nitrostilbene obtained by Knoevenagel and Walter (Abstr., 1905, i, 65), m. p. 75°, a second isomeride is formed.

This separates from light petroleum in darker yellow, stunted crystals, m. p. 128—128·5°, becoming greenish-yellow on exposure to light, and comprises 7—10% of the whole product. Like the isomeride m. p. 75°, it forms a mixture of α and β β-nitro-α-methoxy-αβ-diphenylethane. Each isomeride on heating or distillation is partly converted into the other form.

In addition to these isomerides, three other compounds containing a larger proportion of carbon are formed during the condensation, and separated by distillation of the residue. These are a compound separating in matted, yellow crystals, $C_{21}H_{17}O_2N$, a compound $C_{21}H_{15}ON$, m. p. 212°, and a compound $C_{21}H_{18}O_4N_2$.

This last is probably *αγ-dinitro-αβγ-triphenylpropane*, formed by the condensation of benzaldehyde with two molecules of ω-nitrotoluene. It separates in slender, colourless, matted crystals, m. p. 177—178·5°.

Concentrated alkali hydroxide eliminates NO_2H, and converts it into the compound $C_{21}H_{15}ON$, m. p. 212°. This compound is also formed by the distillation of 7-nitrostilbene, but it is demonstrated that it is formed during the original condensation. It is regarded as 3 : 4 : 5-*triphenyl*iso*oxazole*, $\mathrm{CPh}<\begin{matrix}\mathrm{CPh\cdot O}\\ \mathrm{CPh{:}N}\end{matrix}$, and crystallises in slender, colourless needles.

The compound $C_{21}H_{17}O_2N$ is regarded as *α-nitro-αβγ-triphenylpropylene*, $CH_2Ph\cdot CPh{:}CPh\cdot NO_2$; the yellow, matted needles have m. p. 102—103°.

E. F. A.

Doubly Linked Carbon Atoms and the Carbon–Nitrogen Linking. IX. Arylamino-Alcohols. HERMANN EMDE and ERNST RUNNE (*Arch. Pharm.*, 1911, **249**, 371—382. Compare this vol., i, 714).—α-Amino-α-phenyl*iso*propyl alcohol is obtained in 43·5% yield by treating a 96% alcoholic solution of benzyl methyl ketoxime with sodium amalgam and dilute hydrochloric acid at 0°. Its hydrochloride reacts with methyl iodide and sodium methoxide to form the corresponding trimethylammonium chloride. The decomposition of this chloride by sodium amalgam, or of the corresponding iodide by hydrogen chloride at 170—180°, yields trimethylamine and phenyl*iso*propyl alcohol. *dl-α-iso*Ephedrine (α-methylamino-α-phenyl*iso*propyl alcohol) (this vol., i, 715), in the form of its hydrochloride, decomposes at 250° into benzyl methyl ketone, ammonia, and methyl chloride. α-Phenyl-γ-butanoltrimethylammonium chloride is decomposed by sodium amalgam into α-phenyl-γ-butanol and trimethylamine hydrochloride.

Methyldiethylhydroxyethylammonium iodide, $OH\cdot CH_2\cdot CH_2\cdot NMeEt_2I$, m. p. 249° (decomp.), is obtained by the interaction of hydroxyethyldiethylamine and methyl iodide in methyl alcohol at 0°. The *platinichloride* and the *aurichloride* decompose at 222—223° and 237—238° respectively; the *chloride* is scarcely attacked by sodium amalgam.

C. S.

Preparation of Asymmetric Benzyldialkylacetic Acids. PH. DUMESNIL (*Compt. rend.*, 1911, **153**, 111—113).—The author has obtained the following substances by Haller and Bauer's method. Phenyl ethyl ketone, methyl iodide, and sodamide (1 mol.) in boiling benzene yield *methylethylacetophenone*, $CHMeEt\cdot COPh$, b. p. 109°/10 mm., from which, by a similar process, benzyl chloride produces *benzylmethylethylacetophenone*, $CH_2Ph\cdot CMeEt\cdot COPh$, b. p. 201°/18 mm. When the last substance is heated with sodamide (1 mol.) and a trace of water in boiling xylene for six hours, it yields benzene and the *amide*, $CH_2Ph\cdot CMeEt\cdot CO\cdot NH_2$, from which *a-benzyl-a-methylbutyric acid*, $C_7H_7\cdot CMeEt\cdot CO_2H$, b. p. 180°/18 mm., m. p. 31°, is obtained by hydrolysis with 50% sulphuric acid at 150°.

Ethylpropylacetophenone, $CHEtPr^{\alpha}\cdot COPh$, b. p. 138°/19 mm., and *benzylethylpropylacetophenone*, $CH_2Ph\cdot CEtPr^{\alpha}\cdot COPh$, b. p. 223°/20 mm., m. p. 52°, are produced in a similar manner. When the latter is treated with sodamide and water in boiling xylene, the chief product is *γ-benzylhexane*, $CH_2Ph\cdot CHEtPr^{\alpha}$, b. p. 117°/18 mm. The *amide*, $CH_2Ph\cdot CEtPr^{\alpha}\cdot CO\cdot NH_2$, which is only a secondary product, yields *a-benzyl-a-ethylvaleric acid*, $C_7H_7\cdot CEtPr\cdot CO_2H$, b. p. 200°/18 mm., by hydrolysis. C. S.

Ring Formations in the Peri-Position of the Naphthalene Series. IV. Attempts to Prepare a Six-Membered Carbon Ring. FRANZ SACHS and PERCY BRIGL (*Ber.*, 1911, **44**, 2091—2106).—This paper contains an account of unsuccessful attempts to effect the formation of a six-membered carbon ring in the peri-position by the elimination of water from β-2-ethoxy-1-naphthylacrylic acid, β-2-chloro-1-naphthylacrylic acid, and ω-2-chloro-1-naphthyldiethyl ketone.

In the preparation of 2-hydroxy-1-naphthaldehyde from β-naphthol, hydrocyanic acid, and hydrochloric acid in ethereal solution in the presence of zinc chloride, a small quantity of *tri-2-hydroxy-1-hydronaphthamide*, $(OH\cdot C_{10}H_6\cdot CH{:})_3N_2$, is produced simultaneously. This crystallises from nitrobenzene in slender, microscopic needles of a bright red colour, m. p. 312°, and is hydrolysed by hydrochloric acid to 2-hydroxy-1-naphthaldehyde and ammonia. The formation of this compound is due to the hydrolytic action of traces of water, whereby a small quantity of the aldimine produced in the reaction is converted into 2-hydroxy-1-naphthaldehyde, which then condenses with a further portion of the aldimine, according to the equation:

$$OH\cdot C_{10}H_6\cdot CHO + 2HN{:}CH\cdot C_{10}H_6\cdot OH = (OH\cdot C_{10}H_6\cdot CH{:})_3N_2 + H_2O.$$

2-Ethoxy-1-naphthaldehyde, m. p. 111°, is best prepared by alkylating the hydroxyaldehyde by means of ethyl sulphate in alcoholic solution (compare Bartsch, Abstr., 1903, i, 647). The *anil*,

$$OEt\cdot C_{10}H_6\cdot CH{:}NPh,$$

and *phenylhydrazone* crystallise in light yellow plates, m. p. 73° and 91° respectively; the *semicarbazone*, $C_{14}H_{15}O_2N_3$, crystallises from methyl alcohol in long, white needles, m. p. 214—215°.

2-Ethoxy-1-naphthylhydroxyacetonitrile, $OEt\cdot C_{10}H_6\cdot CH(OH)\cdot CN$, is obtained in an impure condition in the form of large, crystalline plates by the interaction of 2-ethoxy-1-naphthaldehyde and anhydrous hydrocyanic acid in the presence of a small quantity of ammonia. It is exceedingly unstable, and decomposes in solution into its components. 2-Ethoxy-α-naphthaldehyde condenses with malonic acid in alcoholic solution in the presence of aniline, yielding β-naphthacoumarin-3-carboxylic acid (compare Bartsch, *loc. cit.*; Knoevenagel and Schröter, Abstr., 1905, i, 63). Attempts to condense the aldehyde with ethyl acetate and ethyl malonate proved unsuccessful.

ω-ω-2-*Trichloro*-1-*methylnaphthalene*, $C_{10}H_6Cl \cdot CHCl_2$, obtained by heating 2-hydroxy-1-naphthaldehyde with phosphorus pentachloride at 193—205°, crystallises from alcohol in rhombic plates, m. p. 90°; when heated with methyl-alcoholic sodium methoxide it yields 2-*chloro-di*-ω-*methoxy*-1-*methylnaphthalene*, $C_{10}H_6Cl \cdot CH(OMe)_2$, which crystallises in white prisms capped with small pyramids, m. p. 86°.

2-*Chloro*-1-*naphthaldehyde*, $C_{10}H_6Cl \cdot CHO$, prepared by heating the preceding trichloro-compound with dilute acetic acid, or with sodium acetate in aqueous alcoholic solution, crystallises in long, flexible, white needles, m. p. 76°, and gives with strong sulphuric acid a yellow coloration, which becomes blood-red on the addition of nitric acid; the *azine*, $C_{22}H_{14}N_2Cl_2$, forms stout, golden-yellow needles, m. p. 195°, the *semicarbazone*, $C_{12}H_{10}ON_3Cl$, slender, microscopic needles, m. p. 215°. When heated with anhydrous potassium acetate and acetic anhydride at 170°, it yields β-2-*chloro*-1-*naphthylacrylic acid*, $C_{10}H_6Cl \cdot CH:CH \cdot CO_2H$, which crystallises in long needles, m. p. 176°, and furnishes a crystalline *ammonium* and an amorphous *calcium* salt; the salts of the *alkali metals* and of *silver* are also mentioned. On account of its instability, the *chloride* could not be isolated. The *amide*, $C_{10}H_6Cl \cdot CH:CH \cdot CO \cdot NH_2$, crystallises in stout, white needles, m. p. 195°. The acid is reduced by sodium amalgam, chlorine being eliminated from the nucleus at the same time. All attempts to effect an internal condensation in the peri-position by means of sulphuric acid, zinc chloride, or phosphoric oxide were unsuccessful.

Di-2-*chloro*-1-*naphthylideneacetone*, $CO(CH:CH \cdot C_{10}H_6Cl)_2$, is obtained by condensing 2-chloro-1-naphthaldehyde with acetone by means of strong sulphuric acid. It crystallises from ethyl benzoate in canary-yellow needles, m. p. 215°, and gives with concentrated sulphuric acid an indigo-blue coloration.

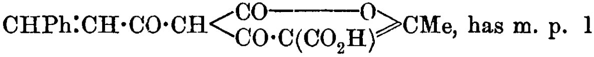
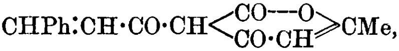
α-2-*Chloro*-1-*naphthyl*-Δ^{α}-*penten*-γ-*one*, $C_{10}H_6Cl \cdot CH:CH \cdot COEt$, prepared by the condensation of 2-chloro-1-naphthaldehyde and methyl ethyl ketone by means of potassium hydroxide in aqueous alcoholic solution, crystallises in flexible, white needles, m. p. 74°, and gives with strong sulphuric acid a reddish-brown coloration, which almost disappears on the addition of nitric acid; the *semicarbazone*,

$$C_{16}H_{16}ON_3Cl,$$

forms lustrous, silky needles, m. p. 185°. When the condensation is carried out in very feebly alkaline solution, α-2-*chloro*-1-*naphthylpentan*-γ-*one*-α-*ol*, $C_{10}H_6Cl \cdot CH(OH) \cdot CH_2 \cdot COEt$, is produced. This crystallises in large double pyramids, m. p. 124°, and is converted by the action of aqueous alcoholic potassium hydroxide into the abovementioned unsaturated ketone.

α-2-*Chloro*-1-*naphthylpentan*-γ-*one*, $C_{10}H_6Cl \cdot CH_2 \cdot CH_2 \cdot COEt$, is obtained in the form of a viscid oil by reducing the unsaturated chloroketone with aluminium amalgam in ethereal solution. Attempts to effect an internal condensation in the peri-position by the action of dehydrating agents yielded no definite results. When treated with semicarbazide, it yields a *substance*, $C_{16}H_{15}ON_2Cl$, the constitution of which has not yet been determined. F. B.

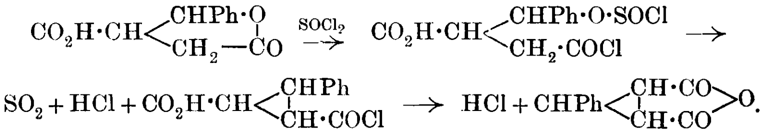
Labile Isomerides of the Same Structure, which can be Converted One into Another. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1911, **34**, 306—353).—The author gives the history of the discovery of the various isomerides of cinnamic acid discovered by Liebermann and Erlenmeyer, sen., and of the additions made to the knowledge of these acids by himself and his pupils. He considers that the following labile acids, of which the crystals have been measured, are known to exist, namely: *iso*Cinnamic acid of Erlenmeyer, sen., the *iso*cinnamic acid in dextrohemihedral and holohedral forms of Liebermann, hemihedral and holohedral forms of *allo*cinnamic acid, and triclinic cinnamic acid. There are, therefore, more isomerides than can be accounted for from the structure and chemical configuration, and the author explains the differences on the assumption of a difference of space disposition in some part of the molecule, the exact character of which is not yet known. He draws the following conclusions from the investigations summarised in this communication. The *iso*-acid as originally described by Erlenmeyer, sen., exists, and possesses the properties originally ascribed to it. It can be changed, however, into the *allo*-acid; it gives with aniline, as Liebermann showed, the aniline salt of the *allo*-acid. The latter acid on treatment with small quantities of an alcoholic solution of zinc bromide is converted into the Erlenmeyer *iso*-acid. The *iso*-acid (E) is also converted into the *allo*-form when left in contact with dilute sulphuric acid. The *iso*-acid of Liebermann prepared from natural sources also exists, and has m. p. 58—59° (from light petroleum); it spontaneously changes into the *allo*-acid, and can be prepared by the reduction of the α-bromo*allo*cinnamic acid. It is an actual modification and not merely a component of the *iso*-acid (L). In addition to existence in nature, it can also be prepared artificially: (*a*) by making the brucine salt of the *allo*-acid, and (*b*) by reduction of the α-bromo*allo*-acid. When the *allo*-acid is neutralised with brucine, two salts can be separated from one another by fractional crystallisation, which differ from one another in solubility, melting point, polarisation, etc. One of these yields the *iso*-acid (L) in hemihedral, and the other the *iso*-acid of holohedral, form. Possibly three brucine salts are formed when the acid is neutralised in this way. S. B. S.

Constitution of Dehydracetic Acid. WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1911, **33**, 1119—1135).—Evidence of a positive and of a negative character is advanced to support Feist's rather than Collie's formula of dehydracetic acid. The negative evidence is based on the fact that sodionitromalonic aldehyde, which reacts very readily with the group $\cdot CH_2\cdot CO\cdot CH_2\cdot$, does not attack dehydracetic acid. The positive evidence is of two kinds. Firstly, Goldschmiedt, Harries, and others have shown that aromatic aldehydes react with saturated asymmetrical ketones in two ways, preferably with the methyl group adjacent to the carbonyl group in alkaline solution, but with the methylene group in the presence of acid. Dehydracetic acid (and also dehydracetocarboxylic acid), constituted in accordance with Feist's views, allows of the formation of one benzylidene derivative by condensation with benzaldehyde. Collie's formulation of the two acids permits of the possibility of three ways of condensation, and the probability of the formation of two benzylidene compounds in acid solution. The facts are, however, that dehydracetic acid and dehydracetocarboxylic acid do not condense with benzaldehyde in acid solution, whilst in aqueous sodium hydroxide, one benzylidene compound of each is obtained; *benzylidenedehydracetocarboxylic acid*,  $CHPh\!:\!CH\cdot CO\cdot CH<\begin{matrix}CO\text{———}O\\CO\cdot C(CO_2H)\end{matrix}>CMe$, has m. p. 147—148° (corr.), and *benzylidenedehydracetic acid*,  $CHPh\!:\!CH\cdot CO\cdot CH<\begin{matrix}CO\text{—}O\\CO\cdot CH\end{matrix}>CMe$, has m. p. 105—106° (corr.), both compounds yielding dehydracetic acid by sublimation.

Further evidence against Collie's formula for dehydracetic acid is obtained by an examination of von Pechmann's synthesis of the acid from acetonedicarboxylic acid and acetic anhydride or acetyl chloride. Both Feist and Collie indicate possible courses of this reaction which lead each to his own constitution of dehydracetic acid. The author shows that acetonedicarboxylic acid, when heated on the water-bath with an excess of benzoic anhydride or benzoyl chloride, yields s-*dibenzoylacetonedicarboxylic acid*, $CO_2H\cdot CHBz\cdot CO\cdot CHBz\cdot CO_2H$, m. p. 162° (corr.), which reacts with acetic anhydride and a few drops of concentrated sulphuric acid, yielding dehydracetocarboxylic and benzoic acids, owing to a displacement of the benzoyl by acetyl groups. There is little doubt, therefore, that the initial step in von Pechmann's reaction is the direct interaction of the methylene hydrogen atoms of acetonedicarboxylic acid with the acetic anhydride; Collie's explanation would not permit of a reaction between acetonedicarboxylic acid and benzoic anhydride.

s-Dibenzoylacetonedicarboxylic acid contains four ionisable hydrogen atoms, decomposes when heated, and is easily hydrolysed to benzoic and acetonedicarboxylic acids. Its *diethyl* ester, $C_{23}H_{22}O_7$, m. p. 70·5° (corr.), contains two ionisable hydrogen atoms, also decomposes when heated, and does not react with acetic anhydride; it is hydrolysed by boiling aqueous barium hydroxide, yielding benzoic and acetonedicarboxylic acids. C. S.

Conversion of Substituted Paraconic Acids into the Isomeric *cyclo*Propanedicarboxylic Acids. PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Compt. rend.*, 1911, **153**, 188—191).—Phenylparaconic acid and terebic acid, when their solutions in about one and a-half times the weight of benzene are heated for twelve hours with thionyl chloride on the water-bath, are converted into the anhydrides of *cis*-3-phenyl*cyclo*propane-1 : 2-dicarboxylic acid and *cis*-3 : 3-dimethyl*cyclo*propane-1 : 2-dicarboxylic acid respectively, sulphur dioxide and hydrogen chloride being evolved. The reaction, which appears to be a general one for lactonic acids, follows probably the course :



$$CO_2H\cdot CH<\begin{matrix}CHPh\cdot O\\ CH_2—CO\end{matrix} \xrightarrow{SOCl_2} CO_2H\cdot CH<\begin{matrix}CHPh\cdot O\cdot SOCl\\ CH_2\cdot COCl\end{matrix} \rightarrow$$

$$SO_2 + HCl + CO_2H\cdot CH<\begin{matrix}CHPh\\ CH\cdot COCl\end{matrix} \rightarrow HCl + CHPh<\begin{matrix}CH\cdot CO\\ CH\cdot CO\end{matrix}>O.$$

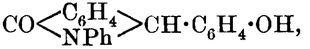
C. S.

Spectrographic Studies in the Phthalein Group. RICHARD MEYER and OTTO FISCHER (*Ber.*, 1911, **44**, 1944—1954).—With the object of ascertaining the cause of the difference in colour exhibited by the *p*-hydroxy- and di-*p*-hydroxy-derivatives of triphenylmethane, the authors have examined the ultra-violet absorption spectra of the sodium salts of phenolphthalein, tetrabromophenolphthalein, fluorescein, quinolphthalein, *p*-hydroxyphenylphthalide, and *p*-hydroxydiphenylphthalide in aqueous solution.

It is found that the spectra of the four first-named compounds are all similar in character, and show well-marked absorption bands, which, however, are lacking in the case of the salts of *p*-hydroxyphenylphthalide and *p*-hydroxydiphenylphthalide, but whether these results support the view put forward by Baeyer (Abstr., 1907, i, 754) that the colour of the disubstituted derivatives of triphenylmethane is due to a rhythmic movement in the molecule, whereby each of the two substituted benzene nuclei alternately acquire a quinonoid structure, has not been determined.

The following new derivatives of *p*-hydroxyphenylphthalide and *p*-hydroxydiphenylphthalide are described.

p-*Benzoyloxyphenylphthalide*, $CO<\begin{matrix}C_6H_4\\ O\end{matrix}>CH\cdot C_6H_4\cdot OBz$, crystallises in colourless, rectangular plates, m. p. 188°. p-*Ethoxyphenylphthalide*, $C_{16}H_{14}O_3$, prepared by the action of ethyl iodide and alcoholic sodium ethoxide on *p*-hydroxyphenylphthalide, forms rhombic plates, m. p. 116° ; the corresponding *benzyl ether*, $C_{21}H_{16}O_3$, crystallises in prismatic needles, m. p. 180°. The *anilide*,

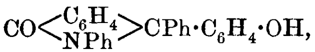


$$CO<\begin{matrix}C_6H_4\\ NPh\end{matrix}>CH\cdot C_6H_4\cdot OH,$$

prepared by heating *p*-hydroxyphenylphthalide with aniline and aniline hydrochloride, forms colourless needles, which become brown at 250° and have m. p. 267°.

p-*Benzoyloxydiphenylphthalide*, $CO<\begin{matrix}C_6H_4\\ O\end{matrix}>CPh\cdot C_6H_4\cdot OBz$, crystallises in triangular prisms, m. p. 139°.

p-*Ethoxydiphenylphthalide*, $C_{22}H_{18}O_3$, forms quadratic plates, m. p. 88° ; the *methoxy*-derivative, $C_{21}H_{16}O_3$, prepared by methylating *p*-hydroxydiphenylphthalide with methyl sulphate and potassium hydroxide, crystallises in rectangular prisms, m. p. 86° ; the *benzyl ether*, $C_{27}H_{20}O_3$, crystallises from glacial acetic acid in rectangular prisms, m. p. 109°.



The *anilide*, $CO{<}\substack{C_6H_4\\NPh}{>}CPh\cdot C_6H_4\cdot OH$, forms hexagonal plates, m. p. 276°. F. B.

Action of Nitric Acid on Trimethylgallic [3 : 4 : 5-Trimethoxybenzoic] Acid and its Methyl Ester. Constitution of Antiarol. HERMANN THOMS and W. SIEBELING (*Ber.*, 1911, **44**, 2115—2125).—When 3 : 4 : 5-trimethoxybenzoic acid in glacial acetic acid solution is treated with fuming nitric acid at – 15°, the carboxyl group is displaced by a nitro-group, with the formation of 5-nitropyrogallol trimethyl ether (compare Schiffer, Abstr., 1892, i, 715). Nitration under similar conditions, but at a higher temperature, results in the formation of 5 : 6-dinitropyrogallol trimethyl ether, which has m. p. 119°, and not 126°, as given by Will (Abstr., 1888, 457).

The nitration of methyl 3 : 4 : 5-trimethoxybenzoate yields either methyl 2-nitro-3 : 4 : 5-trimethoxybenzoate or *methyl* 2 : 6-*dinitro*-3 : 4 : 5-*trimethoxybenzoate*, according to the conditions under which the reaction is carried out. The last-named compound, which crystallises in colourless needles, m. p. 111°, is obtained by the gradual addition of fuming nitric acid to a glacial acetic acid solution of the ester, the reaction being completed by warming the mixture.

2-*Nitro*-3 : 4 : 5-*trimethoxybenzoic acid*, prepared by hydrolysing the corresponding methyl ester with alcoholic potassium hydroxide, crystallises from benzene in colourless prisms, m. p. 163—164°, which lose carbon dioxide when heated at 190—220°; the *silver* and *barium* salts were analysed. When warmed with strong nitric acid the carboxyl group is displaced by the nitro-group with the formation of 5 : 6-dinitropyrogallol trimethyl ether.

2 : 6-*Dinitro*-3 : 4 : 5-*trimethoxybenzoic acid*, $C_6(OMe)_3(NO_2)_2\cdot CO_2H$, obtained by the hydrolysis of the methyl ester with dilute alcoholic potassium hydroxide at the ordinary temperature, forms colourless needles, m. p. 158—160°, which become yellow on exposure to light; the *barium* salt crystallises in pale yellow prisms, the *silver* salt in yellow, microscopic needles. When heated at 194°, it loses carbon dioxide, yielding 4 : 6-*dinitropyrogallol trimethyl ether*,

$$C_6H(NO_2)_2(OMe)_3,$$

which forms large, yellow, transparent crystals, m. p. 85°. On further nitration by means of a mixture of fuming nitric and concentrated sulphuric acids below 20°, it is converted into 4 : 5 : 6-*trinitropyrogallol trimethyl ether*; this crystallises in slender, yellow needles, m. p. 128°.

Reduction of 6-nitropyrogallol trimethyl ether, followed by the displacement of the amino-group by hydroxyl by means of the diazo-reaction, gives rise to 5-hydroxypyrogallol trimethyl ether, m. p. 146°. The latter compound is identical with the phenol first obtained by Will (*loc. cit.*) by the partial methylation of dimethoxyquinol, and subsequently isolated by Kiliani (Abstr., 1897, i, 91) from the sap of *Antiaris toxicata*, under the name of antiarol. F. B.

Synthesis of Methyl Digallatepentamethyl Ether. FERDINAND MAUTHNER (*J. pr. Chem.*, 1911, [ii], **84**, 140—143).—The 3 : 4 : 5 : 2′ : 6′-*pentamethyl ether* of *methyl digallate*,

$$C_6H_2(OMe)_3 \cdot CO \cdot O \cdot C_6H_3(OMe)_2 \cdot CO_2Me,$$

is formed by shaking an ethereal solution of gallyl chloride trimethyl ether (Perkin and Weizmann, Trans., 1906, **89**, 1655) with an aqueous solution of the sodium derivative of methyl syringate (Graebe and Martz, Abstr., 1905, i, 703), and crystallises from a mixture of benzene and light petroleum in needles, m. p. 169—170°. When boiled for ten hours with aqueous alcoholic potassium hydroxide, it yields the trimethyl ether of gallic acid and syringic acid, which can be separated by means of their calcium salts. J. J. S.

Formation of Benzaldehyde and 2 : 4 : 6-Tribromoaniline from 3 : 5-Dibromo-4-aminobenzhydrol by the Action of Bromine. LATHAM CLARKE and GUSTAVUS J. ESSELEN, jun. (*J. Amer. Chem. Soc.*, 1911, **33**, 1135—1140).—*p*-Aminobenzophenone is conveniently obtained by heating benzoyl chloride (2 mols.) and aniline for fifteen minutes at 170—180°, then adding zinc chloride, and heating again for ten hours at 200—210° (compare Chattaway, Trans., 1904, **85**, 394); the resulting *p*-benzoylaminobenzophenone is hydrolysed by alcoholic sodium hydroxide.

By treatment with bromine (2 mols.) in dry chloroform, *p*-aminobenzophenone yields 3 : 5-*dibromo*-4-*aminobenzophenone*, m. p. 146°, which is reduced by aluminium amalgam to 3 : 5-*dibromo*-4-*aminobenzhydrol*, m. p. 147·5°. This substance, by bromination (1 mol.) in dry chloroform, is decomposed into benzaldehyde, hydrogen bromide, and 2 : 4 : 6-tribromoaniline. The formation of the last compound is the proof of the position of the halogen atoms in 3 : 5-dibromo-4-aminobenzophenone. C. S.

Steric Hindrance. PAVEL IW. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1911, [ii], **84**, 143—144. Compare Abstr., 1910, i, 177).—It is pointed out that Stewart (this vol., i, 210) admits that steric hindrance affords a simple explanation of the phenomena met with in the study of cyclic ketones and amines. J. J. S.

The Study of Hydro-aromatic Substances. EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Reports*, 1910, 82—84).—This report deals with the action of ethyl cyanoacetate on 5-chloro-1 : 1-dimethyl-Δ^4-*cyclo*hexen-3-one (Trans., 1910, **97**, 518) with 3 : 5-dichloro-*o*-xylene and 3 : 5-dichlorophthalic acid (Trans., 1910, **97**, 98), and also with the preparation of 1 : 1 : 2-trimethyl*cyclo*hexan-3-one from trimethyldihydroresorcin. T. S. P.

New Method of Synthesis of Methyl Ketones. PHILIPPE BARBIER and RÉNÉ LOCQUIN (*Bull. Soc. chim.*, 1911, [iv], **9**, 722—726). —In a previous paper (this vol., i, 708), mention was made of a new method of preparing methyl ketones. This has now been worked out as a general method, and it has been applied in particular to the preparation of benzyl methyl ketone from methyl dimethylacetoacetate and magnesium benzyl chloride. A 40% yield resulted. In general, organo-magnesium compounds of the type R·Mg·X, by condensation with an ester of the type $\begin{smallmatrix}R_1\\R_2\end{smallmatrix}>C<\begin{smallmatrix}CO\cdot CH_3\\CO_2R_3\end{smallmatrix}$ and subsequent saponification, will yield the ketone $R\cdot CO\cdot CH_3$. Condensation with an ester of the type $CHR_1\colon C<\begin{smallmatrix}CO\cdot CH_3\\CO_2X\end{smallmatrix}$ yields a branched ketone of the type $CH_3\cdot CO\cdot CH_2\cdot CH<\begin{smallmatrix}R\\R_1\end{smallmatrix}$. W. G.

Ketones of the Type of α-Benzyl-αα-dimethylacetophenone. Trialkylacetic Acids and Trialkylmethylcarbinols to which They Give Rise.

Albin Haller and Édouard Bauer (*Compt. rend.*, 1911, **153**, 21—27. Compare Abstr., 1909, i, 654).—The general method already described has been applied to the synthesis of new ketones from phenyl *iso*propyl ketone. The sodium derivative of this substance treated with *o*-xylyl bromide gives *α-o-xylyl-αα-dimethylacetophenone*, $COPh\cdot CMe_2\cdot CH_2\cdot C_6H_4Me$, b. p. 199—200°/15 mm.; the m-*xylyl* derivative is an oil, b. p. 196—197°/12 mm., whilst the p-*xylyl* derivative has b. p. 200—202°/13 mm. *α*-p-*Methoxybenzyl-αα-dimethylacetophenone*, $COPh\cdot CMe_2\cdot CH_2\cdot C_6H_4\cdot OMe$, is a viscid liquid, b. p. 222—224°/15 mm.

The new ketones react normally with sodamide, giving rise to the following amides. o-*Tolyl-α-methyl*iso*butyramide*, pearly spangles, m. p. 62—63°, b. p. 188—192° in a vacuum; o-*tolyl-α-methyl*iso*butyric acid*, $C_7H_7\cdot CH_2\cdot CMe_2\cdot CO_2H$, has m. p. 48°, b. p. 180—181°/16 mm. m-*Tolyl-α-methyl*iso*butyramide* has m. p. 46—47°, and the p-*tolyl* derivative, m. p. 85—86°; the two corresponding *acids* have b. p. 178°/16 mm. and m. p. 53—54°, b. p. 180°/16 mm. respectively. p-*Anisyl-α-methyl*iso*butyramide* separates from ether in prisms probably containing ether of crystallisation, m. p. 72°, after resolidification m. p. 99—100°; the *acid* has m. p. 52—53°.

On reduction with sodium and alcohol, *o*-tolyl-α-methyl*iso*butyramide gives an 80% yield of the *carbinol*, $C_7H_7\cdot CH_2\cdot CMe_2\cdot CH_2\cdot OH$, b. p. 142—143°/15 mm., and a 5—7% yield of o-*xylyldimethylethylamine*, $C_7H_7\cdot CH_2\cdot CMe_2\cdot CH_2\cdot NH_2$, b. p. 129—130°/13 mm.; the *platinichloride* is crystalline. The corresponding m-*xylyl-carbinol* has b. p. 139—140°/16 mm., and the *amine*, b. p. 134—135°/15 mm. The p-*xylyl-carbinol* has m. p. 37°, b. p. 141°/15 mm. p-*Anisyl-β-methyl*iso*butyl alcohol*, $C_7H_7O\cdot CH_2\cdot CMe_2\cdot CH_2\cdot OH$, has m. p. 50°.

W. O. W.

Synthesis of Substituted β-Diketones, Ketonic Esters, and Enolic Esters by means of Ketones and Sodamide.

Albin Haller and Edmond Bauer (*Compt. rend.*, 1911, **153**, 145—152).—The sodium derivative of a ketone, $R\cdot CO\cdot CHR'_2$, reacts with acid chlorides as though $R\cdot CO\cdot CNaR'_2$ and $R\cdot C(ONa)\colon CR'_2$ were both present, but with ethyl β-iodopropionate as though only the former is present. Thus phenyl *iso*propyl ketone, sodamide, and benzoyl chloride yield *ββ-dibenzoylpropane*, CBz_2Me_2, b. p. 195—196°/

15 mm., m. p. 99—100° (*oxime*, NOH:CPh·CBzMe$_2$, m. p. 166°), and *a-phenyl-ββ-dimethylvinyl benzoate*, CMe$_2$:CPh·O·COPh, b. p. 194—196°/13·5 mm., m. p. 53—54°; the latter does not form an oxime, and is hydrolysed by cold alcoholic potassium hydroxide or 1% methyl-alcoholic hydrogen chloride, whilst the former is converted into benzoic acid and phenyl *iso*propyl ketone by boiling alcoholic potassium hydroxide. Similarly, *iso*propyl *tert.*-butyl ketone, sodamide, and benzoyl chloride in benzene yield *β-benzoyl-β-pivaloylpropane*, CMe$_3$·CO·CMe$_2$·COPh, m. p. 35° (*oxime*, m. p. 178°), and an oil which is shown to contain the *benzoate*, CMe$_2$:C(OBz)·CMe$_3$. Pivaloyl chloride, *iso*propyl *tert.*-butyl ketone, and sodamide in benzene yield a liquid, b. p. 213—214° or 102°/18 mm., which doubtless is a mixture of ββ-dipivaloylpropane and the isomeric enolic ester; it does not form an oxime or semicarbazone.

Ethyl β-iodopropionate, phenyl *iso*propyl ketone, and sodamide in ether yield mainly *ethyl γ-benzoyl-γ-methylvalerate*,

CBzMe$_2$·CH$_2$·CH$_2$·CO$_2$Et,

b. p. 183°/13 mm. (*oxime*, m. p. 119—120°), which is hydrolysed by potassium hydroxide to the *acid*, an oil which forms an *oxime*, NOH:CPh·CMe$_2$·CH$_2$·CH$_2$·CO$_2$H, m. p. 123—124°. Under similar conditions ethyl β-iodopropionate and phenyl propyl ketone yield *ethyl γ-benzoylhexoate*, CO$_2$Et·CH$_2$·CH$_2$·CHEtBz, b. p. 189—191°/15 mm. (p-*nitrophenylhydrazone*, yellow crystals, m. p. 205°).

Summarising this and Claisen's work, it is seen that with the sodium derivatives of ketones: (1) acid chlorides and ethyl chloroformate yield isomeric C and O derivatives; (2) ethyl chloro- or bromo-acetate yields glycide esters; (3) ethyl β-iodopropionate, like the alkyl halides, reacts normally and yields δ-ketonic esters. C. S.

Explanation of the Reaction between *p*-Benzoquinone and Hydrogen Chloride. Julius Schmidlin (*Ber.*, 1911, **44**, 1700—1705. Compare Posner, Abstr., 1904, i, 1029; 1909, i, 809; Michael, Abstr., 1904, ii, 164; 1909, i, 494; 1910, i, 748).—The author draws attention to the equilibrium which exists between *p*-benzoquinone and chloroquinol on the one hand, and chloro-*p*-benzoquinone and quinol on the other: $O:C_6H_4:O + C_6H_3Cl(OH)_2 \rightleftharpoons O:C_6H_3Cl:O + C_6H_4(OH)_2$.

In the reaction between hydrogen chloride and quinone the conclusion is drawn that the quinone combines with hydrogen chloride, and that the resulting chloroquinol reacts with the quinone, yielding chloro-*p*-benzoquinone and quinol. The equilibrium is disturbed by the separation of quinol in the form of the sparingly soluble quinhydrone, and thus all the free *p*-benzoquinone is transformed into chloro-*p*-benzoquinone and quinhydrone. A subsidiary reaction is that of hydrogen chloride on the quinone present in the form of quinhydrone, the formation of chloroquinol and quinol, and the reaction between the quinol and chloro-*p*-benzoquinone, resulting in the formation of *p*-benzoquinone and chloroquinol.

Hydrogen bromide behaves in a somewhat similar manner, except that the bromo-*p*-benzoquinone can react with hydrogen bromide, forming dibromoquinol.

When saturated solutions of *p*-benzoquinone and chloroquinol or of chloro-*p*-benzoquinone and quinol are mixed, the precipitate formed consists of nearly pure quinhydrone. The best solvent for the first pair of compounds is water, and for the second pair ether or chloroform.

These results confirm the conclusion drawn by Wichelhaus (Abstr., 1880, 42) that it is impossible to obtain a pure chloroquinhydrone by bringing together quinone and a chlorinated quinol. The products described by Ling and Baker (Trans., 1893, **63**, 1314) are mixtures.

When *p*-benzoquinone and chloroquinol are brought together in benzene solution, a chloroquinhydrone is first formed, but when this is heated with the benzene for some time, reaction takes place, and the non-chlorinated quinhydrone is formed on cooling.

Chloro-*p*-benzoquinone has a pale lemon-yellow, and not a yellowish-red, colour. J. J. S.

Quinonoid Compounds. XXVI. *o*-Quinones. RICHARD WILLSTÄTTER and FRITZ MÜLLER (*Ber.*, 1911, **44**, 2171—2181. Compare Abstr., 1908, i, 731).—The following substances have been prepared in the hope of throwing some light on the conditions of equilibrium of the two desmotropic forms of *o*-benzoquinones. The method is that used previously (*loc. cit.*)—rapid oxidation of the corresponding catechol in dry ether by dry silver oxide in the presence of anhydrous sodium sulphate. All of the quinones form stable, deep red crystals, the colourless form being observed only in the case of homo-*o*-benzoquinone; frequently, however, the product of oxidation is obtained in yellow crystals, which are probably mixtures of the red and the colourless modifications. The red forms are shown to be unimolecular. The instability of the colourless forms negatives the suggestion that they may be polymerides; moreover, since they give the reactions of quinones, whilst the bimolecular forms described below do not, it is justifiable to assume that the colourless forms also are unimolecular.

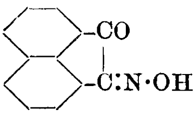
The oxidation of homocatechol under the stated conditions yields *homo*-o-*benzoquinone* [3 : 4-*toluquinone*], $O:C_6H_3Me:O$. Only occasionally, by treating the freshly oxidised solution with petroleum and cooling rapidly in a freezing mixture, have colourless crystals been observed. Usually, by rapid evaporation of the solvent, yellow (mixed) crystals, m. p. 65—67°, are obtained; by recrystallisation they yield the deep red form, m. p. 80—84°, which is more stable than *o*-benzoquinone itself. The substance is readily reduced by cold saturated sulphurous acid. When exposed to sunlight or warmed in ether or acetone, it changes to a *bimolecular* form, $(C_7H_6O_2)_2$, yellow, rhombic prisms, m. p. 124—125°, which has not been depolymerised.

iso*Homo*-o-*benzoquinone* [2 : 3-*toluquinone*], prepared from 2 : 3-dihydroxytoluene, forms unstable dark red prisms and needles, and polymerises, by warming or keeping its ethereal solution, to the *bimolecular* form, m. p. 194—195°, yellow, monoclinic prisms and plates. 3-*Methoxy*-1 : 2-*benzoquinone*, $O:C_6H_3(OMe):O$, m. p. 115—120°, obtained from pyrogallol 1-methyl ether, forms dark red crystals; the stability is such that its solutions in alcohol, water, or dilute sulphuric acid exhibit the reactions of *o*-quinones.

The oxidation of hydroxyquinol by silver oxide yields a quinone which is shown to be *hydroxy*-p-*benzoquinone* by its yellow colour, stability, tendency to form a *quinhydrone* (greenish-black prisms), similarity to the long-known methoxy-*p*-benzoquinone, and difference from 3-methoxy-*o*-benzoquinone. It darkens at 120—124°, and is easily reduced to hydroxyquinol. C. S.

Quinonoid Compounds. XXVII. Chloro-derivatives of Catechol and of *o*-Benzoquinone. RICHARD WILLSTÄTTER and HANS EDUARD MÜLLER (*Ber.*, 1911, **44**, 2182—2191).—Peratoner states that the chlorination of phenols by sulphuryl chloride yields only para-substituted derivatives; with catechol in ether, however, the authors get about 1% of the ortho-isomeride, which is separated by its greater solubility in benzene and its lower b. p. Pure *p*-chlorocatechol has b. p. 136—136·5°/8·5 mm., and a double m. p. It melts at 90—91°; after resolidification, it melts at 59—61°, again becomes solid, and then has m. p. 90° again. The *diacetate* has b. p. 145—147°/7·5 mm., and the *dibenzoate* has m. p. 96—97°. *o*-Chlorocatechol has b. p. 110—111°/11 mm., and m. p. 46—48°; its *dibenzoate* has m. p. 108—109°. 4:5-Dichlorocatechol has m. p. 116—117° (Peratoner and Vitali give 105—106°), and forms a *dibenzoate*, m. p. 140—140·5°. By treating an alcoholic solution of tetrachlorocatechol with water, a *trihydrate*, $C_6Cl_4(OH)_2,3H_2O$, m. p. 94°, is obtained. *o*-Benzoquinone is rapidly dissolved and decolorised by 2% ethereal hydrogen chloride, yielding a mixture of *o*- and *p*-chlorocatechols. 4-*Chloro*-o-*benzoquinone*, m. p. 78° (decomp.), is obtained from *p*-chlorocatechol by the silver oxide method, and crystallises in red needles, which cannot be kept long without decomposing. 3-*Chloro*-o-*benzoquinone*, obtained by oxidising *o*-chlorocatechol with silver oxide or lead peroxide, forms red prisms, which decompose at about 68°. 4:5-*Dichloro*-o-*benzoquinone*, yellow or yellowish-red prisms and plates, m. p. 94° (decomp.), is considerably more stable than the monochlorobenzoquinones. It forms a *quinhydrone*, $C_{12}H_6O_4Cl_4$, glistening, black prisms, decomp. 85°, with the corresponding catechol. The monochloro- and non-halogenated *o*-benzoquinones do not form quinhydrones. C. S.

A New Method for Obtaining Acenaphthenequinone from Acenaphthene. ARNOLD REISSERT (*Ber.*, 1911, **44**, 1749—1752).—A mixture of two isomeric acenaphthenequinone monoximes (annexed constitution) is formed when amyl nitrite (4 mols.) is added to a boiling amyl-alcoholic solution of acenaphthene while a stream of hydrogen chloride is passed through the solution. The amyl alcohol is removed by steam distillation, the oximes extracted with sodium hydroxide solution, and separated by means of their different degrees of acidity. The one oxime is insoluble in hot sodium carbonate solution, and crystallises from glacial acetic acid in soft, faintly yellow crystals, m. p. 207° (decomp.). When the oxime is boiled for some time with glacial acid it yields the isomeric oxime (Francesconi and Pirazzoli, Abstr., 1903, i, 500), which has



m. p. 220°, but then solidifies, and again melts at 290—300°. The quinone can be obtained by hydrolysing the monoxime with 75% sulphuric acid at 100°. J. J. S.

The Catalysis of Borneol and the Catalytic Hydrogenation of Camphor.

Jules Aloy and V. Brustier (*Bull. Soc. chim.*, 1911, [iv], **9**, 733—735).—The authors have employed the method of Sabatier and Senderens (Abstr., 1905, i, 401) in transforming borneol into camphor. The three metals nickel, iron, and copper have been tried, copper being the best. The optimum temperature is 300°, when the yield is theoretical. Above this temperature, terpene-like products are formed.

The hydrogenation of camphor in the presence of reduced nickel was not successful, but in the presence of this metal, camphoroxime was readily transformed into amines, the secondary amine predominating. W. G.

Hydrogenation of Carvone.

Gustave Vavon (*Compt. rend.*, 1911, **153**, 68—71. Compare this vol., i, 657).—The reduction of carvone at the ordinary temperature by hydrogen in presence of platinum-black takes place in three stages, corresponding with the formation of carvotanacetone, tetrahydrocarvone, and carvomenthol. This furnishes the most convenient method for preparing *d*-carvotanacetone; the product has b. p. 227—228°, D_4^{18} 0·937, n_D^{18} 1·4817, $[\alpha]_D$ 59·8°. The final stage of the reduction takes place with greater difficulty. W. O. W.

Specific Rotatory Power of Camphor in Acetone Solution.

H. Malosse (*Compt. rend.*, 1911, **153**, 56—57).—The specific rotation of camphor in acetone at different temperatures and concentrations is shown in a tabular statement. The results have been plotted in the form of a curve, and the equations to the different parts of the curve calculated. W. O. W.

The Isomeric Tanacetyl Alcohols.

Vincenzo Paolini (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 765—769).—By recrystallisation of the hydrogen phthalates of the mixture of alcohols obtained by reduction of tanacetone from the natural oil, and subsequent saponification, the author has isolated a pure *d*-tanacetyl alcohol, and has obtained indications of the presence of the corresponding *l*-compound in the mother liquor. R. V. S.

Some Derivatives of *d*-Tanacetyl Alcohol.

Vincenzo Paolini (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 769—772).—The tanacetyl alcohol employed had b. p. 206—209°, D^{20} 0·925, n_D 1·4635, $[\alpha]_D$ 69·49°. This was dissolved in light petroleum and treated with sodium, and the sodium derivative produced was added to the calculated quantity of phthalic anhydride in light petroleum. The product is a mixture of several esters, from which by repeated crystallisation a pure *tanacetyl hydrogen phthalate*, $C_{18}H_{22}O_4$, was obtained in tufts of colourless needles, m. p. 120°, $[\alpha]_D + 91·27°$. Its *silver* salt, $C_{18}H_{21}O_4Ag$, has m. p. 85—86°. The *calcium* salt, $(C_{18}H_{21}O_4)_2Ca$, was also prepared.

The *strychnine* salt, $C_{18}H_{21}O_4,C_{21}H_{22}O_2N_2$, has m. p. 177—178°, $[\alpha]_D$ 36·78°.

When the phthalate is saponified with alcoholic potassium hydroxide, d-*tanacetyl alcohol* (β-thujyl alcohol) is obtained. It is an oily liquid, b. p. 206°, D 0·9229, n_D^{16} 1·4625, $[\alpha]_D$ 114·67°. When treated with sodium and phthalic anhydride it regenerates the above-mentioned phthalate, and if it is oxidised with chromic acid it yields a ketone, the semicarbazone of which has all the properties of Wallach's β-tanacetonesemicarbazone (Abstr., 1905, i, 147). R. V. S.

Isoprene from Terpene Hydrocarbons. HERMANN STAUDINGER and HELMUT W. KLEVER (*Ber.*, 1911, **44**, 2212—2215).—By passing the vapour of turpentine through an iron tube at a dark red heat, Tilden obtained a small yield of isoprene, the chief products being hydrocarbons of high b. p. (Trans., 1879, **46**, 417). The yield of isoprene is materially increased by working under diminished pressure, but it can be obtained in 60% yield by passing the vapour of dipentene or limonene, under 20—30 mm. or better still 2—3 mm., over an electrically heated platinum spiral. The isoprene thus obtained is almost pure, and contains very little trimethylethylene; the by-products are gaseous substances (olefines and acetylenes) and hydrocarbons, b. p. 100—150°. Terpinolene, terpinene, and camphene give little or no isoprene under these conditions. C. S.

isoCamphane. PETER LIPP (*Annalen*, 1911, **382**, 265—305).—Camphene has been reduced under varying conditions, and the saturated, dicyclic hydrocarbons, $C_{10}H_{18}$, obtained were oxidised in different ways. The symmetrical, saturated cyclic hydrocarbon corresponding with bornylene should be termed bornylane, but as the name camphane has been generally used in chemical literature for this compound, the term is retained and the unsymmetrical, saturated isomeride is termed *iso*camphane (compare Semmler, *Die Aetherische Oele*, 1906, ii, 62).

Technical camphene obtained from pinene hydrochloride was purified by distillation, and the middle fraction, b. p. 155·5—157°/723 mm., after four crystallisations from aqueous alcohol had m. p. 45° and $[\alpha]_D^{22}$ $-18·94°$. The hydrocarbon was not affected when treated with sodium and boiling ethyl alcohol, but was reduced by Sabatier and Senderens' method, using finely-divided nickel distributed over a pumice surface and kept at 170—190°. After a mixture of hydrogen and the vapour of the hydrocarbon had been passed through the tube three times, the product did not decolorise a chloroform solution of bromine. The product consisted of a mixture of an oily and a solid hydrocarbon. The liquid *iso*camphane is formed in small quantities only, and is probably the reduction product of an impurity (Aschan's pinolene) present in the camphene, as it does not appear to be formed when pure camphene, prepared from *iso*borneol, is used. It has b. p. 160—162°, $[\alpha]_D^{19}$ $+1·15°$ in 10% methyl-alcoholic solution, D^{20} 0·8524, and n_D^{20} 1·45733. The solid isomeride crystallises from methyl alcohol in fern-like masses resembling camphene or ammonium chloride; it has m. p. 65—67° after repeated crystallisation, and is practically inactive. A specimen obtained from pure camphene from *iso*borneol had m. p. 61·5—63°. The reduction of inactive camphene by Fokin's method (*Zeitsch. angew. Chem.*, 1909, **22**, 1496) in ethereal solution and in presence of platinum sponge gave a product with b. p. 164°/713 mm. and m. p. 63—64·5° (corr.). A specimen of *l*-camphene with $[\alpha]_D^{19}$ $-80·7°$ and m. p. 44—44·5° when reduced in a similar manner had b. p. 166—166·5° (corr.)/750 mm. and m. p. 62—63° (corr.) after five crystallisations. The solid *iso*camphane has the consistency of paraffin wax, and in appearance closely resembles camphene; its odour is not quite so pronounced, and it is extremely volatile even at the ordinary temperature. It forms an exception to the generalisation that a saturated compound has a lower b. p. than its unsaturated analogue. It has D_4^{67} 0·82757, n_C 1·43982, n_D 1·44186, and n_G 1·45239 at 67°.

Attempts made to reduce *iso*camphane by means of hydriodic acid and iodine under pressure were unsuccessful; after five hours at 240—250° an isomeric hydrocarbon, $C_{10}H_{18}$, with b. p. 157·5—160·5°, D_4^{20} 0·8344, was obtained, but this was not homogeneous.

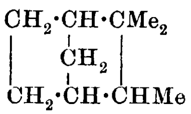
The contradictory statements of Zelinsky (*J. Russ. Phys. Chem. Soc.*, 1904, **36**, 768) and Sabatier and Senderens (Abstr., 1901, i, 159; compare Henderson and Pollock, Trans., 1910, **97**, 1620) are probably due to the fact that Sabatier and Senderens used an impure specimen of camphene and obtained on reduction a solution of solid *iso*camphane in the liquid isomeride.

Contrary to Sabatier's statement, *iso*camphane is comparatively stable towards oxidising agents. It is most readily oxidised by adding powdered permanganate to a warm 50% acetic acid solution of the hydrocarbon. Among the products are unaltered hydrocarbon (60%), a product containing oxygen and with an odour of camphor, a mixture of camphenilone and camphenilanaldehyde, together with camphenilanic acid and *iso*camphenilanic acid (Bredt and Jagelki, Abstr., 1900, i, 134). A mixture of the calcium salts of the two acids is less soluble in hot than in cold water, although each salt independently is more soluble. *Camphenilanaldehydesemicarbazone*, $C_{11}H_{19}ON_3$, crystallises from dilute alcohol in colourless plates, m. p. 200° (decomp.).

When *iso*camphane is oxidised with nitric acid (D 1·4) for 8·5 hours at 100° under pressure, the products are camphene nitrosite, camphenil nitrite, and camphenilone (compare Jagelki, Abstr., 1899, i, 627), together with resinous compounds.

When the hydrocarbon is boiled for twelve hours with the nitric acid the same products are obtained, and in addition *iso*camphoronic acid and carboxy*apo*camphoric acid (camphoic acid: Marsh and Gardner, Trans., 1896, **69**, 74). The normal ammonium salt of the latter acid has m. p. 213—214° (decomp.) (Marsh and Gardner, 198—199°).

The formation of camphenilanic acid and its isomeride indicates that *iso*camphane and camphene have the same ring system, and the annexed structural formula is accepted. The formation of camphoic acid from this hydrocarbon must be accompanied by molecular rearrangement.



$$\begin{array}{l}CH_2\cdot CH\cdot CMe_2\\ \Big| \quad\quad CH_2 \quad \Big|\\ CH_2\cdot CH\cdot CHMe\end{array}$$

The high m. p. for *iso*camphane observed by Vavon (Abstr., 1910, i, 52) is probably due to the presence of camphane. J. J. S.

Constituents of Ethereal Oils. I. Identity of the Aliphatic Terpene from Oil of Hops with Myrcene. II. Methyl Esters of Dicarboxylic Acids. III. Preparation of *iso*Bornylformate. FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1911, **44**, 2009—2012).—I. Chapman (Trans., 1903, **83**, 505) has suggested the identity of the aliphatic terpene, $C_{10}H_{16}$, from oil of hops with myrcene. A colourless, mobile, almost odourless oil is now obtained from oil of hops, b. p. 62—63°/17 mm., D^{20} 0·7937, n_D 1·4716. On reduction, a compound identical with dihydromyrcene is obtained, characterised by the crystalline tetrabromide, m. p. 87°. On heating with sulphuric and acetic acids, myrcenol, $C_{10}H_{18}O$, is formed from the hop oil terpene.

II. *Methyl* iso*fenchonecarboxylate*, $C_{12}H_{20}O_4$, has b. p. 131—132°/14 mm., D^{20} 1·0515, n_D 1·4540.

Methyl camphorate has b. p. 137—139°/14 mm. (Brühl and Braunschweig give 155°/15 mm).

Methyl α-tanacetogencarboxylate, $C_{12}H_{20}O_4$, has b. p. 129—130°/15·5 mm., D^{23}_{20} 1·0525, n_D 1·451.

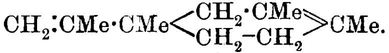
Methyl β-methyladipate has b. p. 122—122·5°/18 mm., D^{20} 1·0372, n_D 1·4336.

III. Camphene when boiled with formic acid yields *iso*bornylformate, $C_{11}H_{20}O_2$, b. p. 91—93°/11 mm., D^{20} 1·005, n_D 1·4726.

E. F. A.

Dimethyldipentene Produced by the Dry Distillation of Dimethylcaoutchouc. A. H. RICHARD (*Compt. rend.*, 1911, **153**, 116—120).—Couturier's βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene behaves, during its polymerisation, exactly like its lower homologue, isoprene. When submitted to the prolonged action of diffused light, it changes into a viscous, bimolecular form, and finally into a white mass having, in physical and chemical properties, a close resemblance to natural rubber. When polymerised by heating at about 150° for some thirty hours, dimethylbutadiene is converted into a viscous liquid, which is separated by distillation with steam into unchanged hydrocarbon and the polymerised product, homocaoutchouc; however long the heating, the reaction seems to be reversible.

By dry distillation, homocaoutchouc yields: (i) βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene, b. p. 69—70°; (ii) a *sesquihomoterpene*, $C_{18}H_{30}$, b. p. 175—180°/22 mm., D^0 0·912; (iii) polyhomoterpenes of higher b. p.; (iv) a *homoterpene*, $C_{12}H_{20}$, b. p. 205° or 97—98°/22 mm, D^0 0·872. The last hydrocarbon should, from analogy to the production of dipentene from isoprene, be *dimethyldipentene*,



$$CH_2{:}CMe{\cdot}CMe<\begin{matrix}CH_2{\cdot}CMe\\CH_2{-}CH_2\end{matrix}\gg CMe.$$

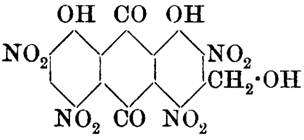
Its molecular refraction, calculated from D^{25}_4 0·85322 and n_D 1·47786, agrees well with the formula $C_{12}H_{20}|\overline{\ }_2$. The substance forms a viscous *tetrabromide* and a *hydrochloronitrosochloride*,

$$C_{12}H_{20},NOCl,HCl,$$

a yellow powder, decomp. 160°, and by reduction with hydrogen and platinum-black yields a *hydrocarbon*, $C_{12}H_{22}$, b. p. 93—95°/20 mm., D_4^{25} 0·842307, and n_D 1·46635. C. S.

Constitution of Nitro-compounds Obtained by the Action of Nitric Acid on Aloins.

EUGÈNE LÉGER (*Compt. rend.*, 1911, **153**, 114—116).—The author has shown previously that barbaloin and *iso*barbaloin are converted by nitric acid into a tetranitroaloemodin, which yields chrysammic acid and 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid by further treatment with nitric acid. Experiments are described now to prove that the trinitro-*m*-hydroxybenzoic acid is formed, not independently of the tetranitroaloemodin, but at the expense of some of the chrysammic acid. Assuming that Robinson and Simonsen's constitution (Trans., 1909, **95**, 1088) of the latter is correct, and remembering that the majority of the compounds obtained from the aloins are derivatives of β-methylanthraquinone, it follows that tetranitroaloemodin must be represented by the annexed constitution. Since the aloins are glucosides of aloemodin and *d*-arabinose, the author is of opinion that the arabinose molecule is attached to the phenolic hydroxyl group in position 1 in barbaloin, and to the phenolic hydroxyl group in position 8 in *iso*barbaloin. C. S.



Glucosides from the Leaves of Digitalis purpurea.

F. KRAFT (*Schweiz. Wochensch. Chem. Pharm.*, 1911, Nos. 12, 13, 17; Reprint, 9 pp.).—*Gitalin*, m. p. 150—155°, obtained from the cold aqueous extract of *Digitalis* leaves by means of chloroform, is a white, amorphous glucoside of neutral reaction, which is soluble in 600 parts of cold water. It is soluble in most of the usual solvents, but the solutions decompose more or less quickly. By the addition of water to its alcoholic solution, the glucoside is converted into crystalline *gitalin hydrate*, m. p. 75°, which is soluble in about 3000 parts of water.

The decomposition of gitalin in solution is accomplished best by the evaporation of an alcoholic solution in a vacuum, whereby *anhydrogitalin*, m. p. 255°, a crystalline glucoside quite insoluble in water, is obtained. Anhydrogitalin is hydrolysed by alcohol and 10% hydrochloric acid on the water-bath, yielding *anhydrogitaligenin*, m. p. 119° (which closely resembles anhydrodigitoxigenin), and two sugars, Kiliani's digitoxose and another, which is not crystallisable.

The literature of digitoxin is very confused. The digitoxin obtained by Keller is claimed by Burmann to be identical with his ψ-digitoxin (which appears to be identical with gitalin). This cannot be so, because Keller's digitoxin is insoluble in water. The author states that gitalin, in the form of its hydrate or of anhydrogitalin, is the chief constituent, not only of Keller's, but of all commercial, digitoxins.

Digitalinum verum was obtained by Kiliani from the seeds of *Digitalinum germanicum*; it is also present in minute amount in the leaves.

Confusion has also arisen in the literature from the fact that the name digitonin is given to two substances, Schmiedeberg's amorphous glucoside, and Kiliani's crystalline, inactive glucoside. The author retains the name for the latter, and calls the former digitsaponin. From the dilute alcoholic extract of digitalis leaves he obtained an inactive *glucoside*, m. p. 265° (decomp.), which he regarded at first as identical with digitonin ; a direct comparison of the two substances, however, shows that they differ in many important properties. By hydrolysis digitsaponin yields amorphous sapogenins and two sugars, one of which is a pentose, the other dextrose. C. S.

Phloridzin- and Phloretin-glycuronic Acids. Jos. SCHÜLLER (*Zeitsch. Biol.*, 1911, **38**, 274—308).—See this vol., ii, 814.

Action of Light of Mercury Lamp on Solutions of Chlorophyll. HENRI BIERRY and J. LARGUIER DES BANCELS (*Compt. rend.*, 1911, **153**, 124—125).—Alcoholic solutions of chlorophyll (from spinach) in quartz vessels are exposed to the light of two mercury vapour lamps for twenty-four to forty-eight hours. The solutions become faintly yellow, and no longer show the absorption bands characteristic of chlorophyll. Tests for urobilinogen were applied, with positive results. A benzene solution of chlorophyll becomes colourless under the same conditions, but does not show the colour reactions of urobilinogen. C. S.

Chemical Nature of *allo*-Chlorophyll. LEON MARCHLEWSKI and J. MARSZAŁEK (*Ber.*, 1911, **44**, 1705—1708. Compare Malarski and Marchlewski, Abstr., 1910, i, 692).—*allo*-Chlorophyllan can be obtained in appreciable amounts from maple leaves : thus, 20 grams of crude chlorophyllan gave 5·76 grams of the *allo*-compound. The compound contains 3% of methoxyl, and prolonged treatment with zinc hydroxide tends to diminish the percentage ; it also yields 31·8% of phytol, and when heated at 105° its properties change. The *allo*-chlorophyllanic acids, obtained by hydrolysing the product dried at 105°, are insoluble in ether. The acids have a cherry-red colour, whilst chlorophyllanic acids are olive-green.

With zinc acetate, *allo*-chlorophyllan yields a zinc derivative, zinc *allo*-chlorophyll, similar to zinc chlorophyll, but with a different absorption spectrum. It is questionable whether *allo*-chlorophyll yields phylloporphyrin, but it is suggested that it contains two carboxyl groups, one present as methyl, and the other as phytyl, ester.
J. J. S.

The Chlorophyll Group. X. Phyllohæmin. II. LEON MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1911, **34**, 275—279). —Phyllohæmin was prepared by treatment of phylloporphyrin in warm acetic acid saturated with sodium chloride with permanganate. The substance which separated, after washing free from excess of sodium chloride and iron salt, was recrystallised by Schalféeff's method, that is, by dissolving in chloroform containing quinine, throwing the solution into acetic acid saturated with sodium chloride and kept at 90°, and allowing the mixture to cool. The measurement of the spectral bands and other properties showed a marked similarity between this preparation and the blood-hæmin. S. B. S.

Quinonoid Compounds. XXV. Aniline Black. V. Richard Willstätter and Carl Cramer (*Ber.*, 1911, **44**, 2162—2171. Compare Abstr., 1909, i, 535, 975).—A criticism of Green and Woodhead's paper (Trans., 1910, **97**, 2388). These authors agree with Willstätter and Dorogi (*loc. cit.*) that the oxidation products of aniline are derivatives of the leuco-base,

$$NHPh\cdot[C_6H_4\cdot NH]_6\cdot C_6H_4\cdot NH_2,$$

but dispute most of their other statements. The chief cause of Green and Woodhead's diverging views which the authors consider erroneous, is the fact that the substance which they have regarded as the leuco-base, $C_{48}H_{42}N_8$, and have obtained by reducing emeraldine with titanium trichloride, is in reality the monoquinonoid black, $C_{48}H_{40}N_8$. The real facts are as follows: Monoquinonoid black, $C_{48}H_{40}N_8$, is obtained by reducing triquinonoid black (emeraldine) with titanium trichloride in the cold, or, better, with phenylhydrazine at 100°. Diquinonoid black, $C_{48}H_{38}N_8$, is easily obtained pure by the spontaneous oxidation of monoquinonoid black or of the leuco-base in the air. Triquinonoid black (emeraldine), $C_{48}H_{36}N_8$, is obtained by oxidising an excess of aniline salt with dichromate, persulphate, chlorate, or other agents. Tetraquinonoid black (nigraniline), $C_{48}H_{34}N_8$, is obtained best by oxidising triquinonoid black with hydrogen peroxide. (By oxidation with dichromate or persulphate, an oxygenated pentaquinonoid black, $C_{48}H_{33}ON_7$, stable to sulphurous acid, is obtained.) All these quinonoid blacks yield the first-mentioned monoquinonoid black by oxidation by Knecht's titanium trichloride process, in the cold or at 90°. The true leuco-base, $C_{48}H_{42}N_8$, is obtained by treating any of these blacks with phenylhydrazine at 150°. (A black which contains iron in its ash must be first boiled with 2*N*-sulphuric acid, otherwise the reaction with phenylhydrazine above 100° proceeds explosively.)

Green and Woodhead state that the salts of nigraniline are very unstable, changing slowly in the cold, rapidly by warming, to emeraldine and *p*-benzoquinone. On the contrary, the authors find that the only change produced by 17% sulphuric acid at 200° is the quantitative hydrolysis of one quinoneimine group.

Green and Woodhead also state that the emeraldine and nigraniline dissolve easily and completely in 80% acetic acid or in 60% formic acid. This, again, is incorrect; only suspensions are obtained.

C. S.

Action of Oxidising Agents on *iso*Pyromucic Acid. Dialdehydes of Dibromomaleic and Bromohydroxymaleic Acids. G. Chavanne (*Compt. rend.*, 1911, **153**, 185—188*).—The constitution of *iso*pyromucic acid previously determined by the author (Abstr., 1905, i, 77), and confirmed by Blaise and Gault (Abstr., 1909, i, 134), is supported by a study of the products of oxidation. Most oxidising agents act too energetically, but hydrogen peroxide in

* and *Bull. Soc. chim. Belg.*, 1911, **25**, 264—279.

alkaline solution at the ordinary temperature produces maleic acid carbon dioxide, and a little formic acid.

It has been shown (*loc. cit.*) that the action of bromine and water on *iso*pyromucic acid yields, under apparently identical conditions, either a substance, $C_5H_4O_4Br_2$, decomp. 104—105°, or a substance, $C_4H_2O_2Br_2$, m. p. 34°. These substances can now be obtained at will. *iso*Bromopyromucic acid forms with bromine an additive *compound*, $C_5H_3O_3Br_3$, large prisms, m. p. 88—89°, which is decomposed by ice water, yielding hydrogen bromide and the substance $C_5H_4O_4Br_2$ previously described (it decomposes at 175° when pure). All attempts to obtain the substance $C_4H_2O_2Br_2$ from the substance $C_5H_4O_4Br_2$ have failed. However, by dissolving the additive compound $C_5H_3O_3Br_3$ in bromine (1 mol.) and adding the solution to a little water at the ordinary temperature, the substance $C_4H_2O_2Br_2$, m. p. 34°, is obtained in good yield. There is no doubt that it is dibromomaleic dialdehyde, because: (i) by oxidation with bromine and water under suitable conditions it gives an almost theoretical yield of bromomucic acid, and (ii) when heated with a large excess of water it decomposes into hydrogen bromide and a *substance*, $C_4H_3O_3Br$, m. p. 83—83·5°, which has acidic properties, forms an *acetyl* derivative, b. p. 118—120°/1·5 mm., *semicarbazone*, decomp. 198°, *phenylhydrazone*, decomp. 126—126·5°, and *trioxime*, decomp. 94—95°, reduces ammoniacal silver nitrate, gives Schiff's test, and is oxidised by bromine and water chiefly to bromomucic acid. The substance, therefore, is α-bromo-β-hydroxymaleic dialdehyde, which reacts in the tautomeric forms: $CHO\cdot C(OH)\colon CBr\cdot CHO$ and $CHO\cdot CO\cdot CHBr\cdot CHO$.

C. S.

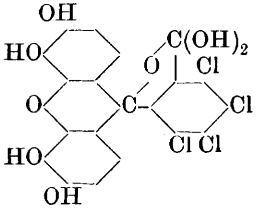
Action of Halogen Acids on Hydroxyarylxanthenols. MOSES GOMBERG and C. J. WEST (*J. Amer. Chem. Soc.*, 1911, 33, 1211—1213).—Many investigators have examined the action of acids on hydroxyarylxanthenols, and report generally that coloured oxonium salts are formed. The authors have made a systematic study of the reaction (as an introduction to the study of the constitutions of fluoran, fluorescein, etc.), and find that, in general, hydroxy- and methoxy-xanthenols yield colourless carbinol chlorides, which tautomerise with extreme readiness to coloured quinocarbonium salts in the presence of excess of acid (compare Gomberg and Cone, Abstr., 1910, i, 55, 869). When one of the two phenyl groups in the xanthone ring contains a hydroxyl group in the para-position to the carbinol carbon atom, the colourless carbinol halide changes spontaneously, even in the absence of excess of acid, to the coloured quinocarbonium salt. Full information is promised in a later paper.

C. S.

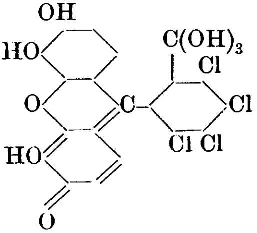
Tetrachlorogallein and Some of its Derivatives. II. WILLIAM R. ORNDORFF and T. G. DELBRIDGE (*Amer. Chem. J*., 1911, **46**, 1—55. Compare Abstr., 1909, i, 733).—A more convenient method of preparing the coloured tetrachlorogallein hydrate is described, in which tetrachlorophthalic acid, pyrogallol, and zinc chloride are heated at 200° in a current of carbon dioxide.

The authors have extended their investigations of the coloured and the colourless derivatives of tetrachlorogallein by the isolation of a colourless tetrachlorogallein hydrate, a colourless tetrachlorogalleincarbinolcarboxylic acid, and two colourless solvates, the diacetonate and the etherate. All colourless derivatives receive a lactonoid constitution, whilst the coloured compounds are represented as quinonoid.

Colourless *tetrachlorogallein hydrate*, $C_{20}H_8O_7Cl_4,H_2O$, is obtained by adding water to an acetone solution of the red hydrate, and passing moist carbon dioxide through the solution; after several days the colourless hydrate crystallises in triclinic needles. Chemically its behaviour is almost identical with that of the red hydrate. It loses H_2O at 157°, and forms tetrachlorogallein. Both hydrates react with dry ammonia to form the same bluish-black *tetra-ammonium* salt as does tetrachlorogallein itself, but whilst the red hydrate absorbs hydrogen chloride to form a red *hydrochloride*, $C_{20}H_8O_7Cl_4,HCl,H_2O$, without loss of water, the colourless hydrate slowly absorbs hydrogen chloride and also loses 1 mol. H_2O, yielding the red hydrochloride, $C_{20}H_8O_7Cl_4,HCl$, identical with that produced from tetrachlorogallein (*loc. cit.*). This difference in behaviour strikingly confirms the constitutions ascribed to the two hydrates:

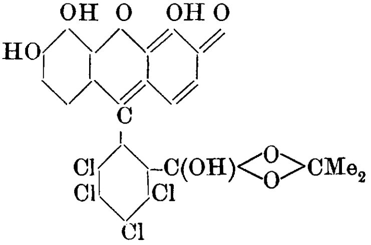


Colourless hydrate.

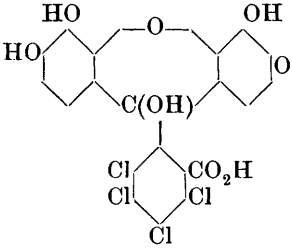


Coloured hydrate.

Tetrachlorogallein diacetonate, $C_{20}H_8O_7Cl_4,2C_3H_6O$, separates in almost colourless crystals from a solution of tetrachlorogallein in dry acetone. It loses acetone in a vacuum over phosphoric oxide, gradually becoming intensely red, and finally, after being heated at 157° in carbon dioxide, colourless again, yielding tetrachlorogallein; the colour is most intense when the composition of the decomposing diacetonate, corresponds with the formula $C_{20}H_8O_7Cl_4,C_3H_6O$. In the air the diacetonate loses its acetone and takes up rather more than one molecule of water to form a mixture of red tetrachlorogallein hydrate with a little of the carbinolcarboxylic acid (see below). The behaviour of the diacetonate accords with the annexed constitution.

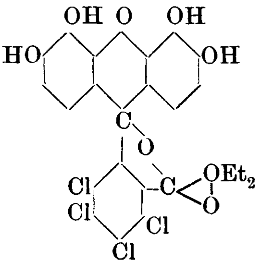


Tetrachlorogalleincarbinolcarboxylic acid, $C_{20}H_{10}O_8Cl_4,H_2O$, is obtained as a white precipitate by adding a cold acetone solution of the preceding diacetonate (or of either of the hydrates or of anhydrous tetrachlorogallein itself) to a large excess of cold acidified water. The substance loses H_2O at 157°, yielding the colourless, anhydrous *carbinolcarboxylic acid* (annexed constitution), which differs from the isomeric red hydrate in that it does not lose more water even at 203°. However, it combines very easily with hydrogen chloride in the cold, forming a red *hydrochloride* (probably the hydrochloride obtained from the red tetrachlorogallein hydrate, since it loses water and hydrogen chloride at 157°, yielding tetrachlorogallein), and with dry ammonia, forming by loss of water the bluish-black tetra-ammonium salt described above. This confirms Baeyer's statements that all carbinols are colourless, and that colour only appears in consequence of loss of water.



Attempts to crystallise tetrachlorogalleincarbinolcarboxylic acid give a mixture of the colourless and the coloured tetrachlorogallein hydrates; also the action of acetic anhydride produces the colourless tetrachlorogallein tetra-acetate, thus showing that the elimination of water from the carbinol acid does not necessarily give a coloured compound.

When tetrachlorogallein diacetonate is shaken with dry ether and filtered, the filtrate yields a colourless *etherate*, $C_{20}H_8O_7Cl_4,C_4H_{10}O$, which loses ether extremely easily, and at 157° in carbon dioxide yields a mixture of equal parts of tetrachlorogallein and its carbinolcarboxylic acid. The etherate becomes pink in air, owing to its conversion, by absorption of water and loss of ether, into colourless tetrachlorogallein hydrate, the carbinolcarboxylic acid, and a little of the coloured hydrate. The etherate is given the annexed constitution. C. S.



New Synthesis of Trihydroxythioxanthones. Fritz Ullmann and Masuo Sone

(*Ber.*, 1911, **44**, 2146—2148).—When warmed gently with concentrated sulphuric acid, aromatic mercaptans and gallic acid readily condense to form trihydroxythioxanthones. Gallic acid and phenyl mercaptan yield Davis and Smiles' 2 : 3 : 4-trihydroxythioxanthone (Trans., 1910, **97**, 1290), the *trimethyl ether* of which has m. p. 153—154°. Gallic acid and *p*-tolyl mercaptan yield 2 : 3 : 4-*trihydroxy-7-methylthioxanthone*, $C_6H_3Me{<}\begin{smallmatrix}CO\\S\end{smallmatrix}{>}C_6H(OH)_3$, yellow needles, darkening above 240°. It forms a reddish-brown solution in dilute alkalis, an orange solution with a faint green fluorescence in concentrated sulphuric acid, and yields with methyl sulphate and potassium hydroxide a *trimethyl ether*, yellow needles, m. p. 135°.

C. S.

Oxythiophens. MAURICE LANFRY (*Compt. rend.*, 1911, **153**, 73—76).—When thiophen is boiled with hydrogen peroxide (6—13 vols.) two substances are obtained, and may be separated by fractionation. *Dioxythiophen*, $C_4H_4O_2S$, has b. p. about 130°, D^{20} 1·26; *tetraoxythiophen*, $C_4H_4O_4S$, has b. p. 158—160°, D^{20} 1·43. The compounds closely resemble one another, and show no phenolic properties; they are colourless liquids with an agreeable odour, unaltered by treatment with sodium, alkali hydroxide, or phenylhydrazine. Nitric or sulphuric acid brings about profound decomposition on boiling. With concentrated sulphuric acid and isatin, they develop a green coloration, destroyed by excess of water. Tetraoxythiophen forms an *octabromide*, $C_4O_4SBr_8$, m. p. 65—66°, by addition and substitution; the existence of this compound indicates that the oxygen in the original substance is united to sulphur.

When the amount of active oxygen in the hydrogen peroxide corresponds with less than 1·5 grams per gram of thiophen, a brown substance is formed, soluble in alkalis. It appears to be a mixture, and under some conditions approximates in composition to the formula $(C_4H_2OS)_n$. W. O. W.

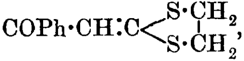
Action of Carbon Disulphide and Potassium Hydroxide on *p*-Tolyl Methyl Ketone and α-Thienyl Methyl Ketone. C. KELBER and A. SCHWARZ (*Ber.*, 1911, **44**, 1693—1700. Compare Abstr., 1892, 340, 1127; 1904, i, 510; 1905, i, 810; 1909, i, 46, 47). —*p*-Tolyl methyl ketone and α-thienyl methyl ketone react with carbon disulphide and alkali in much the same manner as acetophenone (Abstr., 1910, i, 390), the products having the characteristics of thiols.

The *compound*, $C_{10}H_{10}OS_2 = C_6H_4Me \cdot CO \cdot CH{:}C(SH)_2$, obtained from *p*-tolyl methyl ketone, carbon disulphide, finely-powdered potassium hydroxide, and two drops of water by heating on the water-bath and then cooling rapidly, crystallises from light petroleum in glistening, yellow plates, m. p. 84—85°. Carbon dioxide precipitates it from solutions of its alkali salts. The *dimethyl ether*, $C_{12}H_{14}OS_2$, forms pale yellow, glistening needles, m. p. 104—105°; the *dibenzyl ether*, $C_{24}H_{22}OS_2$, broad, yellow needles, m. p. 111·5—112·5°, and the *dibenzoyl* derivative, $C_{24}H_{18}O_3S_2$, pale yellow crystals, m. p. 125°. When heated for four hours at 125° with 0·5*N*-alcoholic potassium hydroxide, the product yields hydrogen sulphide and *p*-toluic acid. Alcoholic ammonia at 140° yields ammonium thiocyanate and *p*-tolyl methyl ketone, and alcoholic hydrochloric acid at 125° yields ethyl mercaptan and *p*-tolyl methyl ketone. When heated on the water-bath with aniline, the product yields a *compound*,

$$C_6H_4Me \cdot CO \cdot CH{:}C(SH) \cdot NHPh \ (?),$$

which crystallises from light petroleum in needles, m. p. 80·5—81·5°, and is readily soluble in alkalis. After prolonged heating with aniline, a *compound*, crystallising in red needles, m. p. 192·5—193°, is formed (N = 8·28%).

The *product*, $C_7H_6OS_3$, obtained from α-thienyl methyl ketone, crystallises from light petroleum in yellow plates, m. p. 90—91°. The *dimethyl ether*, $C_9H_{10}OS_3$, forms compact, yellow needles, m. p. 96·5°, and the *dibenzoyl* derivative, $C_{21}H_{14}O_3S_3$, slender, felted, yellow needles, m. p. 118·5°. Its behaviour towards alcoholic solutions of potassium hydroxide, ammonia, and hydrochloric acid is exactly analogous to the behaviour of the product from *p*-tolyl methyl ketone with these reagents.

The *ethylene ether* of the product previously described (Abstr., 1910, i, 391),  $COPh\cdot CH\dot{:}C<\begin{matrix}S\cdot CH_2\\ |\\ S\cdot CH_2\end{matrix}$, crystallises from light petroleum in long, pale yellow needles, m. p. 80°. Its solution in concentrated nitric acid has a blue to cherry-red colour, and that in concentrated sulphuric acid a deep yellow colour. When reduced with zinc dust and sodium hydroxide solution, the ether yields propiophenone, detected by means of its semicarbazone and ethylene mercaptan,

$$COPh\cdot CH\dot{:}CS_2C_2H_4 + 6H = COPh\cdot CH_2Me + C_2H_4(SH)_2.$$

The *propylene ether*, $COPh\cdot CH\dot{:}CS_2C_3H_6$, m. p. 52—53°, is reduced in an exactly similar manner, and these reactions are used as an argument in favour of the unsaturated dithiol structure previously given to the condensation product from acetophenone. J. J. S.

Cinchona Alkaloids. XIII. Fluorescence Phenomena with Cinchona Alkaloids. Paul Rabe and Oswald Marschall (*Annalen*, 1911, **382**, 360—364. Compare Stokes, *Jahresber.*, 1864, 100).—The phenomena of fluorescence of cinchona alkaloids have been examined qualitatively in order to establish relationships between constitution and fluorescence. The experiments were made with sunlight, light from a uviol lamp, and the ultra-violet rays from an arc lamp. The general method adopted was similar to that used by Tswett (Abstr., 1901, ii, 298; compare also Stobbe, *ibid.*, 1909, ii, 282).

The results show that slight differences in arrangement of the atoms within the molecule, as exemplified by cases of stereoisomerism, produce an appreciable effect on the fluorescence; the examples quoted are the following pairs of substances, which were examined in the solid form by filtered ultra-violet light: cinchonine, blue; cinchonidine, pale blue; quinine, intense blue; quinidine, light blue; quinine hydrochloride, intense blue; quinidine hydrochloride, yellowish-red; deoxyquinine, reddish-blue; deoxyquinidine, sky-blue.

In all cases the fluorescence is more pronounced when working with ultra-violet light than with sunlight; the quality and intensity of the fluorescence varies with the solvent, but no generalisations can be drawn between the two. When water is added gradually to an alcoholic solution, it frequently first produces an increase and ultimately a diminution of the fluorescence.

With quinine salts an important factor is the acid with which the base is combined; thus, when 0·1 gram of the base is dissolved in 20 c.c. of 0·1*N*-acid, the following results are obtained: sulphuric, nitric, phosphoric, hydrofluoric, and trichloroacetic give strongly fluorescent solutions, tartaric and acetic moderately strongly fluorescent, and the halogen hydracids very feebly fluorescent solutions.

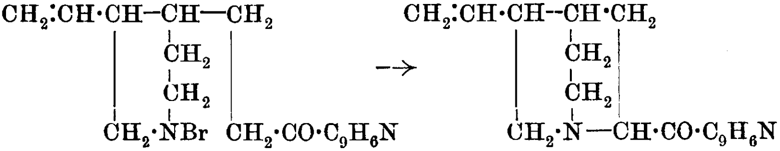
J. J. S.

Cinchona Alkaloids. XIV. Decomposition of Oximinoquinotoxine. Paul Rabe and Ernst Milarch (*Annalen*, 1911, **382**, 365—368. Compare Rabe and Ackermann, Abstr., 1907, i, 546).—The products obtained by shaking phosphorus pentachloride with an ice-cold chloroform solution of oximinoquinotoxine (Rohde and Schwab, Abstr., 1905, i, 228) and then pouring on to ice and water are quinic acid and the nitrile of meroquinine. The oximino-derivative of the tertiary methylquinotoxine behaves in a similar manner, yielding quinic acid and the nitrile of *N*-methylmeroquinine (Rabe and Ritter, Abstr., 1905, i, 811). J. J. S.

Cinchona Alkaloids. XV. Partial Synthesis of Cinchonine.

Paul Rabe (*Ber.*, 1911, **44**, 2088—2091).—An account of the transformation of cinchotoxine into cinchonine.

N-*Bromocinchotoxine* (I), obtained by the action of aqueous sodium hypobromite on cinchotoxine in dilute hydrochloric acid solution at the ordinary temperature, crystallises from alcohol or ether in colourless, elongated prisms, m. p. 153°. It differs from cinchotoxine in being without action towards litmus and methyl iodide. When treated in hot alcoholic solution with sodium ethoxide, it loses hydrogen bromide, and is converted into cinchoninone (II):



(I.) (II.)

The reduction of cinchoninone to cinchonine has been described previously (Rabe and Buchholz, Abstr., 1908, i, 100). F. B.

Ephedrine and ψ-Ephedrine.

Ernst Schmidt [with W. Calliess] (*Apoth. Zeit.*, 1911, No. 37; Reprint 3 pp.).—A preliminary note necessitated by work published by Emde, Fourneau, and Rabe and Hallensleben (compare this vol., i, 396). The synthesis of a base isomeric with ephedrine or ψ-ephedrine starts from phenyl α-bromoethyl ketone. This is converted into *phenyl-α-aminoethyl ketone*, $NH_2\cdot CHMe\cdot COPh$ (*hydrochloride*, m. p. 179°; *nitrate*, m. p. 139—140°; *picrate*, m. p. 160°; *platinichloride*, m. p. 200°; *aurichloride*, m. p. 151°; *mercurichloride*, m. p. 126° or 165°; *stannichloride*, m. p. 219—220°), which is reduced by sodium amalgam in faintly acid solution at 0° to *phenyl-α-aminoethylcarbinol*,

$$NH_2\cdot CHMe\cdot CHPh\cdot OH$$

(*hydrochloride*, m. p. 165°; *aurichloride*, m. p. 130°; *platinichloride*, m. p. 187—188°). This carbinol forms by direct methylation a quaternary base, an aqueous solution of which, by distillation, yields trimethylamine and an oily substance free from nitrogen. The substance $NHMe\cdot CHMe\cdot CHPh\cdot OH$ is obtained by treating phenyl α-bromoethyl ketone with methylamine and reducing the product with sodium amalgam in faintly acid solution.

ω-Aminobenzyl methyl ketone yields by reduction the *carbinol*, $NH_2\cdot CHPh\cdot CHMe\cdot OH$ (*hydrochloride*, m. p. 165—167°), which reacts with methyl iodide in methyl alcohol to form, ultimately, a quaternary base, the distillation of which yields trimethylamine and an oil, as yet unexamined. ω-Bromobenzyl methyl ketone and methylamine yield a *base*, NHMe·CHPh·COMe (*hydrochloride*, m. p. above 200°), which is converted by reduction into ω-*methylaminobenzylmethylcarbinol*, NHMe·CHPh·CHMe·OH, an oil the *hydrochloride* of which has m. p. 190°. C. S.

***d*-Lupanine.** August Beckel (*Arch. Pharm.*, 1911, **249**, 329—353).—A chemical relationship between lupanine, $C_{15}H_{24}ON_2$, and sparteine, $C_{15}H_{26}N_2$, has often been assumed in consequence of the similarity in composition and the occurrence of both alkaloids in the seeds of lupines. The two nitrogen atoms in sparteine are tertiary, and the alkaloid behaves as a diacidic base and forms two isomeric methiodides. The author has examined very thoroughly the behaviour of *d*-lupanine (isolated as the hydrochloride from the seeds of *Lupinus angustifolius*) with methyl iodide, with and without a solvent, at the ordinary temperature, at 100°, and even at 190°, but in no circumstances has a methiodide been isolated other than that described in the literature (m. p. 240°, decomp.); their interaction at 150° results in a partial, at 190° in a complete, conversion of the methiodide into lupanine hydriodide. Lupanine methiodide does not form an additive compound with hydriodic acid. Lupanine an ethyl iodide, alone or in boiling alcohol, yield lupanine hydriodide. Benzyl bromide, but not benzyl chloride, forms an additive compound with lupanine, which is isolated as the *aurichloride*,

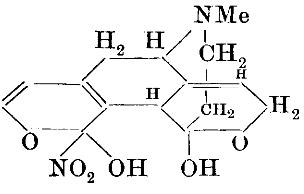
$$C_{15}H_{24}ON_2{\cdot}CH_2Ph,AuCl_4,$$

m. p. 186—187° (decomp.) (*platinichloride*, m. p. 203—204°, decomp.). Lupanine methiodide does not react with ethyl iodide or benzyl bromide at the ordinary temperature or at 100°.

d-Lupanine does not decolorise acidified potassium permanganate, and can be titrated as a mono-acidic base. C. S.

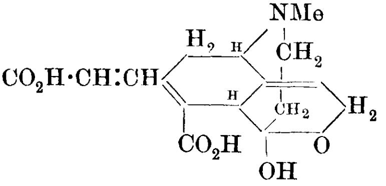
Morphine. I. Heinrich Wieland and Paul Kappelmeier (*Annalen*, 1911, **382**, 306—339).—Knorr's formula for morphine is discussed. Most of the methods used in connexion with the elucidation of the constitution of morphine have been based on Hofmann's degradation process involving a rupture of the nitrogen ring. The author has attempted to use the process of oxidation, but it has not been found possible to obtain definite homogeneous products by direct oxidation. Attempts to obtain acids from 2-nitrosomorphine by hydrolysing to the 2 : 3-quinone and subsequent oxidation also proved unsuccessful. The oxidation of 2-amino- and 2-hydroxy-morphine also gave negative results.

It has been found possible to rupture the morphine ring by means of nitrous gases. When these gases are passed into an aqueous solution of a morphine salt, 2-nitrosomorphine is formed together with the unstable nitrate of a base, $C_{17}H_{18}O_6N_2$. The annexed structural formula suggested for the base is that of a quinnitrole (Zincke, Abstr., 1905, i, 881). The reaction consists in the addition of nitric acid to one ring, of the hydro-

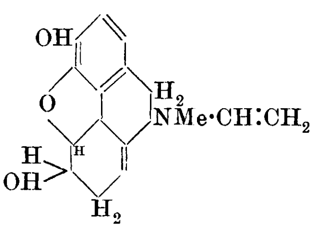


lytic rupture of the oxygen bridge and the oxidation of the secondary alcoholic group to a ketonic group.

When an aqueous solution of the unstable nitrate is warmed, a 30% yield of the colourless nitrate of the base $C_{17}H_{19}O_6N$ is obtained. This compound has acidic properties, is termed morphinic acid, and is regarded as formed by the oxidation of the *o*-quinone, from which the quinnitrole is derived, and is therefore represented by the annexed formula.



The adjacent structural formula for morphine is suggested. According to this the nitrogen atom is attached to carbon atom 9 of the phenanthrene nucleus, but contains a free vinyl group. The actual ring formation occurs with the aid of this vinyl group in the conversion of morphine into methylmorphimethine, *apo*morphine, thebenine, etc. This formula accounts for the readiness with which many morphine derivatives combine with water, and also for the readiness with which the $-N·C·C-$ group is eliminated from morphine.



The compound described by Mayer (*Ber.*, 1871, **4**, 121) as nitrosomorphine is probably morphine nitrite, and differs entirely from 2-*nitrosomorphine*, which is formed when nitrous fumes are passed into a suspension of morphine hydrochloride in water at − 2° to − 3°; the salt dissolves gradually, the liquid turns orange-red, and the nitroso-compound can be isolated as its *sodium* derivative, $C_{17}H_{17}O_4N_2Na,H_2O$, by the addition of cold 20% sodium hydroxide solution. This derivative crystallises from 90% alcohol in brilliant, dark red needles, and turns black when heated, but has no definite m. p. The *silver* derivative forms an insoluble, almost black precipitate, m. p. 181—182° (decomp.), but does not react with methyl iodide. The *hydrochloride*,

$$C_{17}H_{18}O_4N_2,HCl,$$

forms lemon-yellow needles, m. p. 248° (decomp.). 2-Nitrosomorphine, $C_{17}H_{18}O_4N_2,H_2O$, obtained by the action of acetic acid on the sodium derivative or of ammonia on the hydrochloride, crystallises from boiling alcohol in polymorphous forms; the more stable form consists of slender, dark orange-red needles, m. p. 225° (decomp.). It reduces neither Fehling's solution nor ammoniacal silver nitrate, is not appreciably decomposed by acids or alkalis, and its alkali salts give a dark green coloration with ferric chloride. The minutest traces of morphine react with a drop of sodium nitrite solution, yielding a yellow coloration which turns to orange on the addition of alkali, and the reaction is an extremely delicate one for detecting morphine. When reduced with tin and hydrochloric acid, the nitroso-compound yields 2-*aminomorphine*, $C_{17}H_{20}O_3N_2,H_2O$, which forms colourless, glistening crystals or quadratic plates, m. p. 258°. The *hydrochloride*,

$C_{17}H_{20}O_3N_2,2HCl$, is readily soluble in water, and has $[\alpha]_D$ − 90°; the *picrate* forms yellow needles, decomposing at 172°.

The amino-compound is readily diazotised, yielding an *o-diazo-anhydride*; the *hydrochloride*, $C_{17}H_{17}O_3N_3,HCl$, is formed when the amino-compound is suspended in alcohol, treated with alcoholic hydrogen chloride and ethyl nitrite, and precipitated by the addition of ether. The dry salt decomposes at 98°. When warmed with alcohol, the diazo-compound regenerates morphine, but it has not been found possible to obtain pure 2-hydroxymorphine.

Morphine as a phenol couples with diazonium salts, yielding azo-dyes. *Benzeneazomorphine*, $C_{23}H_{23}O_3N_3$, crystallises from alcohol in slender, orange-yellow needles, m. p. 175° (decomp.). Its solutions in acids are orange-brown, and in alkali, blood-red. When reduced with stannous chloride and hydrochloric acid, it yields aniline and amino-morphine.

2-*Aminocodeine*, $C_{18}H_{22}O_3N_2$, obtained by reducing the corresponding nitro-derivative, crystallises from absolute alcohol, has m. p. 226°, and does not possess reducing properties. Its *hydrochloride* is amorphous, and is readily diazotised to a diazonium salt, which couples with an alkaline solution of β-naphthol, yielding a brilliant red dye. When a solution of the diazonium salt is heated, small amounts of 2-*hydroxy-codeine*, $C_{18}H_{21}O_4N$, are obtained in colourless needles, m. p. 176°.

2-Nitroso- and 2-amino-morphine are readily transformed into the corresponding *apo*morphine compounds by the loss of water, for example, when heated with 30% hydrochloric acid at 145° and 130° respectively. 2-*Nitroso*apo*morphine hydrochloride*, $C_{17}H_{16}O_3N_2,HCl$, crystallises from hot water in felted, yellowish-green needles, changes colour at 200°, but has no definite melting point, and reduces ammoniacal silver nitrate, but not Fehling's solution. The free *base*, $C_{17}H_{16}O_3N_2,H_2O$, crystallises from absolute alcohol in red needles, which are not molten at 300°. 2-*Amino*apo*morphine hydrochloride*, $C_{17}H_{18}O_2N_2,2HCl$, crystallises from dilute hydrochloric acid in colourless, felted needles, m. p. 260—265°. It reduces hot Fehling's solution, and with ferric chloride gives a deep violet coloration, which is rapidly transformed to an olive-green. The *base* is more sensitive to oxidation than *apo*morphine itself; it has been obtained as a colourless, amorphous mass, which turns violet-coloured on exposure to the air.

Morphinequinnitrole nitrate, $C_{17}H_{18}O_6N_2,HNO_3,H_2O$, crystallises in brilliant, glistening, orange-yellow prisms when an excess of nitrous fumes is passed into an aqueous suspension of morphine. It cannot be recrystallised, and when its concentrated aqueous solution is warmed, morphinic acid (33%) is obtained, together with dark red, amorphous by-products. *Morphinic acid nitrate*, $C_{17}H_{19}O_6N,HNO_3,H_2O$, crystallises from hot water in colourless prisms, which turn brown on exposure to light. It has no definite melting point, does not give a coloration with ferric chloride, but reduces hot Fehling's solution. *Morphinic acid*, obtained by decomposing the nitrate with concentrated sodium acetate solution, is characterised by the deep green colour which it gives when warmed with water, and this, with a few drops of hydrochloric acid, changes to a cherry-red.

The *hydrochloride*, $C_{17}H_{19}O_6N,HCl,2H_2O$, crystallises in colourless needles.

Chloromorphide, prepared by the action of thionyl chloride on morphine, reacts with diethylamine at 100°, yielding *diethylaminomorphide*, $C_{21}H_{28}O_2N_2$, which crystallises from absolute alcohol in colourless prisms, m. p. 203°. The base is soluble in strong alkalis, but not in ammonia solution. The *hydrochloride* has m. p. 268° (decomp.), and gives a blue coloration with ferric chloride. The *methiodide*, $C_{22}H_{31}O_2N_2I$, has m. p. 268° (decomp.).

Dichlorodiacetylmorphine, $C_{21}H_{21}O_5NCl_2$, obtained by the action of chloroacetyl chloride on anhydrous morphine, crystallises from ether, has m. p. 135°, and readily loses one chloroacetyl group, yielding *chloroacetylmorphine*, $C_{19}H_{20}O_4NCl$, which crystallises from alcohol in colourless needles, m. p. 234° (decomp.).

Benzenesulphonylmorphine benzenesulphonate,

$$C_{23}H_{23}O_5NS,C_6H_5\cdot SO_3H,$$

crystallises from hot water in slender needles, m. p. 140°. The *base* has m. p. 165°. J. J. S.

Strychnine Alkaloids. XI. The Brucine–Nitric Acid Reaction. Preparation of a New Alkaloid, Bis*apo*methylbrucine. HERMANN LEUCHS and RUDOLPH ANDERSON (*Ber.*, 1911, **44**, 2136—2145).—The colour reaction with nitric acid is shown, not only by brucine itself, but also by almost all its known derivatives and degradation products; in two instances, brucinesulphonic acid and brucinolone, substances have been isolated which behave like quinones, in that they can be reduced to the corresponding quinols. The present paper deals with the quinone and quinol corresponding with brucine itself.

Brucine is digested at 0° with 5*N*-nitric acid for half an hour, the red solution is reduced by sulphurous acid at 0°, and the quinol, *bis*apo*methylbrucine*, $C_{21}H_{22}O_4N_2$, prisms darkening at 260° and decomp. 285°, is purified by means of the *hydrochloride*, $C_{21}H_{22}O_4N_2,HCl$. The base develops an indigo-blue coloration with ferric chloride, reduces silver nitrate, and is readily soluble in alkalis.

By treating the red solution of brucine in nitric acid with an excess of cold saturated potassium hydrogen carbonate, a red *substance*, $C_{21}H_{21}O_6N_3$, is obtained, which is converted by chloroform and petroleum into the hydrated *quinone*, $C_{21}H_{20}O_4N_2,H_2O$, dark red needles, from which only one-half of the water can be expelled by intense drying. The anhydrous *quinone*, $C_{21}H_{20}O_4N_2$, red needles, is obtained by oxidising bis*apo*methylbrucine with chromic and sulphuric acids, whereby a red, crystalline *substance*, $C_{21}H_{20}O_4N_2,H_2CrO_4,HCl$, isolated by means of 5*N*-hydrochloric acid, is first obtained, which is converted into the anhydrous quinone by aqueous sodium hydrogen carbonate. After having once been isolated, the quinone and also its hydrate are not readily reduced to bis*apo*methylbrucine. C. S.

The Pyridine Compounds of the Tin Halides. PAUL PFEIFFER [with B. FRIEDMANN, R. LEHNARDT, H. LUFTENSTEINER, RUDOLF PRADE, and K. SCHNURMANN] (*Zeitsch. anorg. Chem.*, 1911, **71**, 97—120. Compare Abstr., 1910, i, 852).—Tin forms four series of pyridine compounds: SnX_4Py_2, $SnRX_3Py_2$, $SnR_2X_2Py_2$, and SnR_3XPy_2, giving, as before, the co-ordination number six, and confirming the constitutional formulæ previously given for the alkylated and phenylated compounds. Only the diphenylated stannic halides yield in addition additive compounds containing more than 2 mols. of pyridine. The iodides are also exceptional, the quantity of pyridine added depending on the number of iodine atoms. The difference is due to the additive power of the iodine atom.

Dipyridine tin tetrabromide, $SnBr_4Py_2$, prepared by adding dry pyridine to well cooled tin tetrabromide, is a white powder. Tin tetraiodide yields an unstable *compound*, $SnI_4Py_2,3Py$. *Dipyridine tin methyl trichloride*, $SnMeCl_3Py_2$, prepared from an ethereal solution of tin methyl chloride, and the *tribromide*, $SnMeBr_3Py_2$, are also amorphous. The tri-iodide yields a yellow additive *compound*, $SnMeI_3Py_2,2Py$. The following compounds have also been prepared: *dipyridine tin dimethyl dichloride*, $SnMe_2Cl_2Py_2$, colourless crystals, m. p. 163° (decomp.); the *dibromide*, $SnMe_2Br_2Py_2$, m. p. 172° (decomp.), and the *di-iodide*, $SnMe_2I_2Py_2$, m. p. 147° (decomp.).

Dipyridine tin dipropyl dichloride, $SnPr_2Cl_2Py_2$, forms colourless, glistening needles, m. p. 114°; the *dibromide* has m. p. 128°. *Dipyridine tin dibutyl dichloride*, $Sn(C_4H_9)_2Cl_2Py_2$, has m. p. 65—66°, and the *dibromide*, m. p. 77—78°.

Dipyridine tin diphenyl dichloride, $SnPh_2Cl_2Py_2$, is stable in air and has m. p. 151°. It also forms an additive *compound* with 2 mols. of pyridine, m. p. 155—156° (decomp.). The *dibromide*, $SnPh_2Br_2Py_2$, forms large crystals, m. p. 155° (decomp.), and also yields an additive *compound*, m.p. 160° (decomp.), with 2 mols. of pyridine. *Dipyridine tin ditolyl dibromide*, $Sn(C_6H_4Me)_2Br_2Py_2$, has m. p. 172—176°; *dipyridine tin triphenyl chloride*, $SnPh_3ClPy_2$, has m. p. 81—84°, and the *bromide*, m. p. 78—84°. C. H. D.

Preparation and Fission of Dihydroindole. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, **44**, 2158—2161).—Dihydroindole, obtained from indole by Carrasco's electrolytic method, forms a *benzenesulphonyl* derivative, fine needles, m. p. 133°, and a *benzoyl* derivative, m. p. 118°. The latter is converted by phosphorus pentachloride in the usual manner into o-*β-chloroethylbenzanilide*, $CH_2Cl{\cdot}CH_2{\cdot}C_6H_4{\cdot}NHBz$, m. p. 120°, in 30% yield. C. S.

Preparation of β-Iodoindole. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **73**, 128—130. Compare Abstr., 1909, i, 512).—2-Iodoindole can be prepared by the action of a solution of iodine in potassium iodide on a solution of indole and potassium hydroxide in water, and just sufficient alcohol to keep the compound in solution. It forms snow-white crystals, m. p. 72°, and turns black on exposure to the air. Scatole (2-methylindole) and tryptophan cannot be converted into iodo-derivatives by either method. J. J. S.

Dihydroquinaldine Bases. GUSTAV HELLER [with SIEGMUND SCHMEJA] (*Ber.*, 1911, **44**, 2106—2115).—It has been shown previously (Heller and Sourlis, Abstr., 1908, i, 914) that 2-methylquinoline, when heated with zinc dust and hydrochloric acid, yields 2-methyldihydroquinoline. This method of reduction has now been applied to the preparation of the dihydro-derivatives of several isomeric methylquinolines and dimethylquinolines. These dihydro-bases are all bimolecular, and cannot be further reduced to the corresponding tetrahydro-compounds. From their indifference towards methyl iodide, and the fact that they yield neither nitrosoamines nor acetyl derivatives, the authors draw the conclusion that the nitrogen atom in these compounds is no longer tervalent. When heated with mercuric oxide in cumene solution or with chromium trioxide in glacial acetic acid solution, the dihydro-bases are oxidised to the corresponding quinolines.

2-*Methyldihydroquinoline hydrochloride*, $C_{10}H_{11}N,HCl$, crystallises in lustrous needles, which become brown at 210°, and have m. p. 250°; the *sulphate*, $2C_{10}H_{11}N,H_2SO_4$, crystallising in lustrous leaflets, becomes brown at 210°, and decomposes at 240°.

2-Methyldihydroquinoline condenses with chloral hydrate, formaldehyde, and phthalic anhydride, but the products thus formed could not be obtained crystalline. When treated with bromine in chloroform solution, it yields *dibromo-2-methyldihydroquinoline*, $C_{10}H_9NBr_2$. This crystallises in lustrous, colourless needles, m. p. 242° (decomp.), and is not oxidised by mercuric oxide. Its stability towards alcoholic potassium hydroxide and reducing agents indicates that the bromine atoms have probably entered the benzene nucleus. Unsuccessful attempts have been made to synthesise the dihydro-compound from *o*-nitrostyryl methyl ketone (Baeyer and Drewsen, Abstr., 1883, 341). The latter compound, when treated with bromine in glacial acetic acid solution, yields the *dibromide*, $NO_2\cdot C_6H_4\cdot CHBr\cdot CHBr\cdot COMe$, which crystallises in colourless needles, m. p. 102°, and is reduced by zinc and acetic acid to 2-methylquinoline and 2-methyltetrahydroquinoline.

2 : 8-*Dimethyldihydroquinoline* crystallises in colourless needles, m. p. 216—217°, and has no basic properties. When treated with bromine in hot alcoholic or glacial acetic acid solution it yields a *tetrabromo*-derivative, $C_{11}H_9NBr_4$ (?), which forms sulphur-yellow crystals, m. p. 171—172°. Bromination in dilute alcoholic solution results in the formation of a *tribromo*-derivative, $C_{11}H_{10}NBr_3$, m. p. 121—122°, whilst in chloroform or benzene solution the action of bromine yields a *substance*, m. p. 240—250°, containing only two atoms of bromine in the molecule.

2 : 6-*Dimethyldihydroquinoline* has m. p. 143°; the *hydrochloride* forms white needles, which become brown at 205°, and have no definite m. p.; the *hydrobromide*, crystallising in lustrous needles, becomes brown at 215°, and has m. p. 260°; the *sulphate*,

$$2C_{11}H_{13}N,H_2SO_4,$$

has m. p. 220° (decomp.), becoming brown at 206°.

The behaviour of 2 : 6-*dimethyldihydroquinoline* towards bromine resembles that of the isomeric 2 : 8-compound; the *tetrabromo*-derivative, $C_{11}H_9NBr_4$, obtained by bromination in hot glacial acetic acid solution, crystallises in pale yellow needles, m. p. 172°.

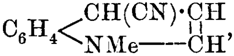
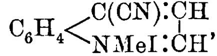
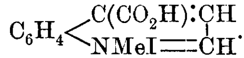
2 : 7-*Dimethyldihydroquinoline* is amorphous, and on account of its feebly basic properties could not be further purified.

The reduction of quinoline by zinc and hydrochloric acid takes place at the ordinary temperature, dihydroquinoline together with a small quantity of tetrahydroquinoline being produced.

8-*Methyldihydroquinoline*, $C_{10}H_{11}N$, has m. p. 144°; the *hydrochloride*, m. p. 278°.

6-*Methyldihydroquinoline* melts indefinitely at 60—105°, forms no salts, and therefore could not be further purified.

By distilling dihydroglauconic acid or by heating 2-methylquinoline hydrochloride with zinc dust, Doebner (Abstr., 1898, i, 384) obtained a substance which he considered to be 2-methyldihydroquinoline. According to the author this consists of 2-methylquinoline, whilst Doebner's dihydro-2 : 6-dimethylquinoline (Abstr., 1900, i, 313) is identical with 2 : 6-dimethylquinoline. F. B.

Cyanodihydrocyclic Amines. IV. Synthesis of Cinchonic Acid. Adolf Kaufmann and Robert Widmer [with Alberto Albertini] (*Ber.*, 1911, **44**, 2058—2065).—On oxidation of 4-cyano-1-methyldihydroquinoline,  $C_6H_4{<}\begin{array}{l}\mathrm{CH(CN)\cdot CH}\\ \mathrm{NMe{-\!-\!-}CH}\end{array}$, with alcoholic iodine solution, it is readily converted into the methiodide of 4-cyanoquinoline,  $C_6H_4{<}\begin{array}{l}\mathrm{C(CN){:}CH}\\ \mathrm{NMeI{:}CH}\end{array}$, which, on hydrolysis, forms the methiodide of cinchonic acid,  $C_6H_4{<}\begin{array}{l}\mathrm{C(CO_2H){:}CH}\\ \mathrm{NMeI{=\!=}CH}\end{array}$. Both iodides are oxidised by alkaline ferric cyanide solution to known α-quinolones, and the betaine of 1-methylcinchonic acid is obtained on treating the methiodide with moist silver oxide.

4-Cyanoquinoline is conveniently prepared by heating 4-cyanoquinoline methiodide in a stream of carbon dioxide at 210—220°, when methyl iodide is eliminated, and the nitrile sublimes in long, colourless needles, m. p. 95°.

In general, cyclaminones when distilled with zinc dust form cyclamine bases; thus, 4-cyano-1-methyl-2-quinolone yields the nitrile of cinchonic acid.

Cyanodihydroacridines are unaffected by alcoholic iodine solution, and the cyano-group cannot be displaced by bromine, which, however, forms a dibromo-derivative, *dibromocyanophenylmethyldihydroacridine*, crystallising in colourless, cubic crystals, m. p. 208—209°. From analogy to the experiments of Dunstan and Oakley (Abstr., 1906, i, 383), the bromine atoms are considered to occupy the 3 : 6-positions.

4-*Cyanoquinoline methiodide* forms red needles, which darken at 180°, m. p. 216° (decomp.).

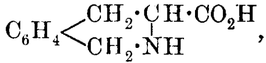
On bromination of phenylmethyldihydroacridone, the *methobromide* of *dibromophenylacridine* is obtained in orange-yellow needles, m. p. 274° (decomp.). Potassium cyanide converts it into the dibromocyanophenylmethyldihydroacridine just described. With alcoholic potassium hydroxide, a reddish-violet coloration is obtained, and yellow needles separate of the *ethyl ether* of 3 : 7-*dibromo*-5-*phenyl*-10-*methyldihydroacridinol*; they become violet at 170°, m. p. 192—195°

(decomp.). 3 : 7-*Dibromo*-5-*cyano*-5 : 10-*dimethyldihydroacridine* forms strongly refractive cubes, which blacken at 220°, m. p. 228°. E. F. A.

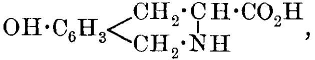
Formation of *iso*Quinoline Derivatives by the Action of Methylal on Phenylethylamine, Phenylalanine, and Tyrosine.

AMÉ PICTET and THEODOR SPENGLER (*Ber.*, 1911, **44**, 2030—2036). — Tetrahydro*iso*quinoline derivatives are obtained directly on condensing substituted phenylethylamines with aldehydes instead of with acids, as in the Bischler-Napieralski synthesis, which leads to unsaturated *iso*quinolines. Thus from formaldehyde and β-phenylethylamine, tetrahydro*iso*quinoline is obtained without difficulty, and the reaction gives still better results with phenylalanine and tyrosine, which yield with formaldehyde, tetrahydro- and hydroxy-tetrahydro-*iso*quinolinecarboxylic acids.

In view of the fact that all these substances are natural plant products, it is very probable that a similar condensation takes place in the plant, and that the relatively simple tetrahydro*iso*quinoline compounds formed after loss of the carboxyl group become methylated and undergo further complication until the various *iso*quinoline alkaloids are obtained. The latter may now be regarded as modified degradation products of vegetable protein. Such alkaloids as laudanosine represent a primary condensation of amino-acid and formaldehyde, and a secondary condensation of this product with a substituted benzaldehyde.

*Tetrahydro*iso*quinoline*-3-*carboxylic acid*,  $C_6H_4<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CH_2\cdot NH\end{matrix}$, prepared from phenylalanine and methylal, crystallises in large, nacreous, colourless plates, m. p. 311° (decomp.). On heating above the melting point, tetrahydro*iso*quinoline is formed.

7-*Hydroxytetrahydro*iso*quinoline*-3-*carboxylic acid*,

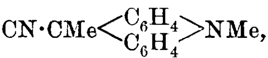
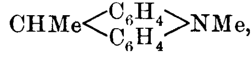


$$OH\cdot C_6H_3<\begin{matrix}CH_2\cdot CH\cdot CO_2H\\ CH_2\cdot NH\end{matrix},$$

forms a colourless, microcrystalline precipitate, m. p. 336—338° (decomp.). When heated, a secondary base, probably 7-*hydroxytetrahydro*iso*quinoline* is obtained, b. p. 210—220°/18 mm.; the *picrate* has m. p. 198—201°. The *hydrochloride*, when distilled with zinc dust, gives *iso*quinoline. E. F. A.

Cyanodihydrocyclic Amines. III.

ADOLF KAUFMANN and ALBERTO ALBERTINI [with ROBERT WIDMER] (*Ber.*, 1911, **44**, 2052—2058. Compare Abstr., 1909, i, 606, 958).—5-Cyano-5-phenyldihydroacridine, probably on account of steric hindrance, could not be converted into the corresponding acid, and, similarly, 5-cyano-10-methyldihydroacridine, on account of the readiness of its oxidation to 10-methylacridone, could not be hydrolysed.

5 - Cyano - 5 : 10 - dimethyldihydroacridine,  $CN\cdot CMe<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>NMe$, however, yields a carboxylic acid, from which carbon dioxide is eliminated on recrystallisation, and the corresponding dihydroacridine,  $CHMe<\begin{matrix}C_6H_4\\ C_6H_4\end{matrix}>NMe$, obtained.

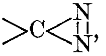
10-*Methylacridine tartrate* crystallises in green needles of silky lustre, m. p. 153—154° (decomp.). The picrate crystallises with a molecule of alcohol in greenish-yellow needles, m. p. 213—214° (Decker gives 220—221°). The *mercurichloride* forms yellow needles, m. p. 258°; the methiodide golden, glistening platelets, decomp. 200°, m. p. 235—245° (Bernthsen, 185°); the *methochloride* separates in glistening, yellow platelets, m. p. 200°, and gives a yellow crystalline precipitate, m. p. 252—255°, with platinum chloride and brown needles, m. p. 193—194° (explosively), with picric acid.

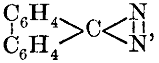
5-*Cyano*-5 : 10-*dimethyldihydroacridine*, formed by the interaction of methylacridine methochloride and potassium cyanide, separates in colourless crystals, m. p. 123°. The *picrate* crystallises in dark brown plates, m. p. 138—139°.

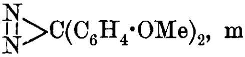
5-*Cyano*-10-*methyl*-5-*benzyldihydroacridine* crystallises in colourless needles, m. p. 125°.

5 : 10-*Dimethyldihydroacridine*-5-*carboxylic acid*, prepared by hydrolysis of the cyano-compound with alcoholic potassium hydroxide, crystallises in colourless, glistening plates, which blacken at 130°, m. p. 160° (decomp.). Carbon dioxide is readily eliminated, and 5 : 10-dimethyldihydroacridine obtained in lanceolate, yellow crystals, m. p. 137° (compare Freund and Bode, Abstr., 1909, i, 514).

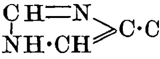
E. F. A.

Action of Hydrazine on Carbonyl Compounds. HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1911, **44**, 2197—2212).—Curtius and his co-workers found that the products obtained from hydrazine and ordinary aldehydes or ketones differed greatly in behaviour from those produced by the interaction of hydrazine and benzil or α-ketonic esters; the former class, therefore, were regarded as hydrazones, $>C:N\cdot NH_2$, and the latter as derivatives of hydrazimethylene, $>C<\begin{matrix}NH\\ |\\ NH\end{matrix}$. The authors now show that the members of both classes all behave alike under suitable conditions, and are therefore constituted alike, although they are unable to state whether the substances are hydrazones or hydrazimethylenes. One of the chief criteria of members of the second class is their oxidation to azomethylenes,  $>C<\begin{matrix}N\\ ||\\ N\end{matrix}$, by mercuric oxide. However, the hydrazones of fluorenone, dimethoxybenzophenone (*dimethoxybenzophenonehydrazone* has m. p. 84—86°), benzophenone, and acetophenone also yield azomethylene derivatives, which decompose in various ways according to their varying stability; these decompositions are initially the formation of nitrogen and the group $RR'C<$, which, by intramolecular change, polymerisation, or interaction with undecomposed azomethylene, may yield non-nitrogenous or nitrogenous compounds. The action of iodine on these azomethylene derivatives also starts with the formation of nitrogen and the group $RR'C<$, which then undergoes change as above or unites with iodine to form substituted methylene iodides.

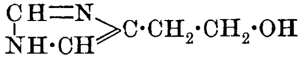
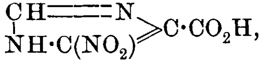
Diphenyleneazomethylene,  $\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}>C<\begin{matrix}N\\ ||\\ N\end{matrix}$, m. p. 94—95°, dark red

needles, is unimolecular (so also are all other azomethylene derivatives); it yields bisdiphenylene-ethylene when decomposed by heat at 130—140° (in the presence of a little benzene or ether), by iodine in boiling alcohol, or by hydrogen bromide in boiling xylene, and is reduced to fluorene by zinc and alcoholic sodium hydroxide. *Dimethoxydiphenylazomethylene*,  $\begin{array}{l}N\\ \|\\ N\end{array}\!\!>C(C_6H_4\cdot OMe)_2$, m. p. 103—104°, deep violet crystals, changes in air or in hot benzene to the ketazine, yields tetramethoxytetraphenylethylene when heated with benzene at 150° in an atmosphere of carbon dioxide, and is converted into dimethoxybenzophenone when shaken in benzene in an atmosphere of oxygen. Diphenylazomethylene is converted completely into the ketazine by heat at 150°.

The formation of azomethylenes by the oxidation of the products of the interaction of hydrazine and carbonyl compounds would suggest that these products are hydrazimethylenes. However, against this assumption and in favour of the hydrazone formula are the facts: (i) the azomethylenes cannot be re-converted into hydrazimethylenes by reduction; (ii) the behaviour of the products is easily explained by the hydrazone formula; (iii) almost all of the products are very easily converted into ketazines; (iv) the acetylation of benzylidenehydrazine yields a substance identical with that obtained from acetylhydrazine and benzaldehyde. All hydrazones behave alike when heated, primarily yielding ketazines and hydrazine, by the further interaction of which methane derivatives may be formed; thus the hydrazone of benzil, which gives deoxybenzoin when heated under Curtius's conditions, is converted into bisbenzilketazine at 240°/11 mm. Similarly, fluorenonehydrazone at 200°/18 mm. yields the ketazine (which is converted into fluorene by an excess of hydrazine hydrate at 200°), and dimethoxybenzophenonehydrazone yields bisdimethoxydiphenylketazine at 280°/20 mm., which is converted into dimethoxydiphenylmethane by an excess of hydrazine at 200°. The hydrazone of Michler's ketone yields the ketazine at 280°/14 mm., which is reduced to tetramethyldiaminodiphenylmethane by an excess of hydrazine at 200°. Benzophenone, benzophenoneanil, and benzophenonephenylhydrazone are reduced to diphenylmethane, and benzylideneazine and benzaldehyde to toluene, by an excess of hydrazine at 200°. C. S.

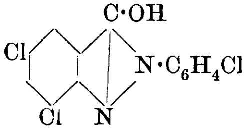
Synthesis of Iminazole [Glyoxaline] Derivatives. ADOLF WINDAUS and H. OPITZ (*Ber.*, 1911, **44**, 1721—1725. Compare Windaus and Vogt, Abstr., 1907, i, 978).—4-*Aminomethylglyoxaline*,  $\begin{array}{l}CH{=}N\\ |\\ NH\cdot CH\end{array}\!\!>C\cdot CH_2\cdot NH_2$, is obtained from glyoxaline-4-acetic acid (Knoop, Abstr., 1907, i, 789) by Curtius' method. The *hydrazide*, $C_5H_8ON_4$, prepared by boiling ethyl glyoxaline-4-acetate for six hours with a 50% hydrazine hydrate solution, crystallises from absolute alcohol in needles, m. p. 189° (decomp.). The *dihydrochloride* crystallises in prisms insoluble in alcohol, has m. p. 230°, and with amyl nitrite and alcohol yields the urethane, and this when hydrolysed with concentrated hydrochloric acid gives 4-*aminomethylglyoxaline hydrochloride*, which crystallises from a mixture of methyl alcohol and ether in long, slender prisms, sintering at 236°.

The *platinichloride*, $C_4H_9N_3Cl_6Pt$, crystallises in compact, rhombic plates, which decompose at 288°; the *picrate* crystallises from hot water in deep yellow, glistening, six-sided plates, m. p. 209°, and the *picrolonate*, $C_{24}H_{23}O_{10}N_{11}$, forms long, yellow needles, m. p. 273° (decomp.).

4-β-*Hydroxyethylglyoxaline*,  $\begin{matrix}CH{=}N\\ NH{\cdot}CH\end{matrix}\!\!>C{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (?), is obtained by the action of barium nitrite on 4-β-aminoethylglyoxaline hydrochloride, and is probably identical with the product formed by the action of yeast on histidine (Ehrlich, this vol., i, 127). The *hydrochloride* crystallises from water in nodular masses of needles; the *platinichloride* forms orange-yellow needles, m. p. 175°, and the *picrolonate* crystallises from alcohol in slender, pale yellow needles, which are much bent, and have m. p. 264° (decomp.). When the hydroxy-compound is treated with 25% nitric acid, the chief product is 5-*nitroglyoxaline*-4-*carboxylic acid*,  $\begin{matrix}CH{=\!=\!=}N\\ NH{\cdot}C(NO_2)\end{matrix}\!\!>C{\cdot}CO_2H$, which crystallises from water in long, colourless prisms, m. p. above 300° (decomp.). J. J. S.

Hydroxyindazoles. IV. Preparation of Hydroxyindazoles from Non-substituted Benzene-azo- or -hydrazo-benzoic Acids.

PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 735—739. Compare Abstr., 1903, i, 371, 585; 1904, i, 121, 667, 699; 1906, i, 544; this vol., i, 577).—The method described gives a ready means for preparing unchlorinated or mono-chlorinated hydroxyindazoles, which up to the present have been difficult to obtain. The transformation consists in a simple dehydration, and proceeds more readily when there are more halogen atoms in the benzene nucleus.



5 : 7-*Dichloro*-3-*hydroxy*-2-p-*chlorophenylindazole* (annexed formula), white needles, m. p. 209—210°, very sparingly soluble in organic solvents, is prepared by the action of phosphorus pentachloride or thionyl chloride on *p*-chlorobenzeneazo-*o*-benzoic acid.

The same method is used for the preparation of several hydroxyindazoles, which have been previously prepared by other methods, and described. 5 : 7-Dichloro-3-hydroxy-2-phenylindazole can be readily obtained from benzeneazo-*o*-benzoic acid in this way (compare Abstr., 1907, i, 158). W. G.

Ring Formation in the Peri-position in the Naphthalene Series. III. Derivatives of 2′ : 4′-Dinitrophenyl-1 : 8-naphthylenediamine.

FRANZ SACHS and R. B. FORSTER (*Ber.*, 1911, 44, 1738—1748. Compare Abstr., 1909, i, 426).—The condensation of 2′ : 4′-dinitrophenyl-1 : 8-naphthylenediamine with various acids and carbonyl derivatives has been studied. In the case of condensing with formic acid, the large, strongly negative dinitrophenyl group has a retarding effect. With acetic anhydride and most acyl chlorides, ring formation does not occur, the product being a monoacyl derivative of the type

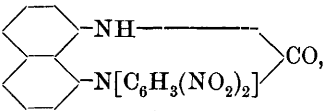
$$R\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2.$$

Carbonyl chloride does not condense at all readily with the nitrated base, but ethyl chlorocarbonate yields the *carbethoxy*-derivative,

$$CO_2Et\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2,$$

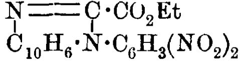
which gives the cyclic compound 1-*op*-dinitrophenyl-1 : 3-dihydro-2-perimidone :

(I.)

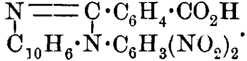


Ethyl oxalate yields a mixture of the two compounds

(II.) $CO_2Et\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2$

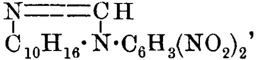
and(III.)  $\begin{array}{l} N{=\!=\!=}C\cdot CO_2Et \\ C_{10}H_6\cdot N\cdot C_6H_3(NO_2)_2 \end{array}$, and succinic anhydride reacts in much the same manner.

Condensation with phthalic anhydride takes place readily when a glacial acetic acid solution of the components is boiled for a short time, the product being 1-*op*-dinitrophenylperimidine-2-benzoic acid,


$$\begin{array}{l} N{=\!=\!=}C\cdot C_6H_4\cdot CO_2H \\ C_{10}H_6\cdot N\cdot C_6H_3(NO_2)_2\cdot \end{array}$$

Acetone, ethyl acetoacetate, and other carbonyl derivatives react with the free amino-group only, ring formation does not occur, and products of the type (IV.) $C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot N{:}CMe_2$ are formed, which are extremely sensitive to acids.

The cyclic perimidine compounds obtained are deeply coloured; their solutions in concentrated sulphuric acid are also coloured, and the colour of the solution is not destroyed by gently heating.

1-op-*Dinitrophenylperimidine*,  $\begin{array}{l} N{=\!=\!=\!=}CH \\ C_{10}H_{16}\cdot N\cdot C_6H_3(NO_2)_2 \end{array}$, crystallises from dilute methyl alcohol in reddish-brown needles, m. p. 175°, and decomposing at 265°. The *picrate*, $C_{23}H_{13}O_{11}N_7$, forms orange-red crystals, m. p. 232°.

1-*Acetylamino*-8-op-*dinitroanilinonaphthalene*,

$$NHAc\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2,$$

separates from alcohol in yellow crystals, m. p. 237°, and yields a *tetranitro*-derivative, m. p. 248°. The corresponding *benzoyl* derivative, $COPh\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2$, crystallises from glacial acetic acid or xylene, and has m. p. 271—272°, and the *cinnamoyl* derivative, $CHPh{:}CH\cdot CO\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2$, separates in yellow crystals from xylene, and has m. p. 258—259°.

1-*Carbethoxylamino*-8-op-*dinitroanilinonaphthalene*,

$$CO_2Et\cdot NH\cdot C_{10}H_6\cdot NH\cdot C_6H_3(NO_2)_2,$$

obtained by heating the dinitrated base with ethyl chlorocarbonate at 100° for seventeen hours, forms orange-coloured crystals, m. p. 184—185°, and decomposing at 260—270°. When heated at 193° under 10—12 mm. pressure for 1½ hours, the compound loses ethyl alcohol and yields 1-op-*dinitrophenyl*-1 : 3-*dihydro-2-perimidone*, $C_{17}H_{10}O_5N_4$, which crystallises from xylene in red, triangular prisms, m. p. 267—268° (decomp.), after changing colour at 150°. The crystals contain 0·5 mol. of xylene, which they lose gradually at 100° under reduced pressure.

8-op-*Dinitroanilino*-1-*naphthylphenylcarbamide*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot NH\cdot CO\cdot NHPh,$$

obtained by heating the components in dry xylene, separates from acetic acid in orange-coloured crystals, m. p. 229—230°, and the corresponding *thiocarbamide*, $C_{23}H_{17}O_4N_5S$, obtained by boiling a chloroform solution of the components for twenty-four hours, separates from a mixture of chloroform and light petroleum in glistening, orange-red crystals, m. p. 182°.

Methyl 8-op-*dinitroanilinonaphthyloxamate*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CO_2Me,$$

obtained by heating the dinitro-base with ten times its weight of methyl oxalate for seven days at 100°, crystallises from dilute acetone, and has m. p. 209—210°. The corresponding *ethyl* ester separates from ethyl acetate in yellow crystals, m. p. 191—192°, and is accompanied by the cyclic compound (III), which forms red crystals, m. p. 171—172°.

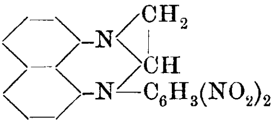
8-op-*Dinitroanilino*-1-*naphthylsuccinamic acid*,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot NH\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H,$$

forms a pale yellow, crystalline powder, turns red at 190°, and decomposes at 227°. When boiled with glacial acetic acid it yields the *anhydro*-compound, $C_{20}H_{14}O_6N_4$, in the form of red crystals sparingly soluble in alcohol and melting at 227°.

1-op-*Dinitrophenylperimidine-2-benzoic acid* forms yellow crystals, m. p. 297°, and when reduced yields the corresponding *diamino*-derivative, which is not molten at 340°, although its *picrate* has m. p. 220°.

The dinitro-base reacts with formaldehyde solution in the presence of glacial acetic acid and dilute hydrochloric acid, yielding a compound, probably of the annexed constitution, which decomposes without melting.



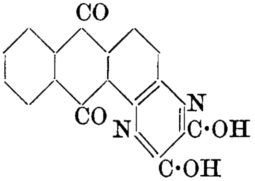
8-op-*Dinitroanilino*-1-*propylideneaminonaphthalene* (IV), from acetone and the dinitro-base, forms yellow crystals, m. p. 166—167°. The corresponding *derivative* from acetophenone,

$$C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot N\colon CMePh,$$

forms red crystals, m. p. 163—164°, and that from ethyl acetoacetate, $C_6H_3(NO_2)_2\cdot NH\cdot C_{10}H_6\cdot N\colon CMe\cdot CH_2\cdot CO_2Et$, has m. p. 167—168°.

J. J. S.

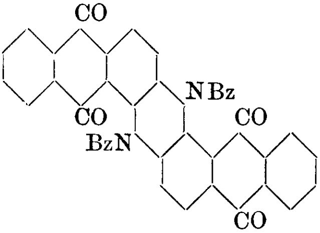
Degradation of Indanthren to Dihydroxypyrazinoanthraquinone and its Behaviour with Benzoyl Chloride and Sodium Ethoxide. Roland Scholl and Siegfried Edlbacher (*Ber.*, 1911, 44, 1727—1737. Compare Scholl and Mansfield, Abstr., 1907, i, 255).—Commercial indanthren powder which has been extracted with hydrochloric and glacial acetic acids can be oxidised by a boiling glacial acetic acid solution of chromium trioxide to *αβ-dihydroxyanthraquinoxalinequinone* (*αβ-dihydroxy-1 : 2-pyrazinoanthraquinone*) (annexed constitution), which crystallises from nitrobenzene in golden-bronzy needles. It begins to sublime at 300°, and chars at 370°. Boiling sulphuric acid or bromine has no action, and distillation with zinc dust yields anthraquinoxaline. Its *sodium* derivative, $C_{16}H_6O_4N_2Br_2$, obtained by the action of sodium ethoxide, forms a brick-red powder.



Nitrodihydroxyanthraquinoxalinequinone, $C_{16}H_7O_6N_3$, obtained by the action of 50% nitric acid, forms a pale yellow powder, and yields a red sodium derivative. The corresponding *amino*-derivative, $C_{16}H_9O_4N_3$, prepared by reducing the nitro-compound with ammonium sulphide, crystallises from nitrobenzene in violet, microscopic needles, m. p. 365°.

αβ-Dihydroxyanthraquinoxalinequinone can be synthesised by condensing 1 : 2-diaminoanthraquinone with anhydrous oxalic acid at 170°.

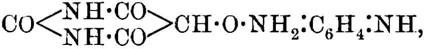
Indanthren yields *N*-benzoyl derivatives (compare Scholl and Berblinger, Abstr., 1907, i, 257) when boiled for an hour with benzoyl chloride or benzoic anhydride. The *dibenzoyl* derivative, *dibenzoyl*-N-*dihydroanthraquinoneazine* (annexed constitution), crystallises from xylene in red needles, forms an unstable blue additive compound with benzoyl chloride, and is hydrolysed by sulphuric acid or by alcoholic potash to indanthren.

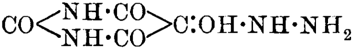
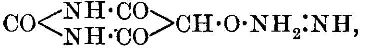


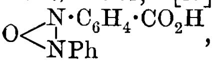
When indanthren is left in contact with a methyl-alcoholic solution of sodium methoxide at the ordinary temperature for twenty-four hours, the colour changes to greyish-green, and, after decanting and washing with methyl alcohol and ether, and finally with absolute ether, a bluish-black sodium compound is obtained. This product is formed by the union of two molecules of sodium methoxide to one of the quinone, probably at the expense of two of the four carbonyl groups originally present. The compound is immediately decomposed by water.

Anthraquinoneazine and sodium methoxide form a green additive compound, $C_{30}H_{18}O_6N_2Na_2$, which is completely decomposed by prolonged treatment with methyl alcohol, yielding anthraquinonazhydrine (Abstr., 1904, i, 110). These compounds are analogous to the additive compounds of sodium alkyl oxides with indigocarmine, indigotin, etc.

J. J. S.

Constitution of Alloxantin. M. M. RICHTER (*Ber.*, 1911, **44**, 2155—2158).—Piloty and Finckh, and also Slimmer and Stieglitz, have suggested that alloxantin is a combination of alloxan and dialuric acid resembling the quinhydrones. Since alloxantin does not exhibit the typical criteria (quinonoid structure, colour, easy dissociation) of quinhydrones, the proof of the suggestion is very difficult, and must be limited to the possibility of preparing quinhydrone-like compounds from *p*-benzoquinone and dialuric acid and from quinol and alloxan. The combination of the former pair is impossible, owing to the sensitiveness of dialuric acid to atmospheric oxidation, but a molecular combination of the latter pair has been described by Böhringer & Söhne (1900, D.R.-P. 107720). That the oxygen atom in alloxan can exert a similar, although milder, oxidising action to that of the oxygen in *p*-benzoquinone is shown by mixing concentrated aqueous solutions of alloxan and *p*-phenylenediamine at 30°, whereby is obtained a bluish-black precipitate of p-*phenylenedi-imine dialurate*,  $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot O\cdot NH_2{:}C_6H_4{:}NH$, the formation of which is explained by the conversion of the *p*-phenylenediamine and the alloxan into *p*-phenylenedi-imine and dialuric acid respectively.

Alloxan and hydrazine hydrate in methyl alcohol yield *alloxan-hydrazine*,  $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>C{:}OH\cdot NH\cdot NH_2$ (according to the author's oxonium formula for quinhydrones), a white, amorphous powder, which in the presence of moisture is transformed into *dialurodi-imine*,  $CO<\begin{matrix}NH\cdot CO\\NH\cdot CO\end{matrix}>CH\cdot O\cdot NH_2{:}NH$, decomposing rapidly into nitrogen and ammonium dialurate. C. S.

Benzeneazoxy-*o*-benzoic Acid. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 739—741).—*Benzeneazoxy*-o-*benzoic acid*,  $O<\begin{matrix}N\cdot C_6H_4\cdot CO_2H\\ | \\ NPh\end{matrix}$, pale yellow spangles, m. p. 110—111°, is prepared by the action of phenylhydroxylamine on *o*-nitrosobenzoic acid in alcoholic solution. It is purified through its barium salt. W. G.

Hydroxyindazoles. III. Preparation of Ortho-substituted Azo-acids. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], 9, 657—661. Compare this vol., i, 577).—Further condensations of nitrosobenzene with *o*-aminobenzoic esters and of amines with *o*-nitrosobenzoic acids have been effected by the method previously described.

Methyl 5-chloroanthranilate and nitrosobenzene when kept for fifteen days at the ordinary temperature in glacial acetic acid yield a reaction product, from which the following substances can be isolated: (1) the yellow compound, $C_{13}H_{11}O_3N_2Cl$, m. p. 137°, previously mentioned (Abstr., 1910, i, 446); (2) *methyl* 2-*benzeneazo*-5-*chlorobenzoate*, which forms red needles, m. p. 64·5°; (3) the *acid*, of which the yellow compound is the methyl ester; (4) azoxybenzene; (5) 2-*benzeneazo*-5-*chlorobenzoic acid*, which, after purification by the crystallisation of its *barium* salt, forms orange-red needles, m. p. 126—127°. The *barium* salt becomes red and anhydrous at 100°.

Methyl bromoanthranilate yields in similar circumstances: (1) a yellow *substance*; (2) the corresponding *acid*; (3) azoxybenzene; (4)

2-benzeneazo-5-bromobenzoic acid, which crystallises in ruby-red prisms, m. p. 142—143°.

By the interaction of *o*-nitrosobenzoic acid and aniline, benzeneazobenzoic acid is obtained, and *p*-tolueneazobenzoic acid and *p*-chlorobenzeneazobenzoic acid may be prepared similarly.

*2-Nitroso-*m*-toluic acid* crystallises in grey prisms, m. p. 172—173° (decomp.). It reacts with *p*-toluidine, yielding *2-*p*-tolueneazo-*m*-toluic acid*, which crystallises in large, red prisms, m. p. 122·5°.

*2-*p*-Tolueneazo-5-chlorobenzoic acid* (from *p*-toluidine and 2-nitroso-5-chlorobenzoic acid) forms orange scales, m. p. 159—160°.

R. V. S.

Sulphur Linkings in Proteins. TREAT B. JOHNSON (*J. Biol. Chem.*, 1911, **9**, 439—448).—The available evidence on the sulphur linkings in protein is summarised and discussed. It is considered that there are other sulphur combinations besides the cystine group which can break down on hydrolysis with the formation of hydrogen sulphide.

E. F. A.

Enzyme Action and Electrolytic Dissociation. HUGO ROHONYI (*Biochem. Zeitsch.*, 1911, **34**, 176—191).—The differences which have been observed between active and inactivated enzyme solutions are experimentally shown by the author to be due to the evaporation of water during the process of inactivation. The increase in conductivity during the course of the hydrolysis of starch by diastase is shown to be due to the setting free of adsorbed salt molecules. No similar increase is observed when ash-free sucrose is hydrolysed by invertin. On the addition of a substrate to an enzyme solution the changes of the conductivity are quantitatively different when active or inactivated enzyme is used. This change is not specific for the substrate, however, as similar differences are noted when indifferent electrolytes are added to the enzyme solutions. The hydrogen ion concentration in the cases investigated remains unchanged during the digestion process, and there is no difference in the hydrogen ion concentration between active and inactivated enzyme solutions.

S. B. S.

Action of Ultra-violet Light on Amylase, Invertase, and a Mixture of These Two Diastases. A. CHAUCHARD and (Mlle.) B. MAZOUÉ (*Compt. rend.*, 1911, **152**, 1709—1711).—Malt amylase is much more sensitive to ultra-violet light than the invertase from yeast. It is therefore possible by exposing a mixture of the two to the light from a quartz-mercury lamp to destroy the activity of one before that of the other.

W. O. W.

The Solubility of the Pancreas Lipase. L. BERCZELLER (*Biochem Zeitsch.*, 1911, **34**, 170—175).—Experiments with pancreas lipase showed that this enzyme is not soluble either in ether, fats, or fatty acids. The conclusion is drawn that the fat scission by lipase takes place in a heterogeneous system.

S. B. S.

Enzymic Decomposition of Hydrogen Peroxide. PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1911, **72**, 226—304. Compare Senter, Abstr., 1905, i, 107; ii, 377).—The decomposition of hydrogen peroxide by the enzymes of blood is not in agreement with a reaction of the first order, nor is it possible to express the course of change by one mathematical expression. There is, however, some proportionality between the enzyme concentration and the amount of hydrogen peroxide decomposed during the first stage of the reaction.

The more highly purified ferment preparations are more susceptible to the adverse influence of impurities. Hydrogen peroxide exerts an adverse influence.

The neutrality or otherwise of the mixture is of great influence on the velocity of reaction, which is quickest at 0° in truly neutral distilled water, and is retarded by the amount of carbon dioxide present in ordinary distilled water or by addition of alkali until indicated by phenolphthalein. At higher temperatures the optimum is in water containing carbon dioxide. When the quantity of acid present is increased, the velocity of change falls at first quickly and later more slowly without the enzyme being damaged. An increase in the amount of alkali decreases the velocity, and the enzyme is also in part destroyed. These changes are more marked at 30° than at 0°. The influence of an increase of temperature on the rate of change is remarkably small so long as the concentration of the hydrogen peroxide is small. E. F. A.

The Reducing Ferments. II. Reduction of Nitrates by the System Perhydrase, Aldehyde, Water. ALEXIS BACH (*Biochem. Zeitsch.*, 1911, **33**, 282—290).—The author has already suggested that the Schardinger enzyme which reduces methylene-blue is a perhydrase which acts together with another substance which can be replaced by aldehydes (this vol., i, 412). The reducing action when methylene-blue is replaced by nitrates was then investigated. It was found that fresh milk contains a catalase, which accelerates the reduction of nitrates by aldehydes to such an extent that nitrites could be detected after one or two minutes' action. The increase of both aldehyde and nitrate concentration increases the rate of action, but the increased rate is less than proportional to the increase of the other two constituents of the system. The increased rate of action is, however, proportional to the concentration of the enzyme when the concentration of the other substances is the same. Side by side with the formation of the nitrites, there is a destruction of the latter substance. The optimum temperature is 60—70°. The acetic acid formed in the process has no appreciable action on the rate. In a mixture of milk, nitrite, and aldehyde at 50°, there is a small disappearance of nitrite, which is not sufficient to account for any appreciable loss in the mixture of nitrate, aldehyde, and ferment, and the reason for the small amount of nitrate formed is not yet accounted for in a satisfactory manner. A similar ferment was obtained from the liver of a calf. S. B. S.

Preparation of a Nitro-1-aminophenyl-4-arsinic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 232879. Compare this vol., i, 594).—The oxanil-4-arsinic acid previously employed for this preparation can be replaced by p-*urethanophenylarsinic acid*, $AsO(OH)_2 \cdot C_6H_4 \cdot NH \cdot CO_2Et$, needles, decomposing at 330—340°, and obtained by adding ethyl chlorocarbonate to a cooled alkaline solution of *p*-aminophenylarsinic acid. The *nitro*-compound prepared by nitrating the foregoing urethane in concentrated sulphuric acid solution crystallises from alcohol in yellow needles, and is converted by heating at 60—80° with sulphuric acid into nitro-1-aminophenylarsinic acid. F. M. G. M.

Quinine Esters of Phenylarsinic Acid Derivatives. K. J. OECHSLIN (*Philippine J. Sci.*, 1911, 6, 23—34).—Arsenophenylglycine and atoxyl have been found by Strong and Teague (*Philippine J. Sci.*, 1910, 5, 29) to be the best drugs which have possibilities as a specific against surra; they have the disadvantage, however, that the dose required to effect a cure is too nearly the lethal dose. The author has tested a number of substances (a list of which is given) for their action on trypanosomata, and in the course of the work has prepared the following quinine esters of phenylarsinic acid derivatives.

A suspension of benzoarsinic acid [*p*-carboxyphenylarsinic acid] in dry chloroform is reduced to benzoarsine dichloride by phosphorus trichloride. After evaporation to dryness in a vacuum on the water bath, chloroform and phosphorus pentachloride (1 mol.) are added to the residue, and the resulting solution is treated with quinine in chloroform, whereby ultimately is obtained the quinine *ester* of benzoarsine dichloride, $C_{20}H_{23}ON_2 \cdot CO_2 \cdot C_6H_4 \cdot AsCl_2$. This substance shows an exceedingly high toxicity for trypanosomata *in vitro*, but on the other hand is equally toxic for the cells of the host *in vivo*, and therefore cannot be used therapeutically. It is oxidised by hydrogen peroxide and hydrochloric acid to the quinine *ester* of benzoarsinic acid, $C_{20}H_{23}ON_2 \cdot CO_2 \cdot C_6H_4 \cdot AsO(OH)_2$, a heavy, white powder, soluble in acids or alkalis, its solutions in the former being fluorescent.

In a somewhat similar manner, di-*p*-benzoarsinic acid is converted into *diquinine dibenzoarsinate*, $C_{54}H_{55}O_8N_4As$, a fine, white powder, and phenylglycinearsinic acid through its acetyl derivative into *quinine acetylphenylglycinearsinic acid*, a heavy, white powder, which is easily soluble in dilute hydrochloric acid, aqueous ammonia, sodium hydroxide, or sodium carbonate. C. S.

Organic Chemistry.

New Catalytic Reaction with Finely Divided Nickel. H. VAN BERESTEYN (*Bull. Soc. chim. Belg.*, 1911, **25**, 293—300).—In attempting to prepare heptyl alcohol from heptaldehyde by the general method of Sabatier and Senderens (compare Abstr., 1905, i, 333), the author, whilst obtaining some of the required alcohol, observed in addition the formation of considerable quantities of *n*-hexylene. This hydrocarbon was also obtained by passing heptyl alcohol over finely divided nickel, in an atmosphere of hydrogen, at 220°, this being the optimum temperature. The reaction is represented by the following equation: $C_7H_{15}\cdot OH = C_6H_{12} + CH_3\cdot OH$.

The methyl alcohol formed is decomposed in the reaction into hydrogen and carbon monoxide, the latter being detected in the gaseous products. W. G.

Optical Investigation of Argentine Petroleum. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 792—793).—Crude Tartahal (Argentine) naphtha is polarimetrically semi-transparent, and the carbonisation constant K is greater than 1%, this being in complete correspondence with the small depths of the deposits. Various other specimens of Argentine petroleum were examined. T. H. P.

Optical Investigation of Petroleum from Southern Bolivia. MICHAEL A. RAKUSIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 791—792). —Two petroleums from the Yacuiba district of S. Bolivia were found to be virtually optically inactive, and to give no reaction with Tschugaeff's cholesterol reagent, trichloroacetic acid. These properties indicate a modification in the properties of the natural petroleum, as originally formed, by a process of filtration. T. H. P.

Presence of Cholesterol in Petroleum. A. K. KOSS (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 697—707).—The author has made a number of experiments with Ledok and Gogor petroleums (from Java), the results being in disagreement with Engler's view that the optical activity of petroleum is due to a product of the destructive distillation of cholesterol. For instance, when cholesterol was dissolved in a lævorotatory fraction of either of these petroleums and the solution completely distilled, the lævorotation of the distillate was found to be identical with that of the original fraction. Also, the magnitudes of the lævorotations are not altered by treatment of these fractions with ozone. T. H. P.

Borislav Ozokerite. A. K. KOSS (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 846—855).—Owing to the difficulty of separating the paraffins unchanged from ozokerite by distillation, the author has used the extraction method, ether, which dissolves part of the asphaltene and the paraffins of lower boiling point, being used first, and the residue being then extracted with acetone. The portion extracted by the latter is divided into several fractions of varying solubility in acetone. The products were suitably purified before examination. Both the liquid and the solid portions of the ozokerite are found to be free from cholesterol.

If the ozokerite exhibits any optical activity, the active constituents belong exclusively to the liquid portion, boiling at 229—305°/10·5 mm. The rotations observed are very slight and are dextrorotations. The higher the m. p. of the paraffin, the higher is the specific gravity and the lower the degree of unsaturation (iodine number). Also, as the degree of unsaturation of the paraffin fractions diminishes, the dispersion decreases and the refraction increases.

According to Krafft, the specific gravities of normal paraffins at their melting points are almost constant, the value of ΔD being very small. With the paraffin fractions under examination, the increase of specific gravity with rise of melting point is much greater than for the normal paraffins, so that isoparaffins are probably present.

T. H. P.

Fluorobromo-derivatives containing Two Atoms of Carbon. V. FRÉDÉRIC SWARTS (*Bull. Acad. roy. Belg.*, 1911, 563—589. Compare *ibid.*, 1897, **33**, 439, and Abstr., 1898, i, 457; 1899, i, 254; 1902, i, 129; 1909, i, 689; 1910, i, 293).—The author has prepared a series of isomeric compounds derived from *as*-tetrabromoethane. A modification of his former method of preparing tribromoethane is given, by which the vinyl bromide formed is separated, collected, and distilled on to the calculated quantity of bromine to give tribromoethane. This is then converted into *as*-dibromoethylene by boiling in alcoholic solution with potassium carbonate and potassium acetate for thirty-six hours. The resulting product after distillation out of contact with air gives on bromination the required *as*-tetrabromoethane, b. p. 112·5°/18 mm. The action of antimony fluoride on this substance is similar to that on bromoform, but is markedly different from that on either *s*-tetrabromoethane or tribromoethane. The reaction with antimony fluoride is somewhat complex. By using $\frac{1}{3}$ mol. of this reagent for every mol. of tetrabromoethane, working at 135°, the principal product is fluorotribromoethane. The other products of the reaction are tetrabromoethylene, and a liquid, b. p. 206—209°, which appeared to be fluorotetrabromoethane.

By using $\frac{2}{3}$ mol. antimony fluoride the principal product is difluorodibromoethane, $CF_2Br\cdot CH_2Br$. The other products are trifluorobromoethane, difluorotribromoethane, pentabromoethane, fluorotetrabromoethane, and tetrabromoethylene.

α-Fluoro-$\alpha\alpha\beta$-tribromoethane (Abstr., 1909, i, 690) is a colourless liquid, b. p. 162·7°/757 mm., $D^{17\cdot5}$ 2·6054, $n_D^{17\cdot5}$ 1·50215; when acted on by potassium ethoxide in an atmosphere of hydrogen, it yields α-fluoro-$\alpha\beta$-dibromoethylene, $CFBr\colon CHBr$, b. p. 88·8°, $D^{17\cdot5}$ 2·2890. On leading oxygen into this substance, *dibromoacetyl fluoride* is produced. Alcohol decomposes this, giving ethyl dibromoacetate.

Another method is given for the preparation of fluorobromoethylene (compare *Bull. Acad. roy. Belg.*, 1909, 709) by the action of zinc dust on fluorotribromoethane. The whole operation is conducted in the absence of air, and the product so obtained has b. p. 6·8°, and can be kept in a sealed tube without showing any signs of alteration after eighteen months.

αα-Difluoro-β-bromoethylene, $CF_2{:}CHBr$, is obtained by boiling an alcoholic solution of difluorodibromoethane with potassium carbonate and potassium acetate. It is a colourless liquid, b. p. 6·2°, D^0 1·82, and is not acted on by air.

Difluorobromodiethyl ether, $CF_2Br{\cdot}CH_2{\cdot}OEt$, obtained by the action of sodium ethoxide on difluorodibromoethane, is a colourless liquid with a pungent odour, b. p. 114—115°, which on oxidation with nitric acid yields bromoacetic and hydrofluoric acids.

α-Fluoro-ααββ-tetrabromoethane, $CFBr_2{\cdot}CHBr_2$, a colourless liquid, b. p. 211°, or 106·4°/24 mm., $D^{17\cdot5}$ 2·9094, results from the action of bromine on the above fluorodibromoethylene.

αα-Difluoro-αββ-tribromoethane, $CF_2Br{\cdot}CHBr_2$, a colourless liquid, b. p. 143·4—143·5°/754 mm., $D^{17\cdot5}$ 2·60769, $n_D^{17\cdot5}$ 1·50215, is obtained by the bromination of αα-difluoro-β-bromoethylene. On treatment with potassium ethoxide in an atmosphere of nitrogen, it yields *difluorodibromodiethyl ether*, $CHBr_2{\cdot}CF_2{\cdot}OEt$, a mobile liquid, b. p. 67·2°/25 mm., $D^{17\cdot5}$ 1·9158, giving with nitric acid, hydrofluoric and dibromoacetic acids.

The author attempted to prepare a tetra-substituted ethylene by the action of potassium carbonate and potassium acetate on difluorotribromoethane. The greater portion of the product was the above ether, and only a small amount of *αα-difluoro-ββ-dibromoethylene* was obtained, which, being difficult to purify, was brominated, giving *αα-difluoro-αβββ-tetrabromoethane*, $CF_2Br{\cdot}CBr_3$, a solid, m. p. 99°, b. p. 185°, having a camphor-like odour. A mixture of antimony fluoride and bromine had practically no action on it.

ααβ-Trifluoro-β-bromoethane, one of the by-products in the action of antimony fluoride ($\frac{2}{3}$ mol.) on tetrabromoethane, is obtained by the action of silver fluoride on αα-difluoro-αβ-dibromoethane in sealed tubes at 120°, as a liquid, b. p. 24·8—25°. It does not react with either mercuric oxide and water at 130°, or with potassium ethoxide at 40°. When treated with sodium methoxide at 150° for seven hours, it gives *methyl trifluoroethyl ether*, $CH_2F{\cdot}CF_2{\cdot}OMe$, b. p. 45°.

The group $:CF_2$ imparts inertia to the molecule, as is shown by the fact that, whereas αβ-difluoro-αββ-tribromoethane, $CFBr_2{\cdot}CHFBr$, can be fluorinated, the corresponding ααβ-trifluoro-αβ-dibromoethane, $CF_2Br{\cdot}CHFBr$, cannot be so acted on. Similarly, the bromine atom in the chain $\cdot CF_2Br$ has very little mobility, and cannot be displaced by potassium ethoxide.

Further, in the ethylenes this group $:CF_2$ gives stability. The compounds $CF_2{:}CH_2$ and $CF_2{:}CHBr$ do not undergo oxidation in air, whilst the compounds $CBr_2{:}CH_2$ and $CFBr{:}CHF$ are oxidised readily. On the other hand, the group $:CFBr$ seems the most reactive towards oxygen, and in the compound $CF_2{:}CFBr$, the group $:CF_2$ cannot inhibit the oxidising action on the group $:CFBr$.

If the general structure of the molecule remains unaltered, the transposition of fluorine and bromine atoms has little or no effect on the b. p. and density of the compound. W. G.

Action of Some Organic Acids on Sodium Formate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 440—442).—By the dry distillation of sodium formate mixed with either malonic, succinic, or tartaric acids in the requisite molecular proportions, formic acid passes over, and may be recognised by its reducing power or by the formation of ethyl formate. Tartaric acid is the least active of the three acids, and, in the case of malonic acid, acetic acid can also be found in the distillate. W. G.

Action of Some Organic Acids on Sodium Formate. II. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 590—591. Compare preceding abstract).—Benzoic and tannic acids readily, gallic acid moderately, the three isomeric hydroxybenzoic acids and cinnamic acid feebly, *p*-nitrobenzoic acid partly, if the operation is carefully conducted, and malic acid only partly, displace formic acid from sodium formate on dry distillation.

Incidentally the author notes certain points as to the behaviour of cinnamic acid on sublimation and dissolution, and mentions ethyl alcohol or pure methyl alcohol as the best solvents for it. W. G.

The Optically Active Modifications of Lactic Acid. REGINALD O. HERZOG and P. SLANSKY (*Zeitsch. physiol. Chem.*, 1911, **73**, 240—246).—Jungfleisch (Abstr., 1904, i, 645) has stated that the two optically active modifications of lactic acid are racemised in alkaline solution at different rates. The two modifications have now been prepared with the aid of morphine by Irvine's method (Trans., 1906, **89**, 935), and heated both in alkaline acid and neutral solution. The rotations were determined in presence of ammonium molybdate under standard conditions. No difference whatever was found in the behaviour of the two antipodes. E. F. A.

Electrolytic Reduction of Lævulic Acid and α-Dimethyllævulic Acid. JULIUS TAFEL and BRUNO EMMERT (*Zeitsch. Elektrochem.*, 1911, **17**, 569—572).—Alkaline solutions of the acids were reduced at a prepared lead cathode at about 20° with a current density of about 0·12 ampere per sq. cm. (Abstr., 1900, ii, 588). With acid solutions, it was necessary to add alcohol in order to prevent the formation of a non-conducting film of valeric acid on the lead cathode, or else to use a cathode of mercury instead of lead.

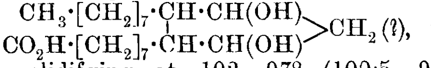
Lævulic and dimethyl-lævulic acid are reduced in alkaline solutions to the corresponding hydroxy-acids or lactones.

In acid solutions lævulic acid is reduced to valeric acid, but dimethyl-lævulic acid yields the corresponding lactone as the principal product, only small quantities of dimethylvaleric acid being formed.

Hydroxyvaleric acid, valerolactone, and α-dimethylvalerolactone are not reduced at all under the conditions used, and these substances cannot therefore be regarded as intermediate products in the reduction to the fatty acids. T. E.

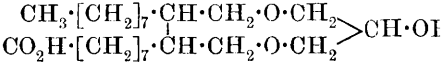
Reactions of Certain Unsaturated Fatty Acids with Formaldehyde. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 809—819).—The author has studied the compounds obtained by the condensation of oleic, elaidic, and undecoic acids with formaldehyde in presence of sulphuric acid. It is found that more definite and non-polymerised products are obtained if the reaction is carried out at low temperatures.

With oleic and elaidic acids the products seem to be identical, and consist of the following acids: (1) A white, crystalline *compound*, $C_{21}H_{40}O_4$ or

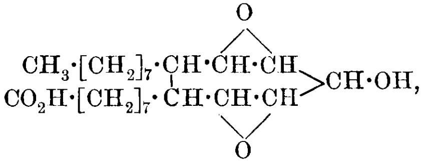


$\begin{matrix} CH_3\cdot[CH_2]_7\cdot CH\cdot CH(OH) \\ CO_2H\cdot[CH_2]_7\cdot CH\cdot CH(OH) \end{matrix} > CH_2$ (?),

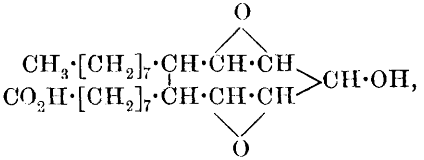
m. p. 112—114° (110—113·5°), solidifying at 102—97° (100·5—94°); the iodine number is 7·6, which indicates the absence of double linkings. The *sodium* and *silver* salts and the *diacetyl* derivative were prepared. (2) An *acid*,



$\begin{matrix} CH_3\cdot[CH_2]_7\cdot CH\cdot CH_2\cdot O\cdot CH_2 \\ CO_2H\cdot[CH_2]_7\cdot CH\cdot CH_2\cdot O\cdot CH_2 \end{matrix} > CH\cdot OH$ or

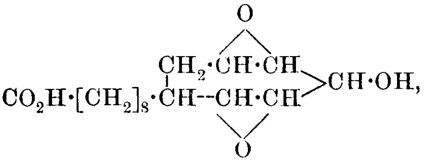


which was obtained as a liquid soluble in light petroleum, and forms a *monoacetyl* derivative. (3) A viscous liquid *acid*, probably



having a bitter taste; it is insoluble in light petroleum, and forms a *monoacetyl* derivative. The *sodium* salt was analysed.

In the case of undecoic acid the principal product is a viscous *liquid*,



soluble in ether.

T. H. P.

The Hæmolytic Action of the Fat of Rice (Oryza sativa, L.) Hæmolysis of Fatty Acids. J. SHIMAZONO (*Arch. expt. Path. Pharm.*, 1911, **65**, 361—366).—The alcoholic and ethereal extracts of rice possess hæmolytic properties which the author traced to the palmitic acid present. This observation led him to study the hæmolytic powers of other fatty acids; working upwards from formic acid, these properties were absent in the lower members, and did not appear until nonoic acid was reached. The higher acids were markedly hæmolytic. It thus appears possible that the hæmolytic action of various organs vaguely ascribed to lipoids, etc., may in reality be due to higher fatty acids. E. J. R.

Cochineal Fat. R. HUERRE (*J. Pharm. Chim.*, 1911, [vii], 4, 56—65).—The fat extracted by boiling ether from "silver cochineal" has m. p. 32°, iodine number 50·53, and the percentage composition free fatty acids 89, glycerides 8, and unsaponifiable matter 3. Liebermann has shown already that the saturated acid present is myristic, and the author finds that the liquid acids are composed of oleic 35% and linoleic 8%, calculated on the "total fatty acids." Oleic acid was isolated by means of the lead salt, but attempts to isolate the linoleic acid in a pure state by Farnsteiner's method (Abstr., 1899, ii, 705) and by the process Haller has used for the separation of oleic acid from saturated fatty acids (Abstr., 1907, i, 9, 10) were unsuccessful, and the presence of linoleic acid was proved by the detection of tetrahydroxystearic acid in the products of oxidation of the liquid fatty acids by permanganate. The unsaponifiable matter is orange-coloured, and has a high iodine number. T. A. H.

Fatty Acids of Cod-liver Oil. ALFRED HEIDUSCHKA and E. RHEINBERGER (*Pharm. Zentr.-h.*, 1911, **52**, 837—838).—It has been shown previously that the fatty acids of cod-liver oil on treatment with Hübl's iodine solution furnish a crystalline derivative, $C_{17}H_{26}O_2Cl_4I_4$, of terapic acid, $C_{17}H_{26}O_2$, in which the iodine can be replaced by chlorine, forming terapic acid octachloride (Abstr., 1910, i, 297).

The first of these derivatives on treatment with zinc and acetic acid furnishes an *acid*, $C_{17}H_{28}O_2$, as a nearly colourless oil, distilling at 154°/75 mm., and having iodine number 264·5. When terapic acid tetrachloride tetraiodide is treated with bromine, the four iodine atoms are replaced by bromine atoms, giving the *compound*,

$$C_{17}H_{26}O_2Cl_4Br_4,$$

m. p. 150°, which forms a yellowish-brown, crystalline powder, soluble in the usual organic solvents.

Terapic acid octachloride forms a *potassium* salt. *Linolenic acid trichloride tri-iodide*, $C_{18}H_{30}O_2Cl_3I_3$, m. p. 95°, formed by the action of Hübl's iodine solution on the mixed fatty acids of linseed oil, is a colourless, crystalline substance, soluble in alcohol or chloroform. T. A. H.

Soya Bean Oil. S. KEIMATSU (*Chem. Zeit.*, 1911, **35**, 839—840).—The oil used had the following constants: D^{15} 0·9265, viscosity at 20° 8·9 to 9·0 (Engler's apparatus), solidifying point −15° to −16°, m. p. −7° to −8°, solidifying point of fatty acids 16—17°, m. p. of fatty acids 23—24°, saponification number 190, iodine value 132—135, and Hehner number 94·2. It contained 0·2% of a phytosterol, m. p. 136—137°, which was not stigmasterol. The fatty acids were separated into saturated and unsaturated by means of the lead salts. The former included palmitic and stearic acids (together 12%). The unsaturated acids on oxidation furnished *iso*linusic, dihydroxystearic, and sativic acids, together with an isomeride of sativic acid, m. p. 158—159° (compare Hartley, Abstr., 1909, ii, 597), and an unidentified acid, m. p. 145—149°, probably impure. These oxidation products indicate the presence in the oil of the following acids, *iso*linolenic, oleic, linoleic (these two together 15%), and an isomeride of linoleic acid (50%). T. A. H.

Preparation of Oxalic Acid by the Fusion of Sawdust with Potassium Hydroxide. A. VON HEDENSTRÖM (*Chem. Zeit.*, 1911, **35**, 853—854).—There being no exact details as to yields, temperature of fusion, etc., in the manufacture of oxalic acid from sawdust, the author has carried out the following experiments, using, in the preliminary work, purified cotton wool instead of sawdust.

Three grams of cotton-wool were heated with 12 grams of potassium hydroxide and 20 c.c. of water in a nickel crucible on a sand-bath, the temperature of the mass being carefully taken. The best yield, 3·72 grams of oxalic acid, was obtained when the temperature was gradually raised to, and maintained at, 280° until no further reaction took place, the fusion then being cooled with continuous stirring. The yield is much less, 1 gram, when the temperature does not exceed 225°, even on prolonged heating. The addition of potassium oxalate in small quantity, as also of potassium permanganate or lead peroxide, further increases the yield of oxalic acid at 280°; the passage of air through the fusion has a similar effect.

Three grams of oak sawdust gave similar results and yields to the cotton-wool. It is thus probable that the lignin substances give oxalic acid as well as the cellulose, and this was confirmed by first extracting the sawdust with a 10% solution of potassium hydroxide at the ordinary temperature, filtering, evaporating the filtrate to dryness, and fusing the residue at 280°. 1·27 Grams of oxalic acid were obtained, which, together with 2·36 grams of oxalic acid obtained from the residual sawdust after extraction, give 3·63 grams, which is practically the same yield as 3·66 grams obtained by direct fusion of 3 grams of sawdust. No oxalic acid was obtained by the extraction of cotton-wool with 10% potassium hydroxide. T. S. P.

Stereoisomeric Dihalogensuccinic Acids. BROR HOLMBERG (*J. pr. Chem.*, 1911, [ii], **84**, 145—168).—The author has measured the velocity of decomposition of dibromosuccinic, *iso*dibromosuccinic, dichlorosuccinic, and *iso*dichlorosuccinic acids, and also of their normal and acid barium salts in (1/30 molar) aqueous solution at 25°, by determining the increase of acidity by means of standard alkali, and finds that the reactions are all of the unimolecular type. The close agreement in the values obtained for the velocity constants indicates that the decomposition of the acids is not affected by the presence of the halogen acid formed in the reaction, and this is confirmed by the comparatively small differences in the constants, obtained for the decomposition of one and the same acid (1) in aqueous solution, (2) in the presence of hydrochloric acid, (3) in the form of its barium hydrogen salt. Although Lossen and Reisch (Abstr., 1898, i, 357) have shown that several reactions take place simultaneously during the decomposition of dibromosuccinic acid in aqueous solution, under the conditions chosen by the author the decomposition occurs mainly according to the scheme:

$$O\cdot CO\cdot CHBr\cdot CHBr\cdot CO\cdot O'' = O\cdot CO\cdot CH{:}CBr\cdot CO\cdot O'' + H^{\circ} + Br'.$$

The behaviour of the isomeric dibromosuccinic acids towards potassium sulphide, potassium xanthate, sodium ethyl sulphide, and potassium trithiocarbonate has also been investigated. When dibromosuccinic acid, in the form of its sodium salt, is allowed to react with these substances in aqueous solution, it is almost quantitatively transformed into fumaric acid, whilst the *iso*-acid, under the same conditions, reacts with difficulty, yielding mainly bromofumaric acid.

Measurements have also been made of the electrical conductivity of the acids and their sodium hydrogen salts, and also of the hydrogen-ion concentration of the same substances in aqueous solution by Bredig and Fraenkel's method (Abstr., 1905, ii, 692); from the results thus obtained, the following values for the primary (k) and secondary (s) affinity constants of the acids have been calculated: dichlorosuccinic acid, $k = 0{\cdot}03$, $s = 8{\cdot}1$; *iso*dichlorosuccinic acid, $k = 0{\cdot}035$, $s = 9{\cdot}9$; dibromosuccinic acid, $k = 0{\cdot}037$, $s = 13{\cdot}6$; *iso*dibromosuccinic acid, $k = 0{\cdot}37$, $s = 4{\cdot}3$.

Unsuccessful attempts to resolve dibromosuccinic acid by crystallisation of the alkaloidal salts are recorded.

The *cinchonine* salt, $C_{42}H_{48}O_6N_4Br_2,6H_2O$, and *strychnine* salt, $C_{21}H_{22}O_2N_2,C_4H_4O_4Br_2$, are described. F. B.

Formation of Cork. S. Zeisel (*J. pr. Chem.*, 1911, [ii], **84**, 317—323).—The author criticises adversely the work of Schmidt (Abstr., 1910, i, 540) on this subject, and maintains that the latter's experiments lend no support to the view that cork is produced by the formation of anhydrides and polymerisation of fatty acids, originally present in young cork in the form of glycerides. F. B.

Sulpho-ethereal Salts or Thionic Esters, R·CS·OR'. Marcel Delépine (*Compt. rend.*, 1911, **153**, 279—282. Compare Abstr., 1910, i, 295).—The following thionic esters have been prepared by the method already indicated (Abstr., 1910, i, 612), or by Matsui's process (Abstr., 1909, i, 463). Experimental details are given for the former.

Ethyl thionacetate, $CH_3\cdot CS\cdot OEt$, b. p. 109—110°, D_4^0 0·9816. Ethyl thionpropionate, b. p. 130—132°, D_4^0 0·9639. *Methyl thion*iso*butyrate*, b. p. 145—148°, D_4^0 0·9577; the *ethyl* ester has b. p. 160—165°, D_4^0 0·9549. *Methyl thion*iso*valerate*, b. p. 160—170° (?). *Methyl thionoctoate*, b. p. 115—120°/12 mm. *Methyl thionbenzoate*, b. p. 110—112°/10 mm. *Methyl thion*cyclo*hexoate*, b. p. 90—100°/12 mm. The last four compounds were not obtained perfectly pure.

The methyl and ethyl esters fume in the air, are strongly phosphorescent, and have an ozone-like odour up to the C_5 terms. The thionbenzoates are also phosphorescent. The higher members of the series as well as the hydroaromatic compounds do not show these properties. W. O. W.

Photochemical Synthesis of Carbohydrates in Absence of Chlorophyll. JULIUS STOKLASA and VENCESLAS ZDOBNICKY (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, **29**, 26—31).—In presence of potassium hydroxide, carbon dioxide and nascent hydrogen interact with production of formic acid. Under the influence of ultra-violet rays a sugar is formed.

Formaldehyde is produced by the interaction of water vapour and carbon dioxide in presence of potassium hydroxide and ultra-violet rays.

Negative results were obtained by submitting (1) water vapour and carbon dioxide, and (2) carbon dioxide, nascent hydrogen, and potassium hydroxide to the action of ultra-violet rays. N. H. J. M.

Instability of Dextrose at the Temperature and Alkalinity of the Body. LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1911, **10**, 3—7).—It is suggested that the very exact regulation of the alkalinity of the body has as one of its principal objects the preservation of a suitable medium for the destruction of dextrose and the regulation of the process. When dextrose is boiled with a mixture of sodium hydrogen phosphate and disodium hydrogen phosphate in varying proportions, the mixture becomes optically inactive within a few hours. Similar solutions preserved with toluene in sealed flasks at 38° for forty-four days showed a slight loss in optical activity.

E. F. A.

Action of Sodium and Potassium Hydroxides on the Optical Behaviour of Dextrose in Solution. S. C. PROFILO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iiia], **17**, 174—181).—In the presence of a fairly high concentration of sodium or potassium hydroxide, a solution of dextrose, which is at first dextrorotatory, slowly diminishes in optical activity and becomes lævorotatory; after a long interval, the lævorotation has diminished to such an extent that the solution is optically neutral. It is suggested that a equilibrium mixture of dextrose, lævulose, and mannose is finally formed, represented by the equation: dextrose $\rightleftarrows$ lævulose $\rightleftarrows$ mannose, and that the sign of the rotation depends on the relative proportions of these substances present. It is possible that after a time the mixture would again become dextrorotatory, but readings ultimately become impossible owing to the depth of colour of the solution. G. S.

Behaviour of Sucrose and its Decomposition Products on Heating. J. E. DUSCHSKY (*Zeitsch. Ver. deut. Zuckerind.*, 1911, 855—879. Compare this vol., i, 607).—Concentrated sucrose solutions of alkaline reaction withstand heating at temperatures up to 130° without appreciable decomposition, as measured either by a fall in the polarisation or by the formation of reducing substances. In cases where a change does take place in solutions which were originally alkaline, it is found that the alkalinity has been destroyed by acid decomposition products, which subsequently facilitate a complete decomposition. Excess of alkali and the nature of the alkali have no influence on the decomposition of concentrated sucrose solutions.

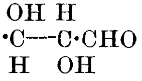
When the reaction is acid, decomposition ensues without any regularity, and its amount is not proportional to the time or temperature of heating. At first dextrose and lævulose are formed, and these are further changed to a series of optically active and inactive substances.

Both in concentrated and in dilute solution the decomposition of sucrose is facilitated before all by the reaction of the medium, and then by the temperature and period of heating. The influence of concentration is subordinate and very irregular.

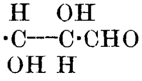
The quantitative results of heating sucrose solutions of alkaline reaction of 50% to 75% concentration for one hour at temperatures from 80° to 135° are contained in a series of tables which give the amount of sugar lost by the process. Heating has but little influence up to 110°; at higher temperatures the loss increases rapidly, amounting to 0·2% to 0·3% at 120°. This indicates that it is inadvisable to warm sugar solutions above a certain limit, and the determinations of the destruction of alkali on heating, which are also tabulated, point to the same conclusion. E. F. A.

Empirical Relation between the Configuration and Rotation of Sugars.

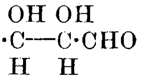
Ernest Anderson (*J. Amer. Chem. Soc.*, 1911, **33**, 1510—1514).—The direction and degree of optical rotation of the sugars are determined by the configuration of the α- and β-carbon atoms. The four possible configurations with their corresponding rotations are:



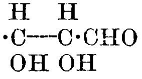
$$\cdot\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\cdot\mathrm{CHO} = \text{strongly dextrorotatory.}$$



$$\cdot\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot\mathrm{CHO} = \text{strongly lævorotatory.}$$



$$\cdot\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}-\overset{\mathrm{OH}}{\underset{\mathrm{H}}{\mathrm{C}}}\cdot\mathrm{CHO} = \text{slightly dextro- or lævo-rotatory.}$$



$$\cdot\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}-\overset{\mathrm{H}}{\underset{\mathrm{OH}}{\mathrm{C}}}\cdot\mathrm{CHO} = \text{slightly dextro- or lævo-rotatory.}$$

It is claimed that this applies to all sugars for which both configuration and rotation are known. The theory is applied to the determination of configuration when the rotatory power is known.

E. F. A.

Action of Oxalic and Malonic Acids on Starch and Dextrin.

William Oechsner de Coninck and A. Raynaud (*Bull. Acad. roy. Belg.*, 1911, 438—439. Compare this vol., i, 423, 607).—With these two dibasic acids the amount of hydrolysis is proportional to the concentration of the acids, and the quantity of dextrin hydrolysed is always greater than that of starch hydrolysed. In the latter respect the two acids under consideration resemble the mineral acids already studied, and differ from the monobasic formic and acetic acids. W. G.

Action of Lactic and Tartaric Acids on Starch and Dextrin. WILLIAM OECHSNER DE CONINCK and A. RAYNAUD (*Bull. Acad. roy. Belg.*, 1911, 592—593. Compare this vol., i, 423, 617, and preceding abstract).—In the case of these two hydroxy-acids the rates of hydrolysis for starch and dextrin are practically the same, the two acids thus resembling formic and acetic acids in their behaviour.

The conclusion drawn from the whole series of experiments is that the rate of saccharification, per molecule of acid, is three or four times greater with mineral than with organic acids. W. G.

New Solvents for Cellulose and their Action on this Substance. HORACE G. DEMING (*J. Amer. Chem. Soc.*, 1911, **33**, 1515—1525).—Cellulose in the form of filter paper is soluble in concentrated aqueous solutions of antimony trichloride, stannous chloride, and zinc bromide. When dissolved in the halogen acids (hydrochloric acid, etc.), these salts and many others dissolve cellulose with great ease. A few salts in solution in formic or trichloroacetic acids also act as solvents for cellulose.

Cellulose attracts metallic salts in solution, forming an adsorption complex, and the salt is distributed between the fibre and the solution. When an agent is present which, like certain dilute acids, can bring about union with water, the complex is brought into solution.

In proof of this view much evidence is adduced. Cellulose modified by acids becomes soluble in aqueous calcium chloride solutions which cannot dissolve pure cellulose. Chlorosulphonic, arsenic, and selenic acids are able to dissolve cellulose.

Celluloses dissolved in acid solutions of salts are precipitated on pouring into water as amorphous compounds with marked reducing properties and easily hydrolysed.

One of the formates of cellulose when hydrolysed by concentrated hydrochloric acid is converted into compounds soluble in water, and finally into dextrose. E. F. A.

β-Aminoethyl Alcohol, a Product of the Hydrolysis of the Lecithin of Bean Meal. GEORG TRIER (*Zeitsch. physiol. Chem.*, 1911, **73**, 383—388).—β-Aminoethyl alcohol is obtained among the products of the hydrolysis of the phosphatide of bean meal (*Phaseolus vulgaris*) with barium hydroxide, and proved to be in all respects identical with the synthetic product. β-Aminoethyl alcohol is regarded as the parent substance of choline, which is evidently derived from it by complete methylation in the plant. E. F. A.

Homocholine and Neosine. E. BERLIN (*Zeitsch. Biol.*, 1911, **57**, 1—74).—The chief point of chemical interest is a comparison of the homocholines obtained by various investigators. The author decides that Malengreau and Lebailly's β-homocholine (Abstr., 1910, i, 545) is identical with Morley's (Abstr., 1881, 151; Morley and Green, *Ber.*, 1885, **18**, 24), and that the constitution $OH\cdot NMe_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$ of Weiss' (*Zeitsch. Naturwiss.*, 1887, **60**, 221) and of Schmidt and Partheil's (Abstr., 1892, 950) γ-homocholine is not proved. The author has prepared γ-homocholine (*mercurichloride*,

$$C_6H_{16}ONCl,6HgCl_2,$$

m. p. 208°; *picrate*, m. p. 255°) by the same method as Malengreau and Lebailly (*loc. cit.*), and has proved its constitution by oxidising it to β-homobetaine by calcium or barium permanganate and warm dilute sulphuric acid. He finds that its aurichloride has m. p. 193—194°, whereas Malengreau and Lebailly give 183°. In consequence of this discrepancy, the author prepares γ-homocholine by another process, and has thereby cleared away much of the confusion in the literature of the homocholines. By exhaustive methylation, γ-aminopropyl alcohol yields two homocholines, which are separated best by means of their mercurichlorides. The less soluble fraction, m. p. 203°, of the mercurichlorides yields an aurichloride, m. p. 187—190°, the base in which is proved to be γ-homocholine by its oxidation to β-homobetaine. The more soluble fraction, m. p. 208°, of the mercurichlorides yields an aurichloride, m. p. 163° [the same as that of Weiss' and of Schmidt and Partheil's γ-homocholine aurichloride (*loc. cit.*)], the base in which is proved to be β-homocholine by its oxidation to betaine. Consequently the so-called γ-homocholine of these two investigators is in reality β-homocholine. A feasible explanation is given for the production of β-homocholine in Schmidt and Partheil's method, and also in the author's second process (above). A discrepancy, as yet unexplained, still remains; Malengreau and Lebailly (*loc. cit.*) give the m. p. of β-homocholine aurichloride as 195—196°.

By-products in the preparation of γ-homocholine from trimethylamine and trimethylene chlorohydrin are the *ether* of γ-homocholine [*platinichloride*, $O(CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_3)_2,PtCl_6$, m. p. 253—254°; *aurichloride*, $C_{12}H_{30}ON_2,2AuCl_4$, m. p. 230—232°] and hexamethyltrimethylenediammonium hydroxide [*platinichloride*,

$$C_9H_{24}N_2,PtCl_6,H_2O,$$

m. p. 258—260° (decomp.)]; the latter is also formed in the author's second process.

Neosine has been isolated from shrimps by Kutscher and Ackermann's method (Abstr., 1908, i, 675). It contains choline, the removal of which is very difficult, but sufficient pure material has been obtained to show, by a comparison of the platinichlorides, mercurichlorides, and aurichlorides, that neosine is not identical with γ-homocholine (compare Kutscher and Ackermann, *loc. cit.*).

Two points of physiological interest are discussed. Firstly, it is shown that γ-homocholine chloride is decidedly more poisonous than choline chloride; thus is disproved Meyer and Schmidt's statement (Abstr., 1905, i, 23) that the physiological activity of the base is weakened when the side-chain is lengthened. Secondly, there has been a controversy as to whether the lowering of the blood-pressure by the injection of choline chloride is due to the substance itself or to an impurity therein. The former view is supported by the author's experiments, since synthetic choline chloride, γ-homocholine chloride, and β-homocholine chloride (in which the presence of such an impurity is almost impossible) all cause a lowering of the blood-pressure. It is remarkable that γ-homocholine ether and hexamethyltrimethylenediammonium dichloride are, comparatively, non-poisonous.

C. S.

d-α-Aminobutyric Acid and l-α-Aminobutyrylglycine. ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1911, 73, 312—313).—*r*-α-Aminobutyrylglycine has been asymmetrically hydrolysed by means of an active enzyme in yeast into d-*α-aminobutyric acid*, $[\alpha]_D^{20}$ +9°, glycine, and l-*α-aminobutyrylglycine*, $[\alpha]_D^{20}$ −86·4°. E. F. A.

Production of Some Amino-acids from the Phenylhydrazones of Ketonic Acids by Aluminium Amalgam, and Preparation of the Optically Active γ-Aminovaleric Acids. EMIL FISCHER and REINHART GROH (*Annalen*, 1911, **383**, 363—372).—When reduced in alcoholic solution by aluminium amalgam and water, the phenylhydrazones of lævulic acid, ethyl acetoacetate, and pyruvic acid yield γ-aminovaleric acid, β-aminobutyric acid (best method of preparation), and alanine respectively in 55—60% yield.

r-γ-Aminovaleric acid, in the form of its benzoyl derivative, is easily resolved by quinine. d-*γ-Benzoylaminovaleric acid*, $C_{12}H_{15}O_3N$, has m. p. 133° (corr.), $[\alpha]_D^{20}$ −21·9° in alcohol, and is less soluble in water than the racemic form. When hydrolysed by 20% hydrochloric acid on the water-bath, it yields d-*γ-aminovaleric acid*, m. p. 214° (corr., decomp.), and $[\alpha]_D^{20}$ 12·0° in water. l-*γ-Benzoylaminovaleric acid*, containing some of the racemic form, has $[\alpha]_D^{20}$ 16·5° in alcohol, and yields an impure l-*aminovaleric acid*, having $[\alpha]_D^{20}$ −10·7° in water. C. S.

Preparation of the Free Esters of Amino-acids. NICOLAI ZELINSKY, A. ANNENKOFF, and J. KULIKOFF (*Zeitsch. physiol. Chem.*, 1911, **73**, 459—470).—The free amino-acid esters may be obtained from their hydrochlorides by heating with excess of lead hydroxide. The procedure is as follows: the hydrochlorides of the esters are prepared as usual by the action of hydrogen chloride on a solution of the amino-acid in absolute alcohol, the alcohol is evaporated in a vacuum, the residue mixed with lead hydroxide, and the mixture distilled in a vacuum, when almost pure ester is obtained with a yield of 85—95% of the possible.

Ethyl α-amino*iso*butyrate has b. p. 38·5—41°/10 mm., D_4^{17} 1·0974, n_D^{17} 1·4169.

Ethyl alanine has b. p. 49—51°/10 mm.; ethyl α-iminodipropionate obtained at the same time showed b. p. 114—115°/10 mm., D_4^{20} 1·0152, n_D^{20} 1·4728.

Ethyl 1-*amino*cyclo*pentane*-1-*carboxylate* has b. p. 80°/10 mm., D_4^{20} 1·0292, n_D^{20} 1·4531. *Ethyl* 1-*amino*cyclo*hexane*-1-*carboxylate* has b.p. 100°/14 mm., D_4^{20} 1·0182, n_D^{20} 1·4614. Both these esters are stable, and do not tend to form a diketopiperazine.

Ethyl methylaspartate is likewise very stable; it has b. p. 112·5—113°/12 mm., D_4^{20} 1·0632, n_D^{20} 1·4332. *Ethyl α-methylaminopropionate* has b. p. 75—76°/65 mm., D_4^{20} 1·4128, n_D^{20} 1·4218, and can be kept for months in sealed tubes without change. E. F. A.

Oxidation of the Amino-acids. II. Alanine and Tyrosine. W. DENIS (*J. Biol. Chem.*, 1911, **10**, 73—76. Compare this vol., i, 616).—The products of oxidation of alanine with alkaline potassium permanganate are ammonia, carbon dioxide, oxalic, acetic and nitric acids. Tyrosine oxidised in the same way yields ammonia, carbon dioxide, oxalic, acetic and nitric acids, with traces of an acid which is probably *p*-hydroxybenzoic. W. D. H.

Conversion of Glycine into Iminodiacetic and Triglycolamic Acids. MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1911, **73**, 194—203. Compare this vol., i, 427).—Much of the work described has been already abstracted (*loc. cit.*).

When glycine and mercuric chloride are set aside at 37° for several days, triglycolamic acid, $N(CH_2\cdot CO_2H)_3$, m. p. 256—257° (decomp.), is obtained.

Alanine is not altered on similar treatment with mercuric chloride.

E. F. A.

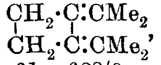
Poulenc's Sodium Glycerophosphate and a Free Glycerophosphoric Acid. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 807—812).—The sodium glycerophosphate of Poulenc is prepared by a patented process by heating monosodium phosphate and glycerol. It has the composition of a *disodium glycerophosphate*, $Na_2(C_3H_7O_2)PO_4$. This indication that it is a chemical individual is confirmed by the fact that the author has prepared pure brucine β-glycerophosphate (Tutin and Hann, Trans., 1906, **89**, 1749) in good yield from the free acid obtained from it by way of the *silver* salt.

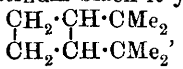
R. V. S.

The Configuration of the Benzene Nucleus. WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1911, **24**, 1759—1760).—Polemical against Lifschitz (this vol., i, 622). T. S. P.

Old and New Benzene Formulæ. ISRAEL LIFSCHITZ (*Zeitsch. angew. Chem.*, 1911, **24**, 1760).—A reply to Vaubel (compare preceding abstract). T. S. P.

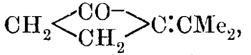
Polymerisation of Diethylene Hydrocarbons. II. Polymerisation and Isomerisation of *as*-Dimethylallene. SERGIUS V. LEBEDEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 820—835. Compare this vol., i, 26).—When *as*-dimethylallene is heated in sealed tubes at 100—225° for two to twenty days, according to the temperature, it yields dipentene, the two following dimerides, and also a trimeride, the investigation of which is now proceeding. It will be seen that these products are both derivatives of *cyclo*butane.

1 : 2-*Diisopropenyl*cyclo*butane*,  $\begin{array}{l}\mathrm{CH_2\cdot C{:}CMe_2}\\ \mathrm{CH_2\cdot C{:}CMe_2}\end{array}$, is a colourless liquid with a faint, aromatic smell, b. p. 61—62°/9 mm., 179—181°/753 mm., D_4^0 0·8571, D_4^{20} 0·8422, $n_D^{19\cdot7}$ 1·50086, $n_G^{19\cdot7}$ 1·52345. It has the normal molecular weight in freezing benzene, and readily oxidises in the air. With nitrous acid, it gives a crystalline *substance*, m. p. 141°. When hydrogenated in presence of platinum black it yields

1 : 2-*Diisopropyl*cyclo*butane*,  $\begin{array}{l}\mathrm{CH_2\cdot CH\cdot CMe_2}\\ \mathrm{CH_2\cdot CH\cdot CMe_2}\end{array}$, which is a faint smell-

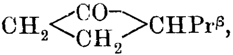
ing liquid, b. p. 157—158·5°/760 mm., D_4^0 0·7901, D_4^{20} 0·7755, n_D^{20} 1·42787, n_G^{20} 1·43755. This compound is also formed, together with a decane, b. p. 153—155·5° (impure), when the hydrogenation is carried out in presence of reduced nickel at 275° and a pressure of 100 atmospheres.

The action of ozone on 1 : 2-di*iso*propenyl*cyclo*butane yields an ozonide which, when decomposed with water, gives 1-iso*propenyl*-2-cyclo*butanone*,



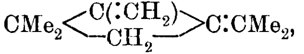
$\mathrm{CH_2}{<}\substack{\mathrm{CO}-\\ \mathrm{CH_2}}{>}\mathrm{C{:}CMe_2}$, as a slightly yellow liquid with a strong odour, recalling that of *p*-benzoquinone, b. p. 57°/11 mm., 171°/760 mm., D_4^{20} 0·9326, n_D^{20} 1·48618, n_G^{20} 1·50571 ; it absorbs oxygen from the air. It forms a *phenylhydrazone*, yellow needles, and a *semicarbazone*, $C_{18}H_{13}ON_3$, m. p. 241°. Attempts to convert the ketone into the corresponding 1 : 2-dione resulted only in the formation of succinic anhydride and condensation products. Oxidation with nitric acid (1 : 1) gave a theoretical yield of succinic acid. In the preparation of the ozonide, the latter is accompanied by succinic anhydride, acetone peroxide, and acetone, these being evidently formed by the decomposition of an unstable diozonide.

1-iso*Propyl*-2-cyclo*butanone*,



$\mathrm{CH_2}{<}\substack{\mathrm{CO}-\\ \mathrm{CH_2}}{>}\mathrm{CHPr^{\beta}}$, obtained by the action of hydrogen on the unsaturated ketone in presence of platinum black, has b. p. 148—150°/770 mm., D_4^{20} 0·8704, n_D^{20} 1·42827, n_G^{20} 1·43843. The *semicarbazone*, $C_8H_{15}ON_3$, m. p. 183°, was prepared.

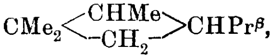
1 : 1-*Dimethyl*-2-*methylene*-3-iso*propenyl*cyclo*butane*,



$$\mathrm{CMe_2}{<}\substack{\mathrm{C({:}CH_2)}\\ -\mathrm{CH_2}-}{>}\mathrm{C{:}CMe_2},$$

is a colourless liquid with an odour resembling that of kerosene, b. p. 37—39°/9 mm., 149—150°/752 mm., D_4^0 0·8143, D_4^{20} 0·7982, $n_D^{19\cdot7}$ 1·46769, n_G^{20} 1·48623. With nitrous acid it gives a crystalline product, m. p. 100° (decomp.).

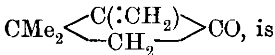
1 : 1 : 2-*Trimethyl*-3-iso*propyl*cyclo*butane*,



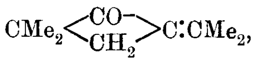
$\mathrm{CMe_2}{<}\substack{\mathrm{CHMe}\\ -\mathrm{CH_2}-}{>}\mathrm{CHPr^{\beta}}$, obtained by hydrogenating the preceding compound under a pressure of 35 atmospheres in presence of platinum black, is a liquid, b. p. 145—146·5°/760 mm., D_4^0 0·7744, D_4^{20} 0·7598, n_D^{20} 1·41997, n_G^{20} 1·42980.

The action of ozone on 1 : 1-dimethyl-2-methylene-3-*iso*propenyl*cyclo*butane yields various condensed products, *as*-dimethylsuccinic acid and an ozonide, which, as would be expected from the unsymmetrical character of the original hydrocarbon and the consequent formation of two mono-ozonides, gives the following two ketones (together with formic acid, acetone, and acetone peroxide) when decomposed with water.

1 : 1-*Dimethyl*-2-*methylene*-3-cyclo*butanone*,



$\mathrm{CMe_2}{<}\substack{\mathrm{C({:}CH_2)}\\ -\mathrm{CH_2}-}{>}\mathrm{CO}$, is a faintly yellow liquid with a pungent odour, b. p. 59—60°/50 mm., D_4^0 0·8854, D_4^{20} 0·8684, n_D^{20} 1·44654, n_G^{20} 1·46123. It readily oxidises in the air, depositing crystals, m. p. 129°, which emit a flash of light when heated. Its *semicarbazone*, $C_8H_{13}ON_3$, has m. p. 160—190° (decomp.).

1 : 1-*Dimethyl*-3-iso*propenyl*-2-cyclo*butanone*,  $CMe_2<\substack{CO-\\CH_2}>C{:}CMe_2$, b. p. 58—65°/11·5 mm., is very unstable, and was not obtained pure. T. H. P.

Hydrogenation in the Presence of Finely Divided Palladium. II. PIERRE BRETEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 764—770. Compare this vol., i, 123).—Phenanthrene can be reduced electrolytically, using spongy palladium deposited on a platinum-iridium gauze cylinder as a cathode. The hydrogenation takes place in an alcoholic sulphuric acid solution with a current of 10 amperes and 8 volts. The tetrahydrophenanthrene after precipitation by water is extracted with ether. W. G.

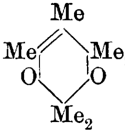
Nitration of *o*-, *m*-, and *p*-Nitrobenzoyl-*p*-anisidines. FRÉDÉRIC REVERDIN (*Compt. rend.*, 1911, **153**, 278—279; *Arch. sci. phys. nat.*, 1911, [iv], **32**, 124—134*).—The nitro-group in the three nitrobenzoyl-*p*-anisidines is without influence on the course of nitration when these substances are treated with nitric acid, alone or in acetic acid solution. In each case, according to the conditions, orange mononitro-derivatives, yellow dinitro-derivatives, or colourless trinitro-compounds are formed. On hydrolysis, these substances give 3-nitro-, 2 : 3-dinitro-, and 2 : 3 : 6-trinitro-*p*-anisidine respectively, thus proving their constitution. The *o*-nitrobenzoyl derivatives and the trinitro-compounds are hydrolysed with ease by sulphuric acid, the others with difficulty.

W. O. W.

Crystallographic Study of Ethyl *iso*Succino-*p*-toluidate. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 921—922). —Ethyl *iso*succino-*p*-toluidate, $C_{13}H_{17}O_3N$ (compare Comanducci and Lobello, Abstr., 1905, i, 271), forms large, colourless, tabular crystals, which belong to the monoclinic system [$a:b:c = 3·4327:1:1·4716$; $\beta = 68°49'$]. R. V. S.

Tetra- and Penta-methyl Orcinol. JOSEF HERZIG and FRANZ WENZEL [with KARL ZEIDLER] (*Monatsh.*, 1911, **31**, 461—489).—Tetramethylorcinol, obtained on methylating orcinol in the nucleus, has been characterised by means of a dibromo-derivative, which is decomposed by dilute alkali hydroxide into fumaric acid and di*iso*propyl ketone.

In addition, a pentamethylorcinol is formed during methylation and characterised by a monobromo-derivative; it probably has the annexed formula. Tetramethylorcinol cannot be further methylated by methyl iodide and potassium hydroxide, and it is not therefore an intermediate product in the formation of pentamethylorcinol.



The yield of tetra- and penta-methylorcinol is unsatisfactory when working in methyl- or ethyl-alcoholic alkali hydroxide solution, and it appears to be more satisfactory in aqueous solution, where, however, pentamethylorcinol preponderates (compare Herzig and Erthal, following abstract).

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* and *Ber.*, 1911, **44**, 2362—2369.

Pentamethylorcinol has m. p. 8°, b. p. 120°/12 mm.

Dibromotetramethylorcinol separates in measurable monoclinic crystals, m. p. 79·5° [$a:b:c=0·7243:1:0·9614$; $\beta=96°18'$]. It is readily decomposed on heating with very dilute potassium hydroxide into di*iso*propyl ketone, fumaric acid, and a saturated monobasic *acid*, $C_{11}H_{16}O_4$, m. p. 165°. With diazomethane a *methyl* ester is formed, m. p. 64—67°, which yields the original substance on hydrolysis. The acid is not decomposed by concentrated potassium hydroxide, and 30% hydrogen peroxide solution is without action. The acid is therefore regarded as a substituted cyclic complex.

[With A. SCHWADRON.]—*Monobromopentamethylorcinol*, after purification by distillation in a vacuum, was obtained in transparent, monoclinic plates [$a:b:c=1·4653:1:0·7528$; $\beta=91°3'$], m. p. 43—45°. It is decomposed by dilute alkali hydroxide, yielding chiefly a neutral *oil*, $C_{12}H_{18}O_3$, insoluble in alkali hydroxide, b. p. 117°/16 mm., 225—229°/760 mm. It is attempted to explain these decompositions by regarding the bromo-compounds as derivatives of norcarane, in which the *cyclo*propane ring undergoes rupture. E. F. A.

Alkylation in the Nucleus. JOSEF HERZIG and BR. ERTHAL (*Monatsh.*, 1911, **32**, 491—504. Compare Abstr., 1910, i, 667).—Tetramethylphloroglucinol when treated with methyl iodide and aqueous potassium hydroxide yields a mixture of hexa- and penta-methylphloroglucinol. Tetraethylphloroglucinol, however, when treated in the same way gives the methyl ether of tetraethylphloroglucinol, m. p. 69—71°, which is characterised by its resistance to alkaline hydrolysis. Phloroglucinol dimethyl ether under similar conditions chiefly yielded the trimethyl ether.

On methylation of orcinol in aqueous alkali, a mixture of tetra- and penta-methyl orcinol is obtained, but the tetramethyl derivative is not converted into the pentamethyl derivative in this manner.

With resorcinol the main product is a methyl ether of trimethylresorcinol, b. p. 102—106°/12 mm. Quinol yields the dimethyl ether.

From phloroglucinol, aqueous potassium hydroxide, and ethyl iodide, the *ethyl ether* of *pentaethylphloroglucinol*, an oil, b. p. 178—181°/15 mm., is obtained.

Silver phloroglucinolcarboxylate and ethyl iodide interact to yield almost entirely ethyl phloroglucinolcarboxylate, m. p. 123°. The amount of secondary action is very small; no product alkylated in the nucleus could be obtained, and the ester could be purified without difficulty. With methyl iodide secondary action takes place, and a product methylated in the ring is obtained.

Phloroglucinol and orcinol when methylated with methyl sulphate form a preponderating quantity of oxygen ethers, and homologues methylated in the nucleus could not be obtained.

Ethyl phloroglucinoldicarboxylate is quantitatively and without difficulty converted by diazomethane into the trimethyl ether, m. p. 88—91°.

Diazomethane is without action on ethyl succinylsuccinate.

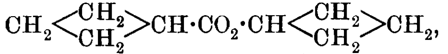
E. F. A

Hexa- and Penta-methylphloroglucinol. JOSEF HERZIG and BR. ERTHAL (*Monatsh.*, 1911, **32**, 505—508. Compare Abstr., 1910, i, 607).—Hexamethylphloroglucinol does not react with *p*-nitrophenylhydrazine, semicarbazide, or amyl nitrite; it could not be reduced. It reacts with magnesium methyl iodide, forming a *compound*, $C_{15}H_{30}O_3$, m. p. 258—260°, which does not contain a methoxyl group, and is resistant towards the usual reagents.

Magnesium methyl iodide reacts with the methyl ether of pentamethylphloroglucinol, forming a *substance*, $C_{13}H_{22}O_2$, m. p. 67—68°, which likewise contains no methoxyl group. E. F. A.

Two Methods of Obtaining *cyclo*Butanol. Certain Transformations of *cyclo*Butanol Accompanied by Isomerisation. NICOLAUS J. DEMJANOFF and M. N. DOJARENKO (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 835—846).—It has been shown by Demjanoff (Abstr., 1908, i, 85) and by Zelinsky and Gutt (Abstr., 1908, i, 14) that the *cyclo*butanol obtained by Perkin (Trans., 1894, **65**, 950) by the action of nitrous acid on *cyclo*butylamine contains an admixture of *cyclo*propylcarbinol. The alcohol obtained by Dalle (Abstr., 1902, i, 525) by the action of nitrous acid on *cyclo*propylmethylamine is also a mixture of *cyclo*propylcarbinol and *cyclo*butanol. In order to prepare pure *cyclo*butanol, the authors have, therefore, had recourse to Simonini's method (Abstr., 1893, i, 391), and to the electrolysis of a solution of potassium *cyclo*butanecarboxylate containing potassium carbonate and potassium hydrogen carbonate (compare Hofer and Moest, Abstr., 1902, i, 736). The principal result of the experiments described below is that the ring of *cyclo*butanol is unstable towards acid reagents, and gives rise to compounds containing a *cyclo*propane ring.

cyclo*Butyl* cyclo*butanecarboxylate*,



$$CH_2{<}{\genfrac{}{}{0pt}{}{CH_2}{CH_2}}{>}CH{\cdot}CO_2{\cdot}CH{<}{\genfrac{}{}{0pt}{}{CH_2}{CH_2}}{>}CH_2,$$

obtained in a 34·5% yield by the interaction of dry iodine and silver *cyclo*butanecarboxylate ($2C_4H_7{\cdot}CO_2Ag + I_2 = C_4H_7{\cdot}CO_2{\cdot}C_4H_7 + CO_2 + 2AgI$), is a liquid, b. p. 198·5—199°/750 mm., D_{15}^{15} 1·003, $D_{18\cdot9}^{18\cdot9}$ 1·007, D_{23}^{23} 0·9980, $n_D^{18\cdot9}$ 1·4551. Hydrolysis of this ester yields *cyclo*butanecarboxylic acid and *cyclo*butanol, b. p. 123°/733 mm., D_{15}^{15} 0·9226, $D_{18\cdot9}^{18\cdot9}$ 0·9206, D_{25}^{25} 0·9181, $n_D^{18\cdot9}$ 1·4339. On oxidation with nitric acid, it yields succinic acid, which is formed only in comparatively small quantity from *cyclo*propylcarbinol under similar conditions.

*cyclo*Butanol and *cyclo*butyl *cyclo*butanecarboxylate are also obtained as the products of hydrolysis of potassium *cyclo*butanecarboxylate.

Oxidation of *cyclo*butanol with chromic oxide and sulphuric acid gives, not *cyclo*butanone, but the isomeric *cyclo*propanealdehyde (compare Abstr., 1908, i, 156).

In spite of small differences in the b. p. and sp. gr., the acid obtained by converting *cyclo*butanol into the bromo-derivative and treating the magnesium compound of the latter with carbon dioxide (*ibid.*) bears a decided resemblance to allylacetic acid. T. H. P.

***p*-Hydroxybenzyl-methylamine and -dimethylamine.** MARC TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 825—828).—p-*Hydroxy-*

benzylmethylamine, $HO\cdot C_6H_4\cdot CH_2\cdot NHMe$, is obtained as the *hydriodide*, m. p. 149—150° (approx.), by the action of hydriodic acid on p-*methoxybenzylmethylamine*, $MeO\cdot C_6H_4\cdot CH_2\cdot NHMe$, D_0^0 1·025, b. p. 121°/14 mm. (*hydrochloride*, m. p. 166°), itself formed by the interaction of anisyl chloride, D_0^0 1·072, b. p. 116—120°/15 mm., or bromide, D_{19}^{19} 1·395, b. p. 129°/6 mm. (approx.), and methylamine in alcohol in a closed tube. Some *di*-p-*methoxybenzylmethylamine*, D_0^0 1·0794, b. p. 210°/15 mm., is also formed in this reaction. On demethylation, it gives *di*-p-*hydroxybenzylmethylamine*, $NMe(CH_2\cdot C_6H_4\cdot OH)_2$, the *hydrochloride* of which has m. p. 197—199°.

p-*Hydroxybenzyldimethylamine*, $HO\cdot C_6H_4\cdot CH_2\cdot NMe_2$, m. p. 112°, reduces ammoniacal silver nitrate, Millon's reagent, or iodic acid, but does not give any coloration with ferric chloride; the *hydrochloride*, m. p. 194°, and the *hydriodide*, m. p. 135°, are both crystalline. It is produced in a manner analogous to its lower homologue by demethylating p-*methoxybenzyldimethylamine*, D_0^0 0·9878, D_{15}^{15} 0·976, b. p. 110—111°/16 mm., which furnishes a *hydrochloride*, m. p. 157°, *hydriodide*, m. p. 145°, and *methiodide*, m. p. 158°. The last-mentioned substance on demethylation by hydriodic acid furnishes p-*hydroxybenzyltrimethylammonium iodide*, $HO\cdot C_6H_4\cdot CH_2\cdot NMe_3I$, m. p. 191°, which is readily transformed by silver chloride into the corresponding *chloride*, m. p. 98°.

p-Methoxybenzyldimethylamine is converted by acetic anhydride into anisyl alcohol and dimethylacetamide, and the demethylated base is similarly transformed by this reagent. T. A. H.

3 : 4 : 5-Trinitroveratrole. ALFONS KLEMENC (*Monatsh.*, 1911, **32**, 457—459).—3 : 4 : 5-Trinitroveratrole, m. p. 144—145°, has been described by Tiemann and Matsmoto (this Journ., 1876, ii, 524) and by Blanksma (Abstr., 1905, i, 277).

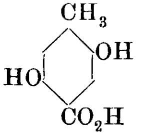
It is now obtained on nitrating hemipinic acid with fuming nitric acid without a solvent and also by heating 5 : 6-dinitro-2 : 3-dimethoxybenzoic acid with fuming nitric acid, a method of preparation which establishes its constitution. E. F. A.

Dehydration of the Glycols of Anethole and *iso*Safrole. VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 940—946).—The author dissociates himself from the attack (Abstr., 1908, i, 901) of his former collaborator Balbiano (compare Balbiano and Paolini, Abstr., 1906, i, 186) on the statements of Tiffeneau and Daufresne (Abstr., 1907, i, 701), and confirms the statements of these authors. R. V. S.

Action of Bromine in Presence of Aluminium Bromide on *cyclo*Hexanol and *cyclo*Hexanone. FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1911, **153**, 349—350).—Hexabromobenzene is formed when *cyclo*hexanol is dropped into excess of bromine containing 1% of aluminium in solution. *cyclo*Hexanone on treatment in the same way forms a *tetrabromo*-derivative crystallising in prisms, m. p. 117° (decomp.). When this is heated at 120—125°, it loses bromine and hydrogen bromide, and becomes converted into a liquid having the properties of a bromophenol. Small quantities of uninvestigated substances of high melting point are also formed in this bromination.

W. O. W.

Position of the Substituents in Hydroxyhomosalicylic [Dihydroxytoluic] Acid. Hans Schmid (*Monatsh.*, 1911, **32**, 435—445).—*Toluquinol monoacetate* crystallises in long, lustrous needles, m. p. 92°. The *diacetate* forms granular crystals, m. p. 49°; on oxidation in neutral solution with potassium permanganate, gentisic acid is obtained.



Dihydroxytoluic acid, prepared by heating toluquinol with potassium hydrogen carbonate and glycerol, forms a *diacetate*, m. p. 129°. This on oxidation with permanganate is converted into 2 : 5-dihydroxyterephthalic acid. Accordingly, dihydroxytoluic acid (hydroxyhomosalicylic acid) is represented by the annexed formula.

E. F. A.

p-Hydroxyphenylglyoxylic, p-Hydroxyphenylacetic, and p-Hydroxyphenylglycollic [p-Hydroxymandelic] Acids. Jules Aloy and Ch. Rabaut (*Bull. Soc. chim.*, 1911, [iv], **9**, 762—764).—By the oxidation of p-acetylaminoacetophenone by alkaline permanganate there results p-*acetylaminophenylglyoxylic acid*,

$$NHAc\cdot C_6H_4\cdot CO\cdot CO_2H,$$

pale yellow crystals, m. p. 186—187°, which yields a white, crystalline *silver* salt, and a yellow *phenylhydrazone*, m. p. 200—202° (decomp.). This acid on hydrolysis and subsequent diazotisation yields p-hydroxyphenylglyoxylic acid (Abstr., 1899, i, 288, 437). From the latter acid by reduction with hydriodic acid, p-hydroxyphenylacetic acid is formed.

p-Hydroxymandelic acid can be obtained from the corresponding glyoxylic acid by the action of sodium amalgam (compare Ellinger and Kotake, Abstr., 1910, i, 384).

W. G.

Theoretical Considerations on the Isomerism in Ethylene Derivatives. Emil Erlenmeyer (*Biochem. Zeitsch.*, 1911, **35**, 149—165).—Substances of the general formula $C(R^1R^2R^3)\cdot C(R^4R^5R^6)$ have been obtained in four modifications. If, however, the models representing these modifications, which are due to relative differences of position of the groups attached to each carbon atom, be twisted about the axis, then, according to van't Hoff, twelve modifications should exist. The author gives reasons for assuming that such do in reality exist, although they have not been definitely isolated. These are (1) the results obtained in the determination of the crystallographic and optical properties of the storax-cinnamic acids; (2) the fact that equimolecular quantities of phenyl-lactic acid and cinnamic acid are obtained by the reduction of phenylbromolactic acid and other similar reactions; (3) the existence of different malic acids, as demonstrated by Mayer and Aberson; (4) the fact that, according to Walden, l-chlorosuccinic acid yields on treatment with potassium hydroxide the *d*-malic acid, whereas by treatment with silver hydroxide the *l*-variety is obtained. If, in the case of ethylene compounds, the double bond between two multivalent elements be represented in the model in a similar manner to the bond between two groups, so as to form an angle, then, by the application of the above-mentioned conceptions as to the rotation of the model in the case of compounds of the $C(R^1R^2R^3)\cdot C(R^4R^5R^6)$ type, a whole series of isomeric derivatives with the ethylene linking should exist. This theory of the author is illustrated by his results with cinnamic acid, and numerous diagrams of the models are given in the paper. S. B. S.

The Possibility of the Existence of Molecular Asymmetric Storax-Cinnamic Acids. EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, **35**, 134—148).—Storax-cinnamic acid was converted into the dibromo-derivative, and this substance, by distillation with steam, into *dl*-phenylbromolactic acid. The latter was separated into its antipodes by means of the cinchonine salts. The *d*- and *l*-bromo-acids were then converted by means of sodium amalgam into the corresponding *d*- and *l*-phenyl-β-lactic acids, which, on treatment with hydrochloric acid at 46°, lose water and are converted into cinnamic acid. In only one case were the cinnamic acids thus obtained from optically active lactic acids themselves directly optically active. As, however, it is probable that optically active cinnamic acids, if they exist, have only a small rotation, it was possible that the amounts of such acids were too small in these preparations to affect the activity. They were therefore converted into the dibromides, and these substances into the sodium salts of the corresponding oxidoacrylates, as the authors have shown that the substances, if optically active, have a large rotation. It was found that the oxidoacrylates prepared from cinnamic acids which were obtained from optically active phenyllactic acids were active, the rotation corresponding in direction with that of the lactic acid from which they were obtained. Furthermore, a few of the crystals of the cinnamic acids obtained from optically active lactic acids showed asymmetric structure, whereas the crystals of storax-cinnamic acid itself were symmetrical.

Attempts were also made to prepare active cinnamic acids by the direct reduction of the active phenylbromolactic acids by means of zinc and alcohol, and it was found that this reaction yielded equal molecules of cinnamic acids and phenyl-β-lactic acids. The changes in the rotation during the reaction were also followed, and it was found that at the end of the reduction very little, if any, changes in the rotation had taken place. As the solution had a considerably higher rotation than could be accounted for by the phenyl-lactic acids they contained, the conclusion was drawn that the zinc salts of the cinnamic acids in the solution were active. On attempting to prepare the free acids from the zinc salts, the authors did not succeed in obtaining optically active acids, although they have obtained preparations from the optically active lactic acids showing distinct traces of asymmetry. They conclude that optically active cinnamic acids exist which are very readily racemised. S. B. S.

The Isomeric Acids of the Cinnamic Acid Series. EMIL ERLENMEYER (*Biochem. Zeitsch.*, 1911, **34**, 355—386).—The differences between the natural storax-cinnamic acid and the synthetic acid obtained from benzaldehyde from various sources are summarised, and the crystalline measurements of the dibromides and dichlorides are given. It is concluded that the synthetic acid is a mixture of the storax acid with heterocinnamic acid; the properties of these latter acids are contrasted, and the crystalline measurements of the dibromides are given. The separation of the two acids present in the synthetic acid can be accomplished (1) by the fractional distillation of the ester; (2) by the incomplete addition of hypochlorous acid, the residue of unacted on acid consisting of the hetero-β-acid; (3) by the fractional precipitation of the acid from a solution of the sodium salt. The evidence is then summarised, which tends to show that the various cinnamic acids are isomerides with the same chemical constitution. (*a*) The evidence is summarised tending to show that the differences are not due to accidental impurities. (*b*) The acids can be converted into dibromides, from which, by various reactions, the original acids can be regenerated in unchanged form. Eight such series of reactions are mentioned. (*c*) It is shown that benzaldehydes of different origin yield different cinnamic acids, those aldehydes containing hydrocyanic acid yielding storax-cinnamic acid, whereas the aldehydes which have been completely separated from hydrocyanic acid yield the synthetic (mixed acids) cinnamic acid. The differences depend therefore on the grouping contained in the benzaldehyde. (*d*) Evidence is summarised to show that the differences are not due to impurities in the aldehyde. (*e*) Finally, evidence is brought forward to show that in the process by removal of the hydrocyanic acid from the natural aldehydes in which calcium hydroxide is used, the aldehyde undergoes isomeric change, due to the presence of alkali. Furthermore, if storax-cinnamic acid be oxidised to benzaldehyde, care being taken to prevent the mixture from becoming alkaline, an aldehyde is obtained from which, by Perkin's synthesis, the original acid can be regenerated. If, however, the oxidation of the acid to benzaldehyde be carried out in alkaline solution, an aldehyde is obtained from which, by the Perkin synthesis, instead of storax-cinnamic acid, a mixture of this and the hetero-β-acid (synthetic cinnamic acid) is obtained. S. B. S.

The Behaviour of Certain Mixtures of Storax Cinnamic Acid with Certain Substituted Cinnamic Acids. EMIL ERLENMEYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1911, **34**, 405—416).—To ascertain definitely whether the synthetic acid differs from the storax acid, owing to the presence of certain impurities, the properties of the mixture of this acid with substituted cinnamic acids (chloro-, hydroxy-, methoxy-, and methyl derivatives) were investigated. Experiments on the separation of *p*-methylcinnamic acid from cinnamic acid were carried out. Crystallographic measurements of the mixtures were also made. The results confirm the statement in a previous paper, that the synthetic acid is not a mixture of cinnamic with a substituted cinnamic acid. S. B. S.

Further Experiments on the Separation of Heterocinnamic Acid. Emil Erlenmeyer and G. Hilgendorff (*Biochem. Zeitsch.*, 1911, **34**, 417—427).—A series of experiments on the fractional precipitation of the synthetic cinnamic acid from the solution of the sodium salt by acid are described, which were undertaken with the object of determining whether the hetero-acid could be further separated into other constituents. As no acid other than the hetero-acid could be isolated by this method, the conclusion is drawn that this is the only acid accompanying the storax-cinnamic acid present in the synthetic product. S. B. S.

Action of Anisaldehyde and Piperonaldehyde on the Sodium Derivative of Phenylacetonitrile. Fernand Bodroux (*Compt. rend.*, 1911, **153**, 350—351).—Anisaldehyde and piperonaldehyde react with the sodium derivative of phenylacetonitrile, forming the unsaturated nitriles, α-phenyl-*p*-methoxycinnamonitrile (Frost, Abstr., 1889, 597) and α-phenyl-3 : 4-methylenedioxycinnamonitrile (Walther and Wetzlich, Abstr., 1900, i, 438) respectively. On hydrolysis these substances yield *α-phenyl*-p-*methoxycinnamic acid*, $OMe\cdot C_6H_4\cdot CH:CPh\cdot CO_2H$, needles, m. p. 188°, and *α-phenyl*-3 : 4-*methylenedioxycinnamic acid*,

$$CH_2:O_2:C_6H_3\cdot CH:CPh\cdot CO_2H,$$

needles, m. p. 233°. W. O. W.

Interchange of Primary, Secondary, and Tertiary Alkyl Groups in the Esters of Organic Acids. Michael Pfannl (*Monatsh.*, 1911, **32**, 509—522. Compare Abstr., 1910, i, 480; also Kommenos, Abstr., 1910, i, 361).—The experiments were made to establish the interchange of secondary and tertiary alcohols with primary, and to show the influence of the nature and structure of the alkyl group on the reaction velocity. The esters of terephthalic acid were allowed to react with methyl alcohol in proportions, so that the equivalent of 0·5 gram of dimethyl terephthalate was present in 10 c.c. of methyl alcohol. Under these conditions about 20% of change is indicated by the crystallisation of the dimethyl ester.

Under similar conditions the diethyl ester required 1 min. 40 sec. for 20% conversion into dimethyl ester, the di-*n*-propyl ester required 3 min. 50 sec., the di-*n*-butyl ester 3 min. 30 sec., the di*iso*butyl ester 5 min. 40 sec., the di*iso*propyl ester 14 min. 10 sec., whilst the di-*tert.*-butyl ester did not react within forty-eight hours. It is obvious that retardation is caused by the branching of the chain, particularly by the secondary and tertiary character of the alkyl.

Whereas methyl is interchanged with the *sec.-iso*propyl group in the esters of terephthalic acid at the ordinary temperature and with very little alkali, the *tert.*-butyl group can only be introduced by using much alkali and heating.

tert.-Butyl benzoate, obtained in this manner from methyl benzoate and *tert.*-butyl alcohol, is a highly refractive, oily liquid, very similar to other esters of benzoic acid; it has b. p. 94°/10 mm., 213°/760 mm., decomposing to benzoic acid when distilled.

Di-*n*-butyl terephthalate forms long, colourless needles, m. p. 16°.

Di-tert.-*butyl terephthalate* crystallises in stout, lustrous prisms, m. p. 118°; it is obtained by fractional distillation of the product obtained by heating the dimethyl ester with *tert.*-butyl alcohol and excess of alkali hydroxide. E. F. A.

Friedel-Crafts' Reaction. OTTOKAR HALLA (*Monatsh.*, 1911, **32**, 637—640).—On heating xanthone with the equivalent quantity of phthalic anhydride, dissolved in benzene containing a little toluene, and aluminium chloride, no interaction with the xanthone was found to take place, but the reaction mixture contained benzoylbenzoic and toluoylbenzoic acids.

Experiments made with varying proportions of toluene showed that when phthalic anhydride, in equivalent quantity to the toluene taken, was used in every case, toluoylbenzoic acid was the sole product.

It was supposed that benzoylbenzoic acid was first formed, and the benzoyl group subsequently displaced by toluoyl, as Heller and Schülke (Abstr., 1908, i, 994) supposed in the case of naphthoylbenzoic acid. This displacement is proved, however, not to take place on heating benzoylbenzoic acid with toluene and aluminium chloride. The change is attributed to the ready substitution of the alkylated benzene nucleus. E. F. A.

Glycocholic Acid and Para-glycocholic Acid. EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1911, **73**, 308—311. Compare Abstr., 1909, i, 587).—Glycocholic acid crystallises with $1\frac{1}{2}H_2O$; it sinters at 126°, m. p. 130°. The anhydrous acid sinters at 130—132°, decomp. 154—155°. When heated at 100° in aqueous suspension for some hours, para-glycocholic acid is formed; it crystallises with $1H_2O$, sinters at 186°, decomp. 198°, or when anhydrous it sinters at 193°, decomp. 198°. The two acids are regarded as isomerides. E. F. A.

Separation and Transformation of the Benzaldehydes. EMIL ERLENMEYER, G. HILGENDORFF, and TH. MARX (*Biochem. Zeitsch.*, 1911, **34**, 386—404).—The attempts made to separate the benzaldehydes from mixtures are described. Fractional distillation led to no satisfactory results. A partial separation could, however, be effected by fractional condensation with sodium acetate and acetic anhydride, or by fractional addition of hydrocyanic acid; owing to the fact that the isomerides possess different velocity fractions in these cases. Experiments are also described to show how the "natural" benzaldehyde can be converted into the "synthetic" benzaldehyde by the action of alkaline reagents, or by heating with platinised abestos; attempts to convert the synthetic acid into the hetero- and storax-acids are also mentioned. S. B. S.

The Electrolytic Reduction of Anisaldehyde. JULIUS TAFEL and WILHELM SCHEPSS (*Ber.*, 1911, **44**, 2148—2154).—In accordance with the results obtained by Tafel (Abstr., 1909, i, 766) on the reduction of methyl *iso*-amyl ketone at cadmium cathodes, it was to be expected that the aldehyde group would undergo reduction to a greater extent at cathodes of this metal than at other cathodes. The authors have, therefore, studied the electrolytic reduction of anisaldehyde in aqueous-alcoholic solution of sulphuric acid, investigating the influence of current density, temperature, and material of which the cathode was made, especially in so far as the yield of *p*-tolyl methyl ether, $C_6H_4Me{\cdot}OMe$, was concerned.

The complete reduction of the aldehyde group takes place to a much greater extent at cadmium electrodes than at electrodes of other metals. Under the conditions of current density and temperature given by Law (Trans., 1906, **89**, 1512, 1520; 1907, **91**, 748; 1911, **99**, 1113), a 37% yield of *p*-tolyl methyl ether was obtained, and the yield could be further increased to 60% by increasing the current density, the temperature not being allowed to rise above 25°. The formation of anisic alcohol takes place to a slight extent only, whereas Law (*loc. cit.*) found the opposite to be the case with copper electrodes.

In addition to *p*-tolyl methyl ether and anisic alcohol, some resin is always formed, together with a mixture of solid substances of high boiling point, which contains the isomeric hydroanisoins, dimethoxystilbene, and probably also dimethoxydibenzyl. The total quantity of these bimolecular products formed depends chiefly on the temperature, increasing very rapidly with rise in temperature. At 35°, however, the amount formed is independent of the strength of the current within fairly wide limits.

The formation of resin was always very small (0·5—7%), only becoming appreciable when very strong or too weak acid was used.

T. S. P.

Phenolic Aldehydes. I. Reactivity of the Aldehyde Group in Phenolic Aldehydes. HERMANN PAULY and RICHARD (FREIHERR) VON BUTTLAR (*Annalen*, 1911, **383**, 230—288).—Attention has been called by several investigators to the fact that certain aromatic aldehydes do not behave normally in the Grignard reaction. Béhal and Tiffeneau, in particular, obtain very poor yields of the expected propenyl compounds from protocatechualdehyde, *p*-hydroxybenzaldehyde, vanillin and *iso*vanillin, and magnesium ethyl bromide, although the neutral ethers react normally (Abstr., 1908, i, 260).

[With KARL LOCKEMANN.]—It is now found that salicylaldehyde and magnesium ethyl iodide give, in 92% yield, a mixture of o-*propenylphenol*, $OH{\cdot}C_6H_4{\cdot}CH{:}CHMe$, m. p. 34·8°, b. p. 229—231°, and a yellow oil, b. p. about 235°/23 mm., which is probably a bimolecular form of *o*-propenylphenol. So also, *o*-vanillin gives 46% of o-iso-*eugenol* (2-*hydroxy*-3-*methoxypropenylbenzene*),

$$OMe{\cdot}C_6H_3(OH){\cdot}CH{:}CHMe,$$

m. p. 81° (*bromo*-o-iso-*eugenol dibromide*, $C_{10}H_{11}O_2Br_3$, m. p. 111°); 2 - 3-dimethoxybenzaldehyde yields 93% of 2 : 3-*dimethoxyphenylmethylcarbinol*, $C_6H_3(OMe)_2{\cdot}CHMe{\cdot}OH$, b. p. 151—152°/15 mm., D_4^{20} 1·1213 (*phenylurethane*, m. p. 127°), and 2 : 3-dihydroxybenzaldehyde yields 85% of a *substance*, which is probably a polymeride, $(C_9H_{10}O_2)_4$, of *o*-propenylcatechol.

The striking difference of behaviour of the preceding aldehydes in the Grignard reaction has induced the authors to examine the reactivity of phenolic aldehydes in other directions. Their conclusions that mono- and di-hydric phenolic aldehydes and their acyl derivatives show, in contrast to their neutral ethers, abnormal behaviour in the following reactions, are based to a large extent on observations already recorded in the literature, and are most concisely represented by the table (*a* = smooth reaction or yield greater than 75%; *b* = fair reaction or yield about 60%; *c* = bad reaction or yield about 30%; *d* = very bad or no reaction).

	Ethers of phenolic aldehydes.	Hydroxybenzaldehydes.			Dihydroxybenzaldehydes.				Vanillins.			*cyclo*Carbonates of dihydroxybenzaldehydes.	
		o-	*m*-	*p*-	2:3,	2:4,	2:5,	3:4.	OH 2, OMe 3,	3, 4,	4. 3.	2:3	3:4.
Cannizzaro reaction	*a*	*d*		*d*		*d*	*d*	*d*			*d*		
Benzoin condensation ……………	*a*	*d*											
Acetal formation (by alcohol and HCl).	*b*	*d*		*d*				*d*		*d*	*d*		*d*
Acetal formation [by $CH(OR)_3$] ………	*a*	*a*	*a*	*a*	*d*	*d*	*d*	*d*					*d*
Hydroxamic acid formation [by $NH(OH)_2$] ………	*a*	*c*	*a*	*d*				*d*		*a*	*d*		*d*
Grignard reaction…	*a*	*a*		*c*	*a*(?)			*d*	*a*(?)	*c*	*c*		*d*
Doebner's reaction ($CH_3·CO·CO_2H$ and $\beta C_{10}H_7·NH_2$)	*a*	*a*	*a*	*b*	*d*	*d*	*d*	*b*	*a*	*a*	*b*		
Schiff's reaction (magenta and H_2SO_3) …………	*a*	*b*	*b*	*d*	*c*	*d*	*b*	*d*	*b*	*c*	*c*	*b*	*b*

The diminution in the reactivity of the aldehyde group does not always coincide with the entrance of the first hydroxyl group, but usually is quite evident when the second hydroxyl group is introduced, particularly in the para-position with respect to the aldehyde group.

Various causes of the abnormalities are suggested and discussed. The original paper must be consulted for a comprehension of the only satisfactory explanation, which is based on Stark's electro-atomistic theory of valency.

The following acetals have been obtained from methyl orthoformate by a modification of Claisen's process. p-*Hydroxybenzaldehyde dimethyl acetal*, $OH·C_6H_4·CH(OMe)_2$, m. p. 60—64°, m-*hydroxybenzaldehyde dimethyl acetal*, b. p. 150°/11 mm. (decomp.); o-*hydroxybenzaldehyde dimethyl acetal*, b. p. about 65°/0·4 mm. These acetals are extremely sensitive to the action of alkalis, and the first and the last, when heated, lose methyl alcohol and yield substances which are apparently mixtures of the hydroxybenzaldehyde and the quinomethyl ether, $O:C_6H_4:CH·OMe$. The following mercaptals are described: m-*Hydroxybenzaldehyde dimethyl mercaptal*, $OH·C_6H_4·CH(SMe)_2$, very viscous oil; p-*hydroxybenzaldehyde dimethyl mercaptal*, m. p. 73·5°; *protocatechualdehyde dimethyl mercaptal*, m. p. 108—109°; o-*protocatechualdehyde di*-p-*nitrobenzyl mercaptal*, $C_6H_3(OH)_2·CH(S·CH_2·C_6H_4·NO_2)_2$, m. p. 177°, yellow prisms; *gentisinaldehyde di*-p-*nitrobenzyl mercaptal*, m. p. 170°, green prisms. The following colours and m. p.'s refer to the substituted β-naphthacinchonic acids obtained by Doebner's method from the corresponding aldehydes: m-*hydroxyphenyl*-, yellow powder, 284·5°; p-*hydroxyphenyl*-, pale yellow powder, 325·5°; m-*hydroxy*-p-*methoxyphenyl*-, citron-yellow powder, 295°; o-*hydroxy*-m-*methoxyphenyl*-, white powder, 251°; mp-*dihydroxyphenyl-β-naphthacinchonic acid*, orange-yellow powder, 317·5°. C. S.

Phenolic Aldehydes. II. Reactivity of the Phenolic Group in Phenolic Aldehydes. HERMANN PAULY, KONRAD SCHÜBEL, and KARL LOCKEMANN (*Annalen*, 1911, **383**, 288—337. Compare preceding abstract).—The acid character of a phenol is enormously increased by the entrance of an aldehyde group into the nucleus. By titration with phenolphthalein as indicator, 2 : 3-, 2 : 4-, and 2 : 5-dihydroxybenzaldehydes behave as monobasic acids, as do also protocatechualdehyde, vanillin, and *o*- and *p*-hydroxybenzaldehydes. The acidifying influence of the aldehyde group, therefore, is exerted on the hydroxyl group in any position in the nucleus, but it is least in the meta-position, and apparently is exerted only on one hydroxyl group, conductivity measurements showing that the *k* values of *p*-hydroxybenzaldehyde and protocatechualdehyde are $2·2 \times 10^{-8}$ and $2·8 \times 10^{-8}$ respectively at 25° (for phenol, *k* $1·3 \times 10^{-10}$ at 18°). Corresponding with the increased mobility (that is, the weakening of the union between the hydrogen and the oxygen atoms) of the hydrogen atom of the hydroxyl group in the para-position in protocatechualdehyde (as compared with the mobility of the hydrogen atom in phenol or catechol), experiment shows that a similar loosening is to be observed in the derivatives of the phenols; thus the *cyclo*carbonate of protocatechualdehyde, by treatment with water, evolves carbon dioxide about seventy-five times as rapidly as the *cyclo*carbonate of catechol. (This ratio is approximately the ratio of the *k* values of protocatechualdehyde and catechol [compare Rivett and Sidgwick, Trans., 1910, **97**, 1677]). Moreover, this loosening of the linking at the oxygen atom in the para-position (or in the ortho-position in the case of derivatives of 2 : 3-dihydroxybenzaldehyde) is seen in the following instances. Protocatechualdehyde *cyclo*carbonate is converted by boiling methyl alcohol into the *m*-methyl carbonate,

$$CHO·C_6H_3(OH)·O·CO_2Me,$$

m. p. 96° (formerly given as 93°), the orientation of which is proved by methylation and subsequent hydrolysis, whereby *iso*vanillin is obtained. Similarly, the *cyclo*carbonate of *o*-protocatechualdehyde is converted into *methyl* o-*protocatechualdehyde*-m-*carbonate*,

$$CHO·C_6H_3(OH)·O·CO_2Me,$$

m. p. 115°, the orientation of the hydroxyl and aldehyde groups being shown by the exact analogy of the substance to salicylaldehyde. Again, protocatechualdehyde *cyclo*carbonate is converted by piperidine into *protocatechualdehyde*-m-*carbopiperidide*,

$$CHO·C_6H_3(OH)·O·CO·C_5NH_{10},$$

m. p. 123° (*phenylhydrazone*, $C_{19}H_{21}O_3N_3$, m. p. 159°), which yields *iso*vanillin by methylation and subsequent hydrolysis. Finally, phenylhydrazine acts on the *cyclo*carbonate to form, first, the *phenylhydrazone*, $CO_3{:}C_6H_3·CH{:}N·NHPh$, m. p. 177°, and then the *phenylhydrazonecarbophenylhydrazide*, $NHPh·N{:}CH·C_6H_3(OH)·O·CO·NH·NHPh$, m. p. 186°.

The salts of phenolic aldehydes with the alkali metals and metals of the alkaline earths are frequently strongly coloured. The authors do not commit themselves by giving a quinonoid constitution to these salts; in fact, they are inclined against this view on account of the persistence of the colour in the presence of even fairly strong reducing agents.

o-Protocatechualdehyde (2 : 3-dihydroxybenzaldehyde) forms an *anil*, $C_6H_3(OH)_2\cdot CH\colon NPh$, scarlet needles, m. p. 135°; *β*-naphthylamine derivative, $C_6H_3(OH)_2\cdot CH\colon N\cdot C_{10}H_7$, bluish-red needles, m. p. 164°; phenylhydrazone, m. p. 167° (not 176° as given previously); *semicarbazone*, m. p. 226° (corr., decomp.), and orange-yellow *barium* salt, $C_7H_4O_3Ba,4H_2O$, which loses $2H_2O$ at 105° and another $2H_2O$ at 170—180°. The 3-*methyl ether*-2-*methyl carbonate*,

$$OCH\cdot C_6H_3(OMe)\cdot O\cdot CO_2Me,$$

m. p. 60°, is obtained from the potassium salt of *o*-vanillin and methyl chlorocarbonate in benzene.

Protocatechualdehyde forms a yellow *barium* salt, $C_7H_4O_3Ba,2H_2O$, which loses one or two molecules of water at 160—170° according to the duration of the heating, and an almost colourless *barium hydrogen* salt, $(C_7H_5O_3)_2Ba,3H_2O$. When the barium salt is heated with methyl sulphate (rather more than 1 mol.) in benzene, vanillin and *iso*vanillin are obtained in equal amount, but when protocatechualdehyde is heated with alcoholic potassium hydroxide (rather more than 1 mol.) and methyl iodide, the ratio of *iso*vanillin to vanillin is 9 : 1.

Vanillin methyl 4-*carbonate*, $CHO\cdot C_6H_3(OMe)\cdot O\cdot CO_2Me$, m. p. 91·5°, is obtained by heating vanillin and methyl-alcoholic potassium hydroxide with methyl chlorocarbonate. iso*Vanillin methyl* 3-*carbonate*, m. p. 121°, is prepared by heating the sodium salt of *iso*vanillin and methyl chlorocarbonate in benzene.

Protocatechualdehyde *cyclo*carbonate forms a *semicarbazone*,

$$CO_3\colon C_6H_3\cdot CH\colon N\cdot NH\cdot CO\cdot NH_2,$$

m. p. 220° (decomp.), and reacts with methyl mercaptan in the presence of hydrogen chloride only at the aldehyde group (compare behaviour with methyl alcohol), forming the *dimethyl mercaptal*, $CO_3\colon C_6H_3\cdot CH(SMe)_2$, m. p. 56·5°.

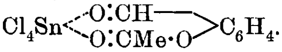
Salicylaldehyde and piperidine (2 mols.) react to form the *dipiperidil*, $OH\cdot C_6H_4\cdot CH(NC_5H_{10})_2$, m. p. 87—88°, colourless plates. Gentisinaldehyde forms a *semicarbazone*, $C_6H_3(OH)_2\cdot CH\colon N\cdot NH\cdot CO\cdot NH_2$, m. p. 249°. An attempt to form an *aci*-ether of salicylaldehyde has not given a conclusive result. C. S.

Theory of the Phenomena of Halochromy. II. PAUL PFEIFFER [and, in part, B. FRIEDMANN, Z. GOLDBERG, E. PROS, and V. SCHWARZKOPF] (*Annalen*, 1911, **383**, 92—155. Compare Abstr., 1910, i, 852).—The author's theory of halochromy is based on the conception that the molecule of the metallic salt or acid (termed the addendum for brevity) unites as a whole co-ordinatively at the carbonyl oxygen atom, thereby neutralising its free affinity, and consequently increasing the free affinity of the carbonyl carbon atom, which thus becomes more unsaturated and acquires the character of a chromophore; the phenomenon of halochromy is ascribed to the presence of such unsaturated carbon atoms.

The halochromatic substances previously described (*loc. cit.*) containing tin tetrahalides as addenda, are almost invariably composed of 2 mols. of the carbonyl compound and 1 mol. of the tin tetrahalide, are represented by the constitution $X_4Sn{<}\begin{matrix}O{:}CRR' \\ O{:}CRR'\end{matrix}$, and are colourless, or nearly so, on account of the relatively simple constitution of the organic component. The substances now described contain aromatic carbonyl compounds, and are usually highly coloured; they are still composed of 2 mols. of the carbonyl compound and 1 mol. of the tin tetrahalide, and therefore receive the constitution given above. Since this constitution is general for halochromatic substances containing a tin tetrahalide, it probably holds for substances containing other addenda.

The colour, but not the composition, of halochromatic substances of the type $X_4Sn{<}\begin{matrix}O{:}CRR' \\ O{:}CRR'\end{matrix}$ (where R and R′ are either or both aromatic) is influenced by the presence of chromophores in R and R′.

The influence of auxochromic groups in R and R′ is interesting. The organic components are the isomeric hydroxybenzaldehydes, methoxybenzaldehydes, and the hydroxyacetophenones, the addendum being a tin tetrahalide, an acid, or an alkali. The presence of the auxochrome intensifies the colour of the halochromatic substance, its influence being greatest when it is ortho to the carbonyl group and least in the para-position; however, when an ethenoid group is present between the aromatic nucleus and the carbonyl group (for example, the isomeric hydroxy- or methoxy-cinnamic acids), the influence of the auxochrome on the colour of the halochromatic substance is normal, being greatest in the ortho- and least in the meta-position. When the hydroxyl group is acetylated, colour disappears; thus *acetylsalicylaldehyde tin tetrachloride* is an unstable, greyish-white, crystalline substance, and has the constitution



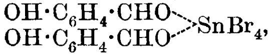
$$Cl_4Sn{<}\begin{matrix}O{:}CH\text{——} \\ O{:}CMe\cdot O\end{matrix}{>}C_6H_4.$$

The dependence of halochromy on the functional nature of the carbonyl compound is illustrated by comparing the halochromy of a series of additive compounds obtained from carbonyl compounds R·CO·A (where A is a hydrogen atom or an alkyl, hydroxy-, alkyloxy-, or amino-group) and an addendum which is either (i) concentrated sulphuric acid, (ii) hydrogen chloride in alcohol or glacial acetic acid, (iii) aqueous potassium hydroxide, (iv) aqueous ammonia, or (v) tin tetrachloride. When R·CO· is a benzoyl, hydroxybenzoyl, or cinnamoyl group, pronounced halochromy is observed only when the addendum is (i) and A is a hydrogen atom or an alkyl group. The explanation of this behaviour is as follows. Evidently the degree of unsaturation of the carbonyl carbon atom (which is essentially the cause of halochromy) must be influenced by the nature of R and A. When these are able to neutralise a portion of the free affinity of the carbonyl carbon atom (as, for example, when A is OH, OR′, NH_2, NR'_2, etc.), its chromophoric character is weakened, and the additive compounds will be colourless or less coloured than those in which A is a hydrogen atom or an alkyl group. (In this connexion it is instructive to contrast the absence of selective absorption in oxalic acid, ethyl oxylate, and oxamide with the yellow colour of glyoxal and of dimethyl diketone.)

The influence of the addendum on halochromy can be ascertained by comparing a series of additive compounds, $X\cdots O:CRR'$, containing different X's. The author's theory requires that the colour should be more intense the stronger the attachment of the addendum to the carbonyl oxygen atom. There is no doubt that such attachment is exceptionally strong when X is H_2SO_4, because almost without exception the colour produced by carbonyl compounds with (i) is more intense than with (ii) or (v) in the list of addenda given above. Unfortunately, there is no method of measuring the attachment of sulphuric acid to the carbonyl oxygen atom. However, according to the ionic theory, the greater the strength of an acid, the more easily is the acidic hydrogen ionised, and therefore the greater the amount of its free affinity. Consequently, carbonyl compounds should form more intensely coloured additive compounds with strong acids than with weak acids of similar constitution. This deduction, which can also be reached by a consideration of Werner's dissociation theory, has been proved by Stobbe and Haertel's experiments on salts of distyryl ketone, etc., and on the colours of solutions of a given ketone in acid having different dissociation constants (Abstr., 1910, i, 43).

When the negative constituent Y of an acid HY unites with a molecule B, forming $HY\cdots B$, a little consideration shows that the carbonyl carbon atom is more unsaturated in the additive compound $RR'CO\cdots HY\cdots B$ than in $RR'CO\cdots HY$; this explains why the hydrochlorides of carbonyl compounds are less coloured than the mercurichlorides and stannichlorides, and also why the acid salts of carbonyl compounds [which the author regards as being constituted like the mercurichlorides; for example, $(CHPh:CH)_2CO\cdots HCl,HCl$] are more coloured than the normal salts.

The author's explanation of the catalytic action of acids or metallic salts (*loc. cit.*) would be greatly strengthened if the unsaturated character of the "binary" compound of the acid or metallic salt and the carbonyl compound could be directly proved by the formation of a "ternary" compound by the addition of a third molecule at the carbonyl carbon atom. Such addition would neutralise more or less the free affinity of the carbon atom, and such "ternary" compounds would be less coloured than the "binary" compounds; thus yellow *disalicylaldehyde tin tetrabromide*,



$$\begin{matrix} OH\cdot C_6H_4\cdot CHO \\ OH\cdot C_6H_4\cdot CHO \end{matrix} > SnBr_4,$$

is easily converted by exposure to the air into a colourless *dihydrate*, $2C_6H_4(OH)\cdot CHO,SnBr_4,2H_2O$, and the orange-red additive compound of distyryl ketone and tin tetrachloride unites with benzene to form an orange-yellow *substance*, $2(CHPh:CH)_2CO,SnCl_4,C_6H_6$.

Meyer states that the additive compounds of metallic salts and quinones correspond completely with the similar compounds of ordinary ketones (Abstr., 1909, i, 395; 1910, i, 179). The author considers, therefore, that the colour phenomena of quinhydrones, of meriquinonoid compounds, and of the compounds of quinones and alkali phenoxides are explicable by his theory of halochromy. In these cases the unsaturated carbonyl carbon atoms are present in a ring, and their influence on selective absorption is materially strengthened by the presence of the ethenoid linkings.

Triphenylmethyl halides form with metallic salts intensely coloured additive compounds, which are generally regarded as $CPh_3X\cdots M$. The methane carbon atom, therefore, becomes unsaturated (triphenylmethyl may be regarded as an extreme case) and chromophoric, and this class of additive compounds falls into line with the author's theory; also, in the triphenylmethane dyes the colour may depend essentially on the presence of the central unsaturated carbon atom, the action of which is increased by auxochromic OH and NH_2 groups.

Finally, by reasoning based on his researches on the molecular compounds of the tin series, the author arrives at conclusions regarding Walden's inversion which do not differ much from those recently expressed by Werner and by Fischer.

The preceding statements are illustrated by reference to compounds in the literature and to the following new substances, which are obtained, as a rule, by the direct interaction of the two components in a non-hydroxylic solvent, usually benzene, occasionally ether or chloroform. (When not given, the formula is normal.) *Disalicylaldehyde tin tetrachloride*, deep yellow crystals, m. p. 152°; *disalicylaldehyde tin tetrabromide*, deep yellow crystals, m. p. 100°; *salicylaldehyde hydrobromide*, $OH\cdot C_6H_4\cdot CHO,HBr$, unstable, yellow prisms; *di*-o-*methoxybenzaldehyde tin tetrachloride*, yellow, crystalline powder, m. p. 180—181°; *di*-o-*methoxybenzaldehyde tin tetrabromide*, yellow, crystalline powder, m. p. 131°; *di*-m-*hydroxybenzaldehyde tin tetrachloride* and the *tin tetrabromide* are yellow, crystalline substances; *di*-m-*methoxybenzaldehyde tin tetrachloride*, yellowish-grey powder; *dipiperonal tin tetrachloride*, yellow, crystalline powder, blackening at 130—190°; *dipiperonal tin tetrabromide*, pale yellow, crystalline powder, m. p. 150°; *di*-p-*dimethylaminobenzaldehyde tin tetrachloride* and also the *tin tetrabromide*, canary-yellow substances; *di*-o-*nitrobenzaldehyde tin tetrachloride*, colourless, prismatic needles, m. p. 80—120°; *di*-m-*nitrobenzaldehyde tin tetrachloride*, colourless, crystalline; *di*-p-*nitrobenzaldehyde tin tetrachloride*, pale yellow, prismatic needles containing C_6H_6, half of which is easily lost, substance then has m. p. 101°; *di*-m-*hydroxyacetophenone tin tetrachloride*, yellow, crystalline, m. p. 99°; *di*-p-*hydroxyacetophenone tin tetrachloride*, colourless, crystalline, m. p. about 190°, reddening at about 150°; *diphorone tin tetrachloride*, colourless crystals, m. p. about 142° (decomp.); *bis-dimethylpyrone tin tetrachloride*, colourless crystals, m. p. 232—235° (decomp.); *dixanthone tin tetrachloride*, sandy-yellow powder, m. p. 245°; *dibenzophenone tin tetrachloride*, colourless crystals; *bis-phenyl styryl ketone tin tetrachloride*, deep yellow crystals; *bis-distyryl ketone tin tetrachloride*, orange powder, m. p. 188° (decomp.); *bis-cinnamylideneacetophenone tin tetrachloride*, Bordeaux-red crystals, m. p. about 160° (decomp.); *bis-dicinnamylideneacetone tin tetra-*

chloride, black precipitate, decomp. below 100°; *dibenzoylpiperidide tin tetrachloride*, colourless, crystalline, m. p. about 213°; *dicinnamoylpiperidide tin tetrachloride*, colourless leaflets, m. p. 221°; *dipiperine tin tetrachloride*, deep yellow crystals; *dipiperine tin tetrabromide*, deep yellow crystals, m. p. 183° (decomp.); *piperine stannichloride*, $2C_{17}H_{19}O_3N.H_2SnCl_6$, compact, yellow crystals (from alcohol containing hydrogen chloride); *piperine stannibromide*, $2C_{17}H_{19}O_3N,H_2SnBr_6$, compact, deep yellow crystals, m. p. 182—184° (decomp.); *piperine hydrochloride*, $C_{17}H_{19}O_3N,HCl$, canary-yellow, crystalline; *piperine dihydrochloride*, $C_{17}H_{19}O_3N,2HCl$, orange powder; *piperine hydrobromide*, $C_{17}H_{19}O_3N,HBr$, canary-yellow, crystalline, m. p. about 170°. Attempts to prepare a substance, $2CPh_3Cl,SnCl_4$, yield only Kehrmann's triphenylmethyl chloride tin tetrachloride, $CPh_3Cl,SnCl_4$.

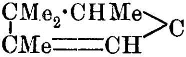
C. S.

Modification of the Friedel and Crafts' Reaction Admitting of the Preparation of α-Naphthyl Ketones to the Exclusion of the β-Isomerides.

E. CAILLE (*Compt. rend.*, 1911, **153**, 393—394).—A solution of the acid chloride in carbon disulphide is cooled to 0°, and treated with aluminium chloride in small portions at a time; crystals separate, consisting of a compound of the ketone with aluminium chloride; after about twenty-four hours these are collected, and decomposed with ice-water acidified with hydrochloric acid. The resulting ketone consists entirely of the α-naphthyl derivative, and the yield is 60—80%.

W. O. W.

2-Methyl-laurenone. A New Ketone Derived from Camphor.

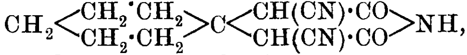
RENÉ LOCQUIN (*Compt. rend.*, 1911, **153**, 284—287. Compare Tiemann, Abstr., 1901, i, 5).—When the lactone, $C_{10}H_{16}O_4$, obtained by Baeyer and Villiger (Abstr., 1900, i, 133) in the oxidation of camphor with Caro's acid is heated with 20% phosphoric acid at 190—200°, it loses carbon dioxide and forms 2-*methyl-laurenone* (2 : 3 : 3 : 4-*tetramethyl*-Δ^1-cyclo*pentenone*-5),  $\begin{matrix}CMe_2\cdot CHMe \\ | \\ CMe{=\!=\!=}CH\end{matrix}\!\!>CO$, b. p. 82—86°/10 mm., 95—96°/18 mm., D_0^4 1·062. The constitution of this substance was established by its conversion by successive oxidation and esterification into *ethyl γ-keto-αββ-trimethylvalerate*, $COMe\cdot CMe_2\cdot CHMe\cdot CO_2Et$, b. p. 105—107°/12 mm., which forms a *semicarbazone*, m. p. 158—159°, and on treatment in the usual way yields the corresponding trimethylsuccinic acid.

2-Methyl-laurenone forms two *semicarbazones*, m. p. 150° and 198° respectively, a normal *oxime*, m. p. 95—96°, b. p. 122—128°/10 mm.; the *phenylcarbanilidoxime* has m. p. 101—102°. When treated with sodium and alcohol, it yields 1 : 2 : 2 : 3-*tetramethyl*-4-cyclo*pentanol*, $C_9H_{18}O$; the *phenylurethane* has m. p. 113—114°. 1 : 2 : 2 : 3-*Tetramethyl*-4-cyclo*pentanone*, b. p. 178—180°, forms two *semicarbazones*, m. p. 182° and 232° respectively.

W. O. W.

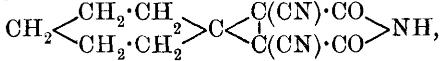
Some New Derivatives of *cyclo*Hexanones.

ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1911, **46**, 662—669. Compare Abstr., 1901, i, 341; Thole and Thorpe, Trans., 1911, **99**, 422).—The *imide* of *aa'-dicyano*cyclo*hexane*-1 : 1-*diacetic acid*,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\ CH(CN)\cdot CO\end{matrix}>NH,$$

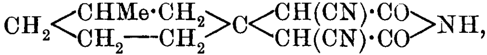
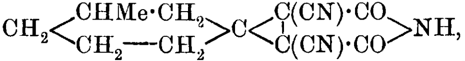
prepared from *cyclo*hexanone and ethyl cyanoacetate, crystallises in colourless needles, m. p. 211—212°. The *ammonium* salt is the primary product. When treated with bromine water, the imide yields quantitatively an additive product containing two atoms of bromine, m. p. 164—165° (with evolution of bromine). This *dibromide* when heated on a water-bath with 50% formic acid until effervescence ceases yields *aβ-dicyano-aβ*-cyclo*hexanesuccinimide*,



$$CH_2<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\ |\\ C(CN)\cdot CO\end{matrix}>NH,$$

which crystallises in lustrous needles, m. p. 238—240°. The removal of bromine from the dibromide can also be effected by warming it in aqueous-alcoholic solution.

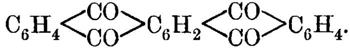
1-Methyl*cyclo*hexan-3-one yields similar products.

The *imide* of *aa'-dicyano*-1-*methyl*cyclo*hexane*-3 : 3-*diacetic acid*,  $CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2-CH_2\end{matrix}>C<\begin{matrix}CH(CN)\cdot CO\\ CH(CN)\cdot CO\end{matrix}>NH$, has m. p. 240—241° (becoming brown; on Maquenne block the m. p. is 244—245°). The *ammonium* salt crystallises well. The imide absorbs two atoms of bromine, and the *dibromide* yields *aβ-dicyano-aβ*-1-*methyl*cyclo*hexane*-3 : 3-*succinimide*,  $CH_2<\begin{matrix}CHMe\cdot CH_2\\ CH_2-CH_2\end{matrix}>C<\begin{matrix}C(CN)\cdot CO\\ |\\ C(CN)\cdot CO\end{matrix}>NH$, m. p. 241—242° (Maquenne block). R. V. S.

"Tagayasan," a Japanese Wood the Dust of which Causes Inflammation. K. IWAKAWA (*Arch. expt. Path. Pharm.*, 1911, **65**, 315—324).—Workmen dealing with Tagayasan timber suffer from inflammation of the eyes. The active principle was extracted by means of benzene, and appears to be identical with chrysophanohydroanthrone, $C_{15}H_{12}O_3$ (compare Abstr., 1900, i, 42), which, however, had not hitherto been found to occur naturally. The pure substance causes the same symptoms as the wood dust. E. J. R.

Synthesis of Linear Diphthaloylbenzene. ERNST PHILIPPI (*Monatsh.*, 1911, **32**, 631—635).—The anhydride of pyromellitic acid condenses with benzene in presence of aluminium chloride to a mixture of 4 : 6-dibenzoyl*iso*phthalic acid and 2 : 5-dibenzoylterephthalic acid. These are separated by making use of their solubility in water and nitrobenzene.

Both isomerides are converted on heating with concentrated sulphuric acid into linear diphthaloylbenzene,



$$C_6H_4<\begin{matrix}CO\\ CO\end{matrix}>C_6H_2<\begin{matrix}CO\\ CO\end{matrix}>C_6H_4.$$

4 : 6-*Dibenzoyl*iso*phthalic acid* crystallises in colourless needles or long plates, m. p. 263—264° (darkening).

2 : 5-*Dibenzoylterephthalic acid* crystallises in long, lanceolate plates or slender needles, which soften at 295°, m. p. 307—309°. On distillation with calcium oxide in a stream of hydrogen under reduced

pressure, *p*-dibenzoylbenzene is obtained; this confirms the constitution.

Diphthaloylbenzene crystallises in bunches of yellow needles, which are not altered at 370°, but sublime at a higher temperature. It forms a dark red vat with alkaline hyposulphite, and dyes cotton first green and then dark blue. E. F. A.

New Method of Formation of Flavanthren. ERWIN BENESCH (*Monatsh.*, 1911, **32**, 447—456).

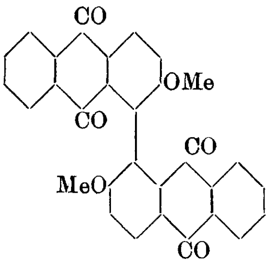
—Flavanthren has been synthesised by the following series of reactions, starting from the methyl ether of 2-hydroxyanthraquinone, which is converted through the *nitro*- and *amino*-derivatives into 1-*iodo*-2-*methoxyanthraquinone*. This, when heated with copper powder, gives 2 : 2′-*dimethoxy*-1 : 1′-*dianthraquinonyl*, which after hydrolysis is converted by ammonia into 2 : 2′-diamino-1 : 1′-dianthraquinonyl; this last changes spontaneously into flavanthren.

On nitration of 2-methoxyanthraquinone, two isomeric mononitro-derivatives, m. p. 271° and 225°, are obtained. The less fusible isomeride does not form flavanthren, and is possibly 3-nitro-2-methoxyanthraquinone.

1-*Nitro*-2-*methoxyanthraquinone* forms yellow crystals, m. p. 271°.

3-*Nitro*-2-*methoxyanthraquinone*, m. p. 225°, is somewhat darker in colour and more soluble than the isomeride.

1-*Amino*-2-*methoxyanthraquinone* is red, and has m. p. 224°. The isomeric 3-*amino*-derivative has m. p. 218—222°.

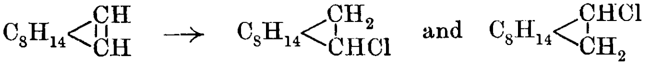


1 - *Iodo* - 2 - *methoxyanthraquinone* forms lustrous, brown crystals, m. p. 265°. The 3-*iodo*-isomeride has m. p. 210—212°.

2 : 2′-*Dimethoxy*-1 : 1′-*dianthraquinonyl* (annexed formula) is a yellow powder, m. p. 346°. On hydrolysis by means of anhydrous aluminium chloride, 2 : 2′-*dihydroxy*-1 : 1′-*dianthraquinonyl* is obtained as a green, amorphous powder. The yields in these operations are but small, and flavanthren itself was not isolated, but its presence was definitely characterised. E. F. A.

Constitution of Camphene. II. Camphene Hydrochloride and Camphene Hydrate. OSSIAN ASCHAN (*Annalen*, 1911, **383**, 1—38. Compare Abstr., 1910, i, 709).

—Since there are at present two competing formulæ, namely, the author's "ethylene" formula and Wagner's "methylene" formula, for camphene, the question of the individual nature of the terpene acquires great importance. The author attempts, admittedly without much success, to answer it by converting camphene (from various sources) through the hydrochloride into camphene hydrate, regenerating camphene therefrom, and comparing the physical properties of the regenerated and the original camphenes. In the course of his experiments, which include the examination of pinene hydrochloride and bornyl and *iso*bornyl chlorides, the author obtains evidence which indicates that (1) crude camphene hydrochloride is a mixture of two stereoisomerides, α and β, derived from camphene (" ethylene " formula), thus:



$$C_8H_{14}\!\left<\begin{array}{l}CH\\ \|\\ CH\end{array}\right. \longrightarrow C_8H_{14}\!\left<\begin{array}{l}CH_2\\ |\\ CHCl\end{array}\right. \text{ and } C_8H_{14}\!\left<\begin{array}{l}CHCl\\ |\\ CH_2\end{array}\right. ;$$

(2) α-camphene hydrochloride, which is not decomposed by dilute aqueous potassium hydroxide, is the main constituent of bornyl chloride, whilst β-camphene hydrochloride is the chief constituent of *iso*bornyl chloride.

Thus camphene (prepared from the hydrochloride of rectified American turpentine), b. p. 159·5—160°, m. p. 40·5—41·5°, and $[\alpha]_D^{20}$ + 12·85° in benzene, is converted by ethereal hydrogen chloride into crude camphene hydrochloride, m. p. 137—140°, and $[\alpha]_D$ − 6·40°. This hydrochloride in benzene is shaken with dilute (approximately 3%) aqueous potassium hydroxide for twelve hours at 60°, and again for twelve hours at 80—90° after the addition of more potassium hydroxide, whereby is obtained camphene hydrate (from the α-camphene hydrochloride), b. p. 206—207·5°, m. p. 149°, $[\alpha]_D$ − 2·89° in benzene, together with some camphene (from the β-camphene hydrochloride), b. p 159·5—160·5°, m. p. 43—44°, D_{50}^{50} 0·8579, $[\alpha]_D^{20}$ + 10·92° in benzene. When boiled with acetic anhydride and sodium acetate, the camphene hydrate yields, together with a little *iso*bornyl acetate, a camphene, b .p. 159—161°, m. p. 44—45°, $[\alpha]_D^{20}$ + 12·63° in benzene, D_{50}^{50} 0·8531, and n_D^{50} 1·45952. Finally, the camphene hydrate in benzene is converted by hydrogen chloride into the original camphene hydrochloride, m. p. 151—153·5° (after recrystallisation from methyl alcohol containing hydrogen chloride), and $[\alpha]_D^{20}$ − 6·495° in benzene. (Camphene hydrate would be expected to form only α-camphene hydrochloride; probably the hydrogen chloride acts as a dehydrating agent, producing camphene, which then unites with the acid to form the mixture of α- and β-camphene hydrochlorides.) The fact that the two camphenes, obtained in the preceding transformations agree very closely with the original camphene in physical properties indicates that the terpene is an individual substance.

Similar results have been obtained with a camphene (from Siberian pine-needle oil), b. p. 159—159·5°, m. p. 47—48°, D_{50}^{50} 0·8548, and $[\iota]_D^{50}$ − 89·29°. A liquid portion of the camphene, b. p. 159—160°, D_{15}^{15} 0·8728, and $[\alpha]_D$ − 75·96°, is converted into the hydrochloride, m. p. 137° (crude) and 149—150° (recryst. from benzene), and $[\alpha]_D^{15}$ 47·33° in benzene, which yields by hydrolysis with dilute potassium hydroxide at 60°, and finally at 80°, camphene hydrate, $[\alpha]_D$ − 1·35° in benzene, from which sodium acetate and boiling acetic acid regenerate a camphene, b. p. 161—163°, m. p. 49·5—51°, and $[\alpha]_D^{20}$ − 76·04° in benzene.

When hydrolysed by dilute potassium hydroxide under the preceding conditions, bornyl chloride (from the *l*-borneol of Siberian pine-needle oil) yields camphene hydrate, m. p. 148—149°, and a trace of camphene, whilst *iso*bornyl chloride (from technical *iso*borneol) yields camphene, b. p. 159—160°, m. p. 50—51°, $[\alpha]_D^{20}$ − 0·45° in benzene, and a trace of camphene hydrate. This evidence is the reason for statement (2) above.

Pinene hydrochloride (from American turpentine), m. p. 126°, $[\alpha]^{20}_{D}$ 6·65°, is scarcely attacked by 2% potassium hydroxide below 100°, but is hydrolysed by a mixture of alcohol, benzene, and milk of lime at 135° and finally at 150°, yielding 7—9% of camphene, b. p. 159·5—161°, m. p. 40—41°, $[\alpha]^{20}_{D}$ +14·52° in benzene, and less than 40% of camphene hydrate, b. p. 206—206·5°, m. p. 149—150°, $[\alpha]^{20}_{D}$ −3·24° in benzene; the camphene obtained from the hydrate by acetic anhydride and potassium acetate has b. p. 159·5—160°, m. p. 43—44°, D^{50}_{50} 0·8542, and $[\alpha]^{20}_{D}$ +15·43° in benzene. Similar results are obtained with a strongly active pinene hydrochloride (from Grecian turpentine), m. p. 128—130°, and $[\alpha]^{20}_{D}$ +28·88° in benzene; the camphene hydrate obtained therefrom has m. p. 149—150° and $[\alpha]^{20}_{D}$ −21·79° in benzene, and yields camphene, b. p. 159—160°, m. p. 44—45°, and $[\alpha]^{20}_{D}$ +85·68° in benzene. There is no doubt, therefore, that the camphene hydrate from pinene hydrochloride is identical with that from camphene hydrochloride.

The higher fractions of the products of the preceding hydrolyses contain chlorine, showing that crude camphene hydrochloride, bornyl chloride, and *iso*bornyl chloride contain a third constituent which is unattacked by 3% potassium hydroxide at 60—80°; it is also resistant to aniline at the ordinary temperature, but is hydrolysed by hot aniline and by alcoholic potassium hydroxide.

Attempts to separate the α- and the β-forms of camphene hydrochloride by crystallisation from petroleum have yielded the less soluble and more stable α-modification, which has m. p. 150—151° in its racemic form and 157—158° in its strongly active form (that from *l*-bornyl chloride). The presence of the β-modification in crude camphene hydrochloride and also in bornyl and *iso*bornyl chlorides is indicated by the rate of hydrolysis of these chlorides by alcoholic potassium hydroxide; the results are expressed graphically.

Camphene hydrate is converted almost quantitatively into *iso*bornyl acetate by heating with sulphuric and acetic acids and a little water at 60—70°. C. S.

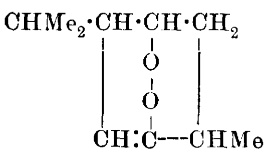
Constitution of Camphene. III. Individuality of Camphene from Various Sources. OSSIAN ASCHAN (*Annalen*, 1911, **383**, 39—51. Compare preceding abstract).—Samples of camphene from seven different sources have been oxidised by potassium permanganate essentially by the process described previously (Abstr., 1910, i, 709), and the products have been separated into their constituents (camphenilone, camphene glycol, camphenilic acid, sodium salt of an *acid*, m. p. 138°, camphenic acid, and other acids soluble in water) always under exactly the same conditions, so that the quantities of each constituent are comparable. It is found in all seven cases that the quantities of the chief oxidation products are, in general, nearly the same, and that the quantities of camphenilic acid and camphenic acid stand in a definite ratio to one another, 1 : 10. These results not only indicate that camphene is an individual substance, but also furnish strong evidence in favour of the author's "ethylene" formula. If camphene has Wagner's "methylene" formula, the formation of the chief oxidation product, camphenic acid, must be explained by assuming an intramolecular change, whereby a five-membered ring becomes a six-membered ring. On the other hand, accepting the "ethylene" formula of camphene, the formation of camphenic acid is a direct process, and the production of the relatively small amount of camphenilic acid (and also of camphenilone and camphene glycol) is explicable by the more rational assumption of the change of a six-membered to a five-membered ring. C. S.

Constitution of Camphene. IV. Stereoisomeric Camphenic Acids. OSSIAN ASCHAN (*Annalen*, 1911, **383**, 52—68. Compare preceding abstracts).—*cis-dl*-Camphenic acid is partly transformed into trans-dl-*camphenic acid*, $C_8H_{14}(CO_2H)_2$, m. p. 122—123° (*diamide*, m. p. 231—232°; dianilide, m. p. 165°), by distillation under 5 mm. pressure, or by heating for twelve hours at 180° with equal parts of acetic acid and 38% hydrochloric acid; the two modifications are separated by alcoholic sodium ethoxide, the sodium salt of the *trans*-acid being the more soluble. The two modifications in approximately equal amounts are also obtained by the reduction of *cis*-α-bromocamphenic acid by zinc and acetic and hydrochloric acids.

The conversion of *cis*-camphenic acid in a normal way into the *trans*-modification is important, since it furnishes a fairly certain proof that the migrating carboxyl group is attached to a ring carbon atom.

The distillation of *cis*-camphenic acid under ordinary pressure yields products which are receiving further examination. C. S.

Chemical Investigation of the Oil of Chenopodium. E. K NELSON (*J. Amer. Chem. Soc.*, 1911, **33**, 1404—1412).—This oil is obtained by distillation of *Chenopodium ambrosioides* var. *Anthelmintica.* It contains about 70% of ascaridole (Abstr., 1908, i, 667), b. p. 96—97°/8 mm., D^{20}_{20} 0·9985, n^{20}_D 1·4769, α^{20}_D +0·7°. [The pure compound may be optically inactive, and this slight activity may be due to a trace of *d*-camphor (see below)]. Ascaridole readily undergoes rearrangement to form a glycol anhydride analogous to pinene oxide, a change indicating that it is an unstable dioxide. Further evidence is afforded by its property of exploding when heated, and by the violence of its reaction with ferrous sulphate and other reagents. The annexed constitution is assigned to it.

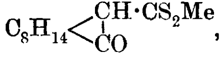


The author prepared *ascaridole glycol* (b. p. 271—272°, m. p. 62·5—64°, D^{20}_{20} 1·0981, n^{20}_D 1·4796, α_D 0) by treatment with ferrous sulphate, also the *monobenzoate*, m. p. 136—137°, and the *dibenzoate*, m. p. 116·5—117·5°, of the glycol.

An old sample of the oil was found to contain *d*-camphor.

E. J. R.

Dithiocamphorcarboxylic Acid. LÉO TSCHUGAEFF and G. PIGOULEWSKY (*Compt. rend.*, 1911, **153**, 388—390).—This substance was obtained in an unsuccessful attempt to prepare a xanthate of the camphor series. Sodium camphor, prepared by means of sodamide, was treated successively with carbon disulphide and methyl sulphate. After heating on the water-bath, the mixture gave *methyl dithiocamphorcarboxylate*,



$C_8H_{14}<\begin{array}{l}CH\cdot CS_2Me\\|\\CO\end{array}$

, as a deep yellow oil, b. p. 179°/8 mm., D^{24} 1·1204, $[\alpha]_D$ +424·58°. The substance is remarkably stable, and has b. p. about 300° under ordinary pressure, practically without decomposition. Alcoholic potassium hydroxide converts it into potassium camphorcarboxylate. *Dithiocamphorcarboxylic acid* is a yellow oil, decomposing on heating into camphor and carbon disulphide. The *copper* salt is deep brown. W. O. W.

Decomposition of Terpenoid Substances by Glowing Metallic Wires.

CARL D. HARRIES and KURT GOTTLOB (*Annalen*, 1911, **383**, 228—229).—An apparatus, termed the "isoprene lamp," is figured and described. A coil of platinum wire, 120 cm. in length and resistance 9Ω at an average red heat, is suspended in the neck of a flask and heated electrically (about 5 amperes at 220 volts). The flask is provided with a vertical condenser containing water at 50°. The liquid in the flask is gently boiled; the undecomposed vapour is condensed and returns to the flask, whilst the volatile decomposition products escape, and are condensed by a freezing mixture. Commercial *r*- or *l*-pinene yields only about 1% of isoprene, whilst commercial carvene yields 30—50%, according to the amount of limonene it contains. C. S.

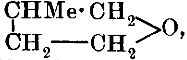
Butadienes and Some Synthetic Caoutchouc Obtained Therefrom.

CARL D. HARRIES (*Annalen*, 1911, **383**, 157—227).—The older processes for the synthesis of isoprene are condemned either on account of the rarity of the initial material, or because the resulting isoprene is contaminated with trimethylethylene or *as*-dimethylallene. The following process is adopted to obtain pure isoprene in quantity sufficient for the determination of its physical constants.

[With KARL NERESHEIMER.]—Ethyl pyrotartrate is reduced by sodium and alcohol to *iso*pentane-αδ-diol,

$$OH\cdot CH_2\cdot CH_2\cdot CHMe\cdot CH_2\cdot OH,$$

b. p. 124—125°/13 mm., D^{18}_{18} 0·9954, n^{18}_D 1·45173 (*diacetate*, b. p. 116—117°/17 mm., D^{20}_{20} 1·0434, n^{20}_D 1·42717; *oxide*,



$\begin{array}{l}CHMe\cdot CH_2\\|\\CH_2—CH_2\end{array}{>}O$,

b. p. 86—87°, D^{20}_{20} 0·8643, n^{20}_D 1·41122; s-*diphenyldiurethane*, m. p. 97°; *tetraphenyldiurethane*, m. p. 102°). The glycol is converted by 60% hydrobromic acid at 100° into αδ-dibromo-β-methylbutane (Abstr., 1907, i, 743), b. p. 84—86°/11 mm., D^{17}_{17} 1·6986, n^{17}_D 1·51217, which reacts with 33% alcoholic trimethylamine at 100° to form the corresponding bis-quaternary ammonium bromide, the base of which, by distillation, yields isoprene (in 50% yield), b. p. 36—37°, D^{21}_{21} 0·6804, D^{21}_4 0 6793, n^{21}_D 1·42267, n^{21}_α 1·41807, n^{21}_γ 1·44340.

For the technical preparation of isoprene, Hofmann's (Elberfeld) process with *p*-cresol is recommended as giving very pure isoprene. The author obtains most of his (pure) isoprene by heating turpentine or, better, dipentene or limonene over a glowing platinum spiral (preceding abstract), but also obtains a fair amount by dropping $\beta\gamma$-dibromo-β-methylbutane (obtained from acetone through the amyl alcohol) on soda-lime at 600°. The soda-lime is advantageously previously saturated with carbon dioxide (the reagent thus prepared is more porous than calcium carbonate or similar substances), and the process, for which a special apparatus has been designed, is applicable to the preparation of other homologous hydrocarbons. When heated with quinoline, $\beta\gamma$-dibromo-β-methylbutane is converted into a substance, b. p. 39—40°, D_4^{17} 0·6719, n_D^{17} 1·40188, which probably consists chiefly of *as*-dimethylallene.

Erythrene ($\Delta^{\alpha\gamma}$-butadiene) is conveniently obtained from phenol by the Elberfeld process. A satisfactory laboratory method starts from *sec.*-butyl alcohol. This is converted by phosphoric oxide into the olefine, the dibromide of which yields butadiene by the hot soda-lime process.

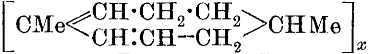
$\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene can be obtained by the author's method with pinacone hydrochloride and hot soda-lime, but is best prepared from pinacone and potassium hydrogen sulphate by the Elberfeld process.

Each of the preceding butadienes yields by suitable polymerisation a "normal" caoutchouc and a "sodium" caoutchouc, which are similar in appearance, but differ in their behaviour with ozone.

"Normal" caoutchoucs are obtained when the polymerisation is effected by the acetic acid process or, better, by heat alone, as in the Elberfeld method. Experiments with "normal" isoprene caoutchouc show that in order to secure a product of good quality it is necessary, not only to use pure isoprene, but also to exclude oxygen during the process of polymerisation. Synthetic caoutchoucs are very sensitive to autoxidation, and the higher the temperature of polymerisation, the more readily does the caoutchouc undergo autoxidation.

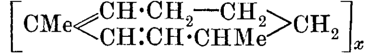
The quality of a synthetic caoutchouc is conveniently tested by submitting the caoutchouc to a process of cold vulcanisation (the hot process requires costly apparatus and a large amount of material, and is unsuitable for laboratory experiments), and examining the solidity and elasticity of the product. As tested by this method, the best synthetic caoutchouc is produced when isoprene is polymerised by heat alone at the lowest possible temperature.

The comparison of synthetic with natural caoutchouc is very difficult, because only the nitrosites and tetrabromides are available for comparative purposes, and these compounds are amorphous, difficult to purify, and have no definite m. p. The author, therefore, prefers to rely on a comparison of the ozonides and of their products of decomposition. He thus finds that "normal" isoprene caoutchouc (and, still more distinctly, "normal" dimethylbutadiene caoutchouc) must contain a small amount of another caoutchouc, because the decomposition products of its ozonide contain some substances (methylglyoxal ?) which are not found among the products of decomposition of the ozonide of natural caoutchouc. Moreover, a small portion of the synthetic caoutchouc is very much more difficultly ozonised than is natural caoutchouc. The constitution



$$\left[\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{\cdot}CH_2{\cdot}CH_2}\\ \mathrm{CH{:}CH{-}CH_2}\end{matrix}{>}\mathrm{CHMe}\right]_x$$

or



$$\left[\mathrm{CMe}{<}\begin{matrix}\mathrm{CH{\cdot}CH_2{-}CH_2}\\ \mathrm{CH{:}CH{\cdot}CHMe}\end{matrix}{>}\mathrm{CH_2}\right]_x$$

is suggested for the second synthetic caoutchouc.

A comparison of "normal" isoprene caoutchouc and purified Para caoutchouc with regard to their behaviour with Budde's brominating solution shows that hydrogen bromide is more copiously evolved during the reaction of the synthetic caoutchouc, and that the resulting tetrabromide is easily and completely soluble in carbon disulphide.

The action of nitrous fumes on "normal" isoprene caoutchouc yields, as in the case of natural caoutchouc, a yellowish-green, insoluble *nitrosite* "*a*," decomp. 115—120° or 130—135°, and a soluble *nitrosite* "*c*," decomp. 158—162°, the composition of which approximates to the formula $C_{10}H_{15}O_7N_3$ less exactly than does that of the nitrosite "*c*" of carefully purified natural caoutchouc, which also has decomp. 158—162°. When distilled in a vacuum, the synthetic caoutchouc behaves like natural rubber, and so also when treated with ozone (with the two reservations mentioned above).

When heated in glacial acetic acid at 110—120° for ten days, $\Delta^{\alpha\gamma}$-butadiene yields "normal" *butadiene-caoutchouc*, $(C_8H_{12})_x$, a pure product being obtained when oxygen is excluded during the polymerisation. This caoutchouc resembles gelatin, is non-elastic and easily torn, and is sparingly soluble except in chloroform. It forms a yellow, amorphous, easily soluble *nitrosite*, decomp. above 80°, and yields an explosive, oily *ozonide* (in chloroform), or a white, solid ozonide (in carbon tetrachloride), the latter closely resembling the ozonide of $\Delta^{1:5}$-*cyclo*octadiene. When polymerised by heat alone, butadiene yields a solid, the distillation of which at 100—110°/0 mm. furnishes a *hydrocarbon*, C_8H_{12}, b. p. 36°/23 mm., D_4^{16} 0·8523, n_D^{16} 1·46768, which resembles the terpenes. The residue contains the caoutchouc, which is quite similar to that obtained by the acetic acid process, except that it is insoluble even in chloroform, and is unaffected by nitrous acid or ozone.

Dimethylbutadiene polymerises very much more slowly than isoprene. The acetic acid process yields a yellow, friable product. When heated in a sealed tube at 100° for about twenty-three days, dimethylbutadiene is converted into a viscous mass, which is distilled at ordinary pressure to remove the unchanged hydrocarbon, and then at 110°/0 mm. to separate the small amount of terpene by-product. An ethereal solution of the residue yields, by the addition of alcohol, "normal" *dimethylbutadiene-caoutchouc*, $(C_{12}H_{20})_x$, which can scarcely be distinguished from isoprene caoutchouc in its external appearance. It can be vulcanised, and forms a *tetrabromide*, $C_{12}H_{20}Br_4$, evolving hydrogen bromide at about 130°, and a *nitrosite*, $C_{12}H_{19}O_7N_3$, darkening at 120°. When ozonised in carbon tetrachloride, it gives a mixture of two *ozonides*, the decomposition of which by hot glacial acetic acid yields acetonylacetone and other substances which reduce Fehling's solution.

"Sodium" *butadiene-caoutchouc*, $(C_8H_{12})_x$, is obtained almost quantitatively when $\Delta^{\alpha\gamma}$-butadiene is heated with a little sodium wire in a sealed tube at 35—40° for three hours, and the resulting viscous, brown mass is washed with dilute alcohol. When freshly prepared, it is pale yellow, transparent, and soluble in ether, chloroform, and benzene, but it loses these properties after keeping, and becomes viscous and stringy. It can be vulcanised (hot or cold process), yielding a product which surpasses all other synthetic caoutchoucs in elasticity. The *nitrosite* (approximately $C_8H_{12}O_3N_2$) and *bromide* (approximately $C_8H_{12}Br_4$) are described. In chloroform, 6—7% ozone produces an impure, oily *diozonide*, $C_8H_{12}O_6$, whilst 12—14% ozone produces a very explosive *substance*, which is apparently an ozonide, $C_8H_{12}O_4$; the decomposition products of these substances are being examined.

"Sodium" *isoprene-caoutchouc*, $(C_{10}H_{16})x$, is obtained almost quantitatively by heating pure isoprene with sodium at 60° for about fifty hours. It resembles the "normal" caoutchouc in its physical properties (except appearance), but is more soluble. It can be vulcanised, forms a white *tetrabromide* very similar to the "normal" tetrabromide, and yields with nitrous acid a mixture of two *nitrosites*, one insoluble, the other soluble; the latter is a yellowish-white powder, darkening at 170—180°. The "sodium" caoutchouc in carbon tetrachloride is attacked very slowly by 12—14% ozone, and yields a mixture of an ozonide and diozonide. With 6—7% ozone in chloroform, it forms a solid *diozonide*, $C_{10}H_{16}O_6$, which is quite different from the diozonide of ordinary caoutchouc, since its products of decomposition do not give the pyrrole reaction, and do not contain any characteristic substance except a very small amount of lævulaldehyde.

"Sodium" *dimethylbutadiene-caoutchouc*, obtained by heating dimethylbutadiene with sodium at 60° for ten to twelve days and nights, forms, after purification, a mass like gutta-percha. Its behaviour with ozone is similar to that of "sodium" isoprene caoutchouc; evidence of the presence of the "normal" caoutchouc is also obtained. The *tetrabromide* is a white powder, which evolves hydrogen bromide at 130°; the *nitrosite* is also described.

The paper concludes with some remarks on the constitution of natural caoutchouc and a reply to Pickles' criticisms (Trans., 1910, **97**, 1085). C. S.

Chemistry of Caoutchouc. II. Physico-chemical Investigation of the Extraction of Resin. David Spence and J. H. Scott (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 83—85. Compare this vol., i, 657).—Measurements have been made of the quantities of resin extracted from caoutchouc by boiling acetone during successive equal intervals of time. When the percentage of extracted resin is plotted against time, a curve is obtained which closely resembles the corresponding curve representing Bayliss's data for the rate of extraction of salts from gelatin by water. From this, it appears probable that a portion, at least, of the resin is present in the caoutchouc in the adsorbed condition.

Reference is made to the extraction experiments of Zilchert (*Gummi Zeit.*, 1911, **25**, 716), in which different kinds of caoutchouc were examined. The differences met with are supposed by the authors to be due to differences in the degree of dispersity of the colloidal system. H. M. D.

New Synthetic Glucosides. EMIL FISCHER and BURCKHARDT HELFERICH (*Annalen*, 1911, **383**, 68—91. Compare Abstr., 1910, i, 716).—With the object of obtaining as many synthetic glucosides as possible for comparison with natural products, the authors have applied König and Knorr's process to geraniol, *cyclo*hexanol, benzyl alcohol, cetyl alcohol, and ethyl glycollate. In every case except the last two the glucosides are split by emulsin, and therefore belong to the β-series; there is no doubt that the two exceptions also belong to the same series. The same method is used for each alcohol, except in the case of ethyl glycollate, where a solvent is not employed. The alcohol and bromoacetoglucose dissolved in ether are shaken for several hours with freshly prepared dry silver oxide until a filtered sample no longer gives a precipitate of silver bromide when boiled with aqueous silver nitrate.

*Tetra-acetyl-β-benzyl-*d*-glucoside*, $CH_2Ph\cdot C_6H_7O_6Ac_4$, white needles, m. p. 96—101° (corr.), has $[\alpha]^{22}_D$ $-49{\cdot}51°$ in alcohol, and is hydrolysed by aqueous barium hydroxide to *β-benzyl-*d*-glucoside*, $CH_2Ph\cdot O\cdot C_6H_{11}O_5$, flexible needles, m. p. 123—125° (corr.), $[\alpha]^{20}_D$ $-55{\cdot}76°$ in water, which has a very bitter taste, does not reduce Fehling's solution, and is rapidly hydrolysed by dilute hydrochloric acid or emulsin.

*Tetra-acetyl-β-*cyclo*hexyl-*d*-glucoside*, $C_6H_{11}\cdot C_6H_7O_6Ac_4$, long needles, m. p. 120—121° (corr.), $[\alpha]^{22}_D$ $-29{\cdot}74°$ in alcohol, yields *β-*cyclo*hexyl-*d*-glucoside*, $C_6H_{11}\cdot O\cdot C_6H_{11}O_5$, m. p. 133—137° (corr.), $[\alpha]^{20}_D$ $-41{\cdot}55°$ in water, by hydrolysis as above. *Tetra-acetyl-β-geranyl-*d*-glucoside*, $C_{10}H_{17}\cdot C_6H_7O_6Ac_4$, white needles, m. p. 29—30°, $[\alpha]^{22}_D$ $-25{\cdot}17°$ in alcohol, is hydrolysed by aqueous alcoholic barium hydroxide, yielding *β-geranyl-*d*-glucoside*, $C_{10}H_{17}\cdot O\cdot C_6H_{11}O_5,H_2O$, long needles, m. p. 58°, $[\alpha]^{27}_D$ $-38{\cdot}12°$ in water. *Tetra-acetyl-β-cetyl-*d*-glucoside*, $C_{16}H_{33}\cdot O\cdot C_6H_7O_5Ac_4$, glistening needles, m. p. 71—73° (corr.), $[\alpha]^{20}_D$ $-20{\cdot}19°$ in alcohol, is not attacked by dilute hydrochloric or sulphuric acid, and is hydrolysed by boiling alcohol and 10% sodium hydroxide, yielding *β-cetyl-*d*-glucoside*, $C_{16}H_{33}\cdot O\cdot C_6H_{11}O_5$, colourless needles, $[\alpha]^{24}_D$ $-22{\cdot}02°$ in alcohol, which is tasteless, melts indefinitely between 110° and 145°, is not attacked by Fehling's solution, by dilute mineral acids, or by emulsin, but is hydrolysed on the water-bath by acetic acid containing a few drops of hydrochloric acid. *Ethyl tetra-acetyl-β-*d*-glucosidoglycollate*, $CO_2Et\cdot CH_2\cdot O\cdot C_6H_7O_5Ac_4$, colourless needles, m. p. 83—84° (corr.), $[\alpha]^{20}_D$ $-40{\cdot}62°$ in alcohol, is hydrolysed by *N*/5-barium hydroxide in twenty hours, yielding *β-*d*-glucosidoglycollic acid*, $CO_2H\cdot CH_2\cdot O\cdot C_6H_{11}O_5$, clusters of stout leaflets, m. p. 165—167°, $[\alpha]^{21}_D$ $-44{\cdot}11°$ in water, which has an acid taste, is not attacked by Fehling's solution or emulsin, and forms amorphous *calcium*, *barium*, *zinc*, *lead*, and *mercury* salts, and a crystalline *sodium* salt. *β-*d*-Glucosidoglycollamide*, $NH_2\cdot CO\cdot CH_2\cdot O\cdot C_6H_{11}O_5$, obtained by saturating with ammonia a methyl-alcoholic solution of ethyl tetra-acetylglucosidoglycollate in a freezing mixture, has m. p. 167° (corr.)

and $[\alpha]_D^{18} - 43{\cdot}24°$, is hydrolysed by boiling dilute hydrochloric acid or by emulsin, and has a sweet taste and bitter after-taste; attempts to prepare the corresponding nitrile by boiling acetic anhydride result in the formation of *penta-acetylglucosidoglycollamide*, $C_{18}H_{25}O_{12}N$, white needles, m. p. 146—149° (corr.).

Pentabenzoyldextrose ($[\alpha]_D^{20} + 25{\cdot}40°$ in chloroform) reacts like penta-acetyldextrose with hydrogen bromide in glacial acetic acid, forming *bromo-β-benzoglucose*, $C_6H_7O_5Bz_4Br$, white needles, m. p. 125—128° (corr.), $[\alpha]_D^{19} + 145{\cdot}1°$ in toluene, which interacts with methyl alcohol and silver oxide to produce *tetrabenzoyl-β-methyl*-d-*glucoside*, $CH_3{\cdot}C_6H_7O_6Bz_4$, white needles, m. p. 160—162° (corr.), $[\alpha]_D^{20} + 30{\cdot}99°$ in chloroform; the last substance is converted into β-methylglucoside by shaking with alcoholic sodium ethoxide. C. S.

The Glucoside of Leaves of the Pear Tree, its Presence in the Leaves of Different Varieties, its Detection in the Trunk and Root. ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*Compt. rend.*, 1911, **153**, 468—471. Compare Abstr., 1910, i, 273; ii, 742).—Arbutin has been obtained from the leaves of four new varieties of pear tree in addition to those already studied. Probably all varieties of *Pirus* contain arbutin. This glucoside also occurs in the trunks and roots of the trees. W. O. W.

Bile Pigments. I. HANS FISCHER (*Zeitsch. physiol. Chem.*, 1911, **73**, 204—239).—Maly's hydrobilirubin and the urobilin described by Garrod and Hopkins (Abstr., 1896, i, 712) are shown to be mixtures. Hæmopyrrole is not the urobilinogen of the urine; the urobilin prepared from hæmopyrrole has quite different properties from that of urine.

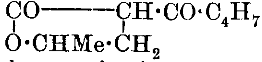
Bilirubin dissolves to form colloidal solutions in presence of taurocholic and glycocholic acids. When reduced by means of sodium amalgam, bilirubin forms *hemibilirubin*, $C_{16}H_{22}O_3N_2$ or $C_{16}H_{20}O_3N_2$, crystallising in short, colourless prisms, which tend to become red and belong to the monoclinic system [$a : b : c = 1{\cdot}8 : 1 : 0{\cdot}7$; $\beta = 110°20'$], m. p. 192° (decomp.). It gives an intense red coloration with sodium hydroxide and copper sulphate, forms dyes with diazonium salts, and changes on exposure to the air, first to a reddish-orange dye and then to a brown dye with a green surface reflex: these show all the urobilin reactions.

A new biliary acid, *lithocholic acid*, $C_{24}H_{40}O_3$, is isolated from ox gall stones. This crystallises in long prisms, m. p. 184—186° (corr.), $[\alpha]_D^{20} + 32{\cdot}14°$; it is tasteless, and crystallises from acetic acid without a molecule of the solvent.

The composition of coprosterol given by Bondzynski and Humnicki is confirmed; this has m. p. 112—116°, $[\alpha]_D^{20} + 24{\cdot}53°$.

Deoxycholic acid was obtained from fæces in colourless needles, m. p. 145°, $[\alpha]_D^{20} + 53{\cdot}38°$. E. F. A.

Hypericin (Hypericum Red). C. ČERNÝ (*Zeitsch. physiol. Chem.*, 1911, **73**, 371—382. Compare Wolff, *Pharm. Centr.-h.*, 1875, **16**, 193).—The flowers of *Hypericum perforatum* contain a brilliant red pigment in addition to a yellow pigment. The red colouring matter has an absorption spectrum very similar to that of oxyhæmoglobin. About 1 gram of pigment has now been isolated from 2470 grams of dried flowers having approximately the formula $C_{16}H_{10}O_5$; the possibility of it being a flavone dye is suggested. Solutions of hypericin in organic solvents are blood-red; on dilution they become somewhat violet, and show a fire-red fluorescence. Measurements have been made of the absorption spectrum under various conditions in extension of those of Wolff (*loc. cit.*). E. F. A.

Constitution of Divalolactone. SIMA M. LOSANITSCH (*Compt. rend.*, 1911, **153**, 390—392).—Fittig (Abstr., 1890, 286) regarded divalolactone, the product of the action of sodium ethoxide on valerolactone, as an ether containing two lactonic oxygen atoms. The present author believes the third atom of oxygen to be ketonic, and the substance to have the formula  $\begin{array}{l}\mathrm{CO}\text{——————}\mathrm{CH{\cdot}CO{\cdot}C_4H_7}\\ \mid\qquad\qquad\quad\ \mid\\ \mathrm{O{\cdot}CHMe{\cdot}CH_2}\end{array}$. Fittig's divalolactonic acid would then have the constitution

$$\mathrm{OH{\cdot}CHMe{\cdot}CH_2{\cdot}CH(CO_2H){\cdot}CO{\cdot}C_4H_7}.$$

The following observations support these conclusions: Magnesium methyl iodide acts on valerolactone, giving *βε-dihydroxy-β-methylhexane*, b. p. 121°/14 mm., whereas divalolactone does not give the analogous diol, but loses water, forming *dimethylanhydrovalolactone*, $C_{12}H_{20}O_2$, b. p. 104—105°/13·5 mm. This is a ketone, since on further treatment with magnesium methyl iodide, it yields a *compound*, $C_{13}H_{24}O_2$, b. p. 136—137°/13 mm., whilst the analogous ether, 2 : 5 : 5-*trimethyltetrahydrofuran*, b. p. 102—103°, does not react with the Grignard reagent. On treating divalolactonic acid with methyl sulphate and sodium hydroxide, it yields, according to conditions, the corresponding *methyl* ester, b. p. 114°/13 mm., or divalolactone.

The C_4H_7 group in these compounds is under investigation.

W. O. W.

Catalytic Preparation of Substituted Ketohydrofurans. GEORGES DUPONT (*Compt. rend.*, 1911, **153**, 275—277. Compare this vol., i, 554).—The conversion of dimethyl-Δ^γ-hexinene-$\beta\epsilon$-diol into a tetrahydrofuran derivative by the catalytic action of mercuric sulphate has been extended to other diols of the type

$$\mathrm{OH{\cdot}CRR'{\cdot}C{\vdots}C{\cdot}CRR'{\cdot}OH}.$$

When R and R′ are saturated and of low molecular weight, the change is rapid and quantitative, but secondary reactions intervene when the radicles are unsaturated, aromatic, or of high molecular weight.

The following *diols* are new: *Acetylenediacraldehyde*,

$$\mathrm{CH_2{:}CH{:}CH(OH){\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}CH{:}CH_2},$$

b. p. 146°/15 mm., D^{24} 1·0341, n_D 1·5040; *acetylenedicrotonaldehyde*, $\mathrm{CHMe{:}CH{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}CH{:}CHMe}$, m. p. 90—92°; the *tetrabromide* has m. p. 137°; *acetylenedi*isovaleraldehyde,

$$\mathrm{CH_2Pr^\beta{\cdot}CH(OH){\cdot}C{\vdots}C{\cdot}CH(OH){\cdot}CH_2Pr^\beta},$$

b. p. 158—160°/15 mm., D^{24} 0·92475, n_D 1·4614; *acetylenedibutyrone*, $\mathrm{OH{\cdot}CPr_2{\cdot}C{\vdots}C{\cdot}CPr_2{\cdot}OH}$, pearly spangles, m. p. 120°.

3-*Keto*-2 : 5-*dimethyltetrahydrofuran* has b. p. 143°, D^{15} 0·9894, n_D 1·4267 ; the *compound*, $C_6H_6(SO_4Hg_2O)$, was isolated as an intermediate product in its formation. Pinacone gives a similar *compound*, $C_6H_{10}(SO_4Hg_2O)$, when treated with Denigès' reagent. The new ketone reduces Fehling's solution, and gives a *semicarbazone*, m. p. 168—170°. 3-*Keto*-2 : 5-*dimethyl*-2 : 5-*diethyltetrahydrofuran*, b. p. 192°, D^{15} 0·9317, n_D 1·4368, forms a *semicarbazone*, m. p. 136—138°. 3-*Keto*-2 : 5-*di*iso*butyltetrahydrofuran*, b. p. 112—114°/15 mm., D^{24} 0·9066, n_D 1·4385. 3-*Keto*-2 : 2 : 5 : 5-*tetraethyltetrahydrofuran*, b. p. 110°/18 mm., D^{24} 0·9275, n_D 1·4486. 3-*Keto*-2 : 5-*dipentamethylenetetrahydrofuran*, $C_3H_6<\substack{CH_2\\CH_2}>C<\substack{CO\cdot CH_2\\—O—}>C<\substack{CH_2\\CH_2}>C_3H_6$, has b. p. 152—154°/18 mm., D^{24} 1·0268, n_D 1·4904 ; the *semicarbazone* has m. p. 216°.

W. O. W.

Condensation of *p*-Dibromobenzene with Xanthone ; Quinocarbonium Salts.

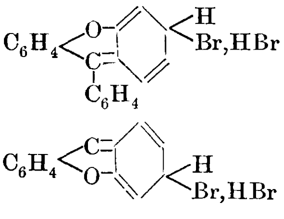
LEE H. CONE and C. J. WEST (*J. Amer. Chem. Soc.*, 1911, **33**, 1538—1548).—By the action of xanthone on the products resulting from dibromobenzene and magnesium, p-*phenylenedixanthenol*, $\left(O<\substack{C_6H_4\\C_6H_4}>C\cdot OH\right)_2C_6H_4$, is formed in addition to *p*-bromophenylxanthenol (Gomberg and Cone, Abstr., 1909, i, 55; 1910, i, 869). This is the simplest member of a new series of xanthenols with two reactive nuclei ; with hydrochloric acid a coloured diacid chloride and a colourless normal dichloride are formed. The influence of the bridge oxygen is brought to light by a comparison with tetraphenyl-*p*-xylylene glycol, $OH\cdot CPh_2\cdot C_6H_4\cdot CPh_2\cdot OH$ (Thiele and Balhorn, Abstr., 1904, i, 491).

This glycol gives with hydrogen bromide in acetic acid solution a colourless bromide, which with metallic silver or copper yields a quinonoid orange-coloured hydrocarbon, tetraphenyl-*p*-xylylene, which is not at all an analogue of triphenylmethyl.

p-Phenylenedixanthenol gives with hydrogen chloride a coloured dihydrochloride, from which a colourless simple chloride can be prepared. Silver removes the chlorine from this chloride, forming an unsaturated hydrocarbon, which is a true isologue of triphenylmethyl. A colourless bromide could not be obtained.

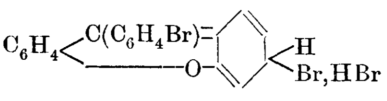
p-*Phenylenedixanthenol* forms colourless crystals, m. p. 176—177°. The *chloride-hydrochloride* is a bright red, crystalline powder; on heating a suspension in benzene, hydrogen chloride is evolved and a clear, colourless solution of the *chloride*, $C_6H_4\left(CCl<\substack{C_6H_4\\C_6H_4}>O\right)_2$, remains. This darkens at 210°, m. p. 259—260°. It forms a number of salts characterised by their great insolubility and high melting points. The *ferrichloride* forms orange-red crystals ; the *zincichloride* is somewhat darker in colour ; the *stannichloride* separates in finely divided orange crystals ; the *mercurichloride* gives dull red crystals ; the *perbromide* forms yellow crystals ; the *periodide* is a dark brown, nearly black, powder ; the *perchlorate* separates in fine reddish-yellow crystals, and the *hydrogen sulphate* is a crystalline powder.

p-*Phenylenediquinoxanthenol bromide hydrobromide* (annexed formula) is obtained in reddish-brown crystals; the *bromide* is a red solid, and has not been obtained in a colourless form.



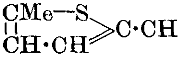
The following salts of *p*-bromophenylxanthenol are described: *ferrichloride*, orange-yellow needles, m. p. 218°; *zincichloride* double salt, large, shimmering, dark orange plates, m. p. 235°; *stannichloride*, dark yellow crystals, m. p. 185°; *mercurichloride*, light orange-yellow crystals, which turn bright yellow at 160°, soften at 250°, m. p. 257° to a dark liquid. The *perbromide* of the *chloride* forms fine glistening, light orange needles, m. p. 201—202°; the *periodide* appears in dark purple, shining needles, m. p. 188°. The *hydrogen sulphate* crystallises in large plates, which are brown in transmitted light, and have a green metallic lustre in reflected light, m. p. 77—78°.

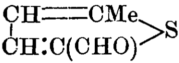
p-*Bromophenylquinoxanthenol bromide hydrobromide* (annexed formula), prepared by the addition of acetyl bromide to a solution of the xanthenol, forms very hygroscopic, dark orange-red crystals. It loses hydrogen bromide, forming p-*bromophenylxanthenol bromide*, $C_{19}H_{12}OBr_2$, which is colourless.



The *zincibromide* separates in bright red crystals, m. p. 250° to a dark red liquid; the *mercuribromide* yields yellow crystals, m. p. 247—248° to a dark red liquid. The *bromide perbromide* is obtained as orange crystals, m. p. 188°; the *bromide periodide* forms deep purple, lustrous crystals, m. p. 211—212° to a dark purple liquid.

E. F. A.

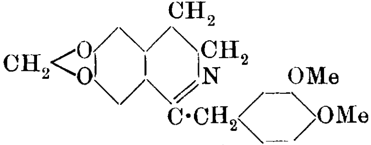
5-Methylthiophen-2-aldehyde. E. Grishkewitsch-Trochimowsky (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 803—806. Compare this vol., i, 481).—In ethereal solution, 2-iodo-5-methylthiophen readily reacts with magnesium, forming the corresponding iodomagnesium derivative, which, when treated with ethyl orthoformate, yields the *acetal*,  $\begin{matrix}CMe{-}S\\ CH{\cdot}CH\end{matrix}{>}C{\cdot}CH(OEt)_2$, as a colourless, viscous liquid with a pleasant fruity odour, b. p. 236·5—238°/747 mm., $D_4^{19·5}$ 1·0388, $n_D^{19·5}$ 1·48953.

5-*Methylthiophen-2-aldehyde*,  $\begin{matrix}CH{=\!=}CMe\\ CH{:}C(CHO)\end{matrix}{>}S$, obtained by hydrolysing the acetal with hydrochloric acid in a current of carbon dioxide, is a colourless, refractive liquid with an odour of bitter almonds, b. p. 218—219·5°/749 mm., D_4^{21} 1·1698, n_D^{21} 1·58166. Its *phenylhydrazone*, $C_{12}H_{12}N_2S$, forms faintly yellow needles, m. p. 116—117°.

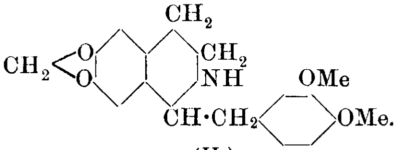
An ethereal solution of the aldehyde saturated with ammonia in the cold gradually deposits the *hydramide*, $(C_4H_2SMe{\cdot}CH{:})_3N_2$, in rosettes of colourless needles, m. p. 124·5—125·5°; the hydramide is decomposed into its components when gently heated with dilute mineral acid.

The action of carbon dioxide on the above iodo-magnesium complex gives 5-methylthiophen-2-carboxylic acid in almost quantitative yield. T. H. P.

Synthesis of Berberine. Amé Pictet and Alphonse Gams (*Compt. rend.*, 1911, **153**, 386—388; *Ber.*, 1911, **44**, 2480—2485. Compare this vol., i, 483).—The complete synthesis of berberine has now been accomplished in the following steps. Homopiperonylamine condenses with homoveratroyl chloride to give *homoveratroylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}C_6H_3(OMe)_2$, long needles, m. p. 136°. This loses $1H_2O$ when boiled with phosphoric oxide in xylene solution, and forms the unsaturated *compound*, m. p. 68—70° (I).



(I.)



(II.)

Reduction of this tertiary base with tin and hydrochloric acid leads to the formation of *veratrylnorhydrohydrastinine*, slender needles, m. p. 208—210° (II). A methylene group is introduced between the imino-group and the veratryl ring by condensing the product with methylal in presence of hydrochloric acid. The tetrahydroberberine so obtained is identical with that prepared by Perkin from natural berberine, and yields this substance when treated with oxidising agents. W. O. W.

The Alkaloids of the Toadstool and "Artificial" Muscarine. J. Honda (*Arch. expt. Path. Pharm.*, 1911, **65**, 454—466).—A method is described by which muscarine can be obtained from toadstools and freed from the choline also invariably present. In addition to these two substances, two other alkaloids were also isolated, and named α- and *β-myketosine*. The quantities obtained were too small for analysis.

The muscarine thus isolated has the same physiological action as "artificial" muscarine obtained by the oxidation of choline platinichloride. E. J. R.

Cyclic Ammonium Bases. Herman Decker and Adolf Kaufmann (*J. pr. Chem.*, 1911, [ii], **84**, 219—246).—The first part of this paper is mainly a review of previous work on the constitution of the ψ-ammonium bases. This is followed by a discussion of the subjects enumerated below.

(I) *Constitution of the Carbinol Bases.*—The author criticises the view that the ψ-ammonium bases have an aldehydic or ketonic structure. The formation of anhydrides of the carbinol bases observed by Kaufmann and Strübin (this vol., i, 321) furnishes no evidence in support of the aldehydic structure. Reference is made to the formation of symmetrical ethers of carbinol bases of other classes, and the preparation of the *anhydride* of 2-hydroxy-9-phenylxanthen-9-ol, $(C_{19}H_{13}O_2)O$, m. p. 246°, is described.

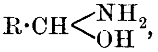
(II) *Constitution of the Cyanines.*—In this section the author discusses the constitution of the cyanine dyes, and explains the mechanism of the reactions by which they are formed.

(III) *The Negative Properties of the Nitrogen Atom in Aromatic Rings.*—The substitution processes occurring in heterocyclic rings are readily explicable on the assumption that the nitrogen atom exercises an orientating influence, similar to that of a strongly negative group, such as the nitro-group. The mobility of the atoms or groups in the 2- or 4-position of the pyridine ring is referred by the author to the same negative property of the nitrogen atom.

(IV) *Constitution of the* apo*Cyanines.*—The negative influence referred to in the preceding section is the factor which determines the formation of the *apo*cyanines. Owing to this negative property of the nitrogen atom, the hydrogen occupying the 2-position in the quinoline molecule is very reactive, and condensation, therefore, readily takes place in this position. Kaufmann and Strübin's (this vol., i, 328) assumption that 1 : 2-dihydroquinoline is an intermediate product in the formation of the *apo*cyanine dyes thus becomes unnecessary.

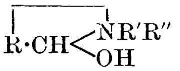
(V) *The Aldehydic Function of Carbinol Bases.*—In this section attention is drawn to the great similarity in the reactions of aldehydes and carbinol bases, and to the remarkable activity of the hydroxyl group.

(VI) *The Cause of the Aldehydic Function of Carbinol Bases.*—A comparison of the formulæ of the aldehyde-ammonias (I) and the ψ-ammonium bases (II) at once reveals the fact that these compounds are similarly constituted:



$R\cdot CH<^{NH_2}_{OH}$,

(I.)



$R\cdot CH<^{NR'R''}_{OH}$

(II.)

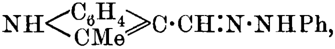
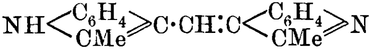
It is to this similarity of structure that the remarkable resemblance in the reactions of aldehydes and ψ-ammonium bases is due. F. B.

The Splitting of the Pyrrolidine Ring by Bacteria.

DANKWART ACKERMANN (*Zeitsch. Biol.*, 1911, **57**, 104—111).—*dl*-Proline, obtained by the hydrolysis of gelatin with baryta according to Fischer and Boehner's method, was acted on by a mixed culture of putrefaction bacteria in a culture solution containing Witte's peptone and dextrose. The solution was kept slightly alkaline. If the decomposition proceeded in the manner usual for amino-acids, pyrrolidine should be formed, but this substance could not be detected; instead, the ring was broken and δ-aminovaleric acid was formed by the addition of two atoms of hydrogen. Arginine is also decomposed by bacteria with formation of the same acid. E. J. R.

The Reactivity of the β-Unsubstituted Pyrrole Ring.

W. KÖNIG (*J. pr. Chem.*, 1911, [ii], **84**, 194—219).—The reactions of β-unsubstituted indole and pyrrole derivatives are compared with those of primary amines and of compounds containing a reactive methylene group. It is shown that there is a remarkable resemblance in the chemical behaviour of these three groups.

Guided by this similarity, the author attempted to prepare 2-methylindole-3-aldoxime by heating a methyl-alcoholic solution of 2-methylindole with mercury fulminate and hydrochloric acid, but obtained, instead of the aldoxime, the mercurichloride of a red dye, which proved to be identical with that prepared by Ellinger and Flamand (this vol., i, 329) from 2-methylindole-3-aldehyde and dilute sulphuric acid. From the analysis of numerous salts, and from quantitative experiments on the formation of the perchlorate and mercurichloride, as well as from many other considerations, the author conclusively proves that the dye base has the composition $C_{19}H_{16}N_2$, and not $C_{28}H_{23}N_3$, as stated by Ellinger and Flamand. When heated with phenylhydrazine, it yields 2-methylindole and *2-methylindole-3-aldehydephenylhydrazone*,  $\mathrm{NH}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CMe}\end{matrix}{>}\mathrm{C\cdot CH{:}N\cdot NHPh}$, which crystallises in lustrous, colourless needles, m. p. 201°. Both this reaction and the similar decomposition by hydrolysis into 2-methylindole and 2-methylindole-3-aldehyde are in agreement with the formula,  $\mathrm{NH}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CMe}\end{matrix}{>}\mathrm{C\cdot CH{:}C}{<}\begin{matrix}\mathrm{C_6H_4}\\ \mathrm{CMe}\end{matrix}{>}\mathrm{N}$, proposed by the author. The dyes are therefore derivatives of 3 indyl-3-indolidenemethane, and not of tri-indylmethane, as supposed by Ellinger and Flamand.

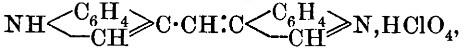
The *mercurichloride*, $C_{19}H_{17}N_2Cl,HgCl_2$, crystallises with one molecule of methyl alcohol in large, apparently rhombic plates with a green lustre, m. p. 197°; these lose their methyl alcohol at 120°, and are transformed into red needles having a violet lustre. The *mercuribromide*, prepared from 2-methylindole, mercury fulminate, and hydrobromic acid, forms brownish-red crystals, also containing one molecule of methyl alcohol, m. p. 193°.

Similar mercurihalides have been obtained from 2:5-dimethylindole and 2-phenyl-5-methylpyrrole.

2-Methylindole-3-aldoxime, $C_{10}H_{10}ON_2$, prepared by heating the aldehyde with hydroxylamine hydrochloride and pyridine, crystallises in long, colourless needles, m. p. 154°. When boiled with acids, it is slowly converted into the above-mentioned dye; the transformation takes place much more readily in the presence of mercuric chloride.

The salts of the dye are best prepared by the addition of a slight excess of the requisite acid to 2-methylindole-3-aldehyde dissolved in six to eight times its weight of alcohol. The *hydrochloride*, $C_{19}H_{16}N_2,HCl$, m. p. 248°; the *hydrobromide*, m. p. 218°; the *hydriodide*, m. p. 228—230°, and the *perchlorate*, $C_{19}H_{16}N_2,HClO_4$, m. p. 248° (decomp.), all crystallise in red or brownish-red needles containing one molecule of methyl alcohol; the sulphate, m. p. 215° with previous sintering, has the composition $C_{19}H_{16}N_2,H_2SO_4$ (compare Ellinger and Flamand, *loc. cit.*).

A general method for the preparation of the dyes of the 3-indyl-3-indolidenemethane series is described. Ethyl orthoformate (1 mol.) and indole or its derivatives (2 mols.) are dissolved in the smallest possible quantity of alcohol and treated with the calculated amount of the acid, the salt of which is required. The following compounds were prepared in this manner: the *perchlorate* of the dye from indole (3-indyl-3-indolidenemethane),



$$NH<\overset{C_6H_4}{\underset{CH}{}}>C\cdot CH:C<\overset{C_6H_4}{\underset{CH}{}}>N,HClO_4,$$

crystallising in ruby-red needles with a green lustre, m. p. 276°; the corresponding sulphate (compare Ellinger and Flamand, Abstr., 1909, i, 846), and the *perchlorate*, $C_{21}H_{20}N_2,HClO_4$, from 2:5-dimethylindole; the latter compound crystallises with one molecule of alcohol in long, bright red needles, which lose their alcohol at 120°, and have m. p. 245°.

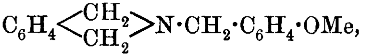
Similar salts have been prepared from 1-alkylindoles, 2-phenyl-5-methylpyrrole, and 3-methylindole.

The dyes of this series are also obtained in small yield by the action of hydrocyanic acid and hydrogen chloride on indole and its derivatives in the presence of aluminium chloride. F. B.

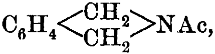
p-Hydroxybenzylamine. MARC TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 819—824. Compare this vol., i, 778).—The author has undertaken the investigation of this phenolic base and of certain of its homologues in view of their close connexion with hordenine, and analogous substances, of marked physiological activity (compare Barger, Trans., 1909, **95**, 1123, 2193, and Barger and Walpole, *ibid.*, p. 1720).

p-Hydroxybenzylamine, prepared from anisylamine by the action of hydriodic acid, was used in the form of the *hydrochloride*, m. p. 195°; the *hydriodide* melts at 198—200°.

2-p-*Methoxybenzyl*-1 : 3-*dihydro*iso*indole*,



$$C_6H_4<\overset{CH_2}{\underset{CH_2}{}}>N\cdot CH_2\cdot C_6H_4\cdot OMe,$$

m. p. 83°, obtained by von Braun's method (Abstr., 1910, i, 506) from *o*-xylylene bromide and anisylamine, crystallises in needles, and is very soluble in alcohol; the *hydrobromide*, m. p. 234°, crystallises in spangles, and the *methiodide* has m. p. 183°. When boiled with acetic anhydride, anisyl acetate and 2-*acetyl*-1 : 3-*dihydro*iso*indole*,  $C_6H_4<\overset{CH_2}{\underset{CH_2}{}}>NAc$, m. p. 77°, b. p. 180—200°/15 mm., are formed. The latter crystallises in needles from boiling light petroleum. T. A. H.

Hydrazones. ROBERTO CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 803—807. Compare Abstr., 1910, i, 196).—The *p*-nitrophenylhydrazones of benzaldehyde, and *o*-, *m*-, and *p*-nitrobenzaldehyde exhibit chromoisomerism similar to that previously discussed. The *p*-nitrophenylhydrazone of anisaldehyde, however, was not obtained in two modifications. Benzaldehyde-*p*-nitrophenylhydrazone (compare Hyde, Abstr., 1899, i, 688) when recrystallised from alcohol forms orange needles, m. p. 195—196°. When precipitated from warm alcohol with water, it is transformed into yellow scales, m. p. 195°. If, however, the precipitation is effected in the cold, a red form is obtained in needles or scales, which become yellow at 140° and melt at 194°. The yellow variety can be transformed into the other by recrystallisation from formamide, from which solvent only the red form is deposited. The red and yellow modifications thus appear to be distinct, whilst the orange-coloured products, which can be prepared by the action of various solvents, represent one or more mixtures, combinations, or solid solutions of these two.

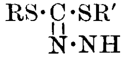
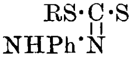
o-Nitrobenzaldehyde-*p*-nitrophenylhydrazone when recrystallised from glacial acetic acid forms orange-red needles, which become red at 190°, and melt at 250—251°. By precipitation with water from alcohol, it is converted into an orange-yellow modification, m. p. 250—251°.

m-Nitrobenzaldehyde-*p*-nitrophenylhydrazone (Hyde, *loc. cit.*) crystallises from acetic acid in orange-red crystals, m. p. 250—251°, which, by precipitation with water from alcohol, are converted into the yellow form, m. p. 248°. This form when heated to 130° acquires an increasing red tint, but regains its original colour on cooling (thermochromism).

p-Nitrobenzaldehyde-*p*-nitrophenylhydrazone (Hyde, *loc. cit.*) crystallises from glacial acetic acid in brick-red scales, m. p. 247°. From alcohol an orange-yellow form, m. p. 245°, is obtained.

Anisaldehyde-p-*nitrophenylhydrazone* forms small, reddish-violet needles, m. p. 160°; only one modification could be isolated, but the addition of water to its solution in acetone gives a yellow precipitate which becomes red immediately. R. V. S.

Isomeric Hydrazones of Dithiocarbonic Esters. MAX BUSCH and HERMANN KRAPF (*J. pr. Chem.*, 1911, [ii], 84, 293—304).

—It has been shown previously (Abstr., 1901, i, 430) that the phenylhydrazones of unsymmetrical esters of dithiocarbonic acid exist in two stereoisomeric forms,  $\begin{array}{l}\mathrm{RS{\cdot}C{\cdot}SR'}\\ \quad\ \|\\ \quad\mathrm{N{\cdot}NHPh}\end{array}$ and  $\begin{array}{r}\mathrm{RS{\cdot}C{\cdot}SR'}\\ \|\quad\ \ \\ \mathrm{NHPh{\cdot}N}\quad\ \ \end{array}$, which appear to be equally stable. In extending the investigation to the *p*-tolylhydrazones and *p*-bromophenylhydrazones, the authors have met with a marked difference in the stability of the isomerides. Thus, of the isomeric *p*-tolylhydrazones of methyl *p*-nitrobenzyl dithiocarbonate, the more fusible modification is the less stable form, and is completely transformed at 100° into the less fusible, stable isomeride.

The isomeric hydrazones described below were prepared by successively introducing two different groups into *p*-tolyldithiocarbazinic acid or *p*-bromophenyldithiocarbazinic acid by the action of alkyl or aryl halides on the potassium salts of the acids, or of their esters in aqueous alcoholic solution, at the ordinary temperature, the different modifications being produced by varying the order of introduction of the groups R′ and R″:

$$\mathrm{NHR{\cdot}NH{\cdot}CS_2H \longrightarrow NHR{\cdot}NH{\cdot}CS_2R' \longrightarrow NHR{\cdot}N{:}C(SR'){\cdot}SR''}.$$

The isomerides are distinguished by naming the two groups in the order in which they are introduced. It is assumed that the group first introduced and the hydrazine residue occupy the *anti*-positions.

The *phenylhydrazone* of *benzyl* o-*nitrobenzyl dithiocarbonate*, $\mathrm{C_7H_7{\cdot}S{\cdot}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2){:}N{\cdot}NHPh}$, prepared from *o*-nitrobenzyl chloride and benzyl phenyldithiocarbazinate, crystallises in clusters of red needles, m. p. 67°. The isomeric o-*nitrobenzyl benzyl dithiothio-*

carbonate phenylhydrazone, prepared from benzyl chloride and *o*-nitrobenzyl phenyldithiocarbazinate, forms lustrous, light red columns, m. p. 88°. Both forms have the same solubility, and, when heated separately at 100°, are converted into a mixture consisting of the two isomerides in equal proportions.

The interaction of *p*-nitrobenzyl chloride and potassium *p*-tolyldithiocarbazinate yields p-*nitrobenzyl* p-*tolyldithiocarbazinate*,

$$C_7H_7{\cdot}NH{\cdot}NH{\cdot}CS_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

which crystallises in stout, yellow needles, m. p. 127°, together with the p-*tolylhydrazone* of *di*-p-*nitrobenzyl dithiocarbonate*,

$$C_7H_7{\cdot}NH{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2\ ;$$

the latter compound forms lustrous, red, pointed needles, m. p. 116°

o-*Nitrobenzyl* p-*tolyldithiocarbonate*, prepared in a similar manner to the preceding *p*-nitro-compound, crystallises in yellow needles, m. p. 147°, which become green when kept. It is accompanied by *di*-o-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*, crystallising in very slender, felted, golden-yellow needles, m. p. 134°.

Methyl p-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*,

$$SMe{\cdot}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2){:}N{\cdot}NH{\cdot}C_7H_7,$$

prepared from methyl *p*-tolyldithiocarbazinate and *p*-nitrobenzyl chloride, forms lustrous, garnet-red, pointed needles, m. p. 115°; the isomeric p-*nitrobenzyl methyl dithiocarbonate* p-*tolylhydrazone*, prepared by methylating *p*-nitrobenzyl *p*-tolyldithiocarbazinate, crystallises in tufts of glassy, golden-yellow needles, m. p. 57°. The former isomeride is the stable form, and remains unchanged when heated above its m. p.

Ethyl p-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*, $C_{17}H_{19}O_2N_3S_2$, crystallises in lustrous, red leaflets, m. p. 70°; the *isomeride* is a red oil.

The p-*tolylhydrazone* of *benzyl* p-*nitrobenzyl dithiocarbonate*,

$$NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}S{\cdot}C(S{\cdot}C_7H_7){:}N{\cdot}NH{\cdot}C_7H_7,$$

prepared from *p*-nitrobenzyl chloride and benzyl *p*-tolyldithiocarbazinate, is identical with the hydrazone obtained by the interaction of benzyl chloride and *p*-nitrobenzyl *p*-tolyldithiocarbazinate; it crystallises in tufts of red needles or garnet-red, quadrilateral plates, m. p. 119°.

o-*Nitrobenzyl* p-*nitrobenzyl dithiocarbonate* p-*tolylhydrazone*,

$$C_7H_7{\cdot}NH{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2,$$

forms slender, orange needles, m. p. 124°; the *isomeride*, light red columns, m. p. 80°.

p-*Nitrobenzyl* p-*bromophenyldithiocarbazinate*,

$$C_6H_4Br{\cdot}NH{\cdot}NH{\cdot}CS_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

crystallises in long, transparent, light yellow needles, m. p. 135—136°; it is obtained together with the p-*bromophenylhydrazone* of *di*-p-*nitrobenzyl dithiocarbonate*, $C_6H_4Br{\cdot}NH{\cdot}N{:}C(S{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$, which forms lustrous, red needles, m. p. 132°, by the interaction of *p*-nitrobenzyl chloride and potassium *p*-bromophenyldithiocarbazinate.

o-*Nitrobenzyl* p-*bromophenyldithiocarbazinate*, prepared in a similar manner, crystallises in slender, white needles, m. p. 156—157°; the accompanying *di*-o-*nitrobenzyl dithiocarbonate* p-*bromophenylhydrazone* forms slender, felted, light red needles, m. p. 119°.

The p-*bromophenylhydrazone* of *methyl* p-*nitrobenzyl dithiocarbonate*, $NO_2\cdot C_6H_4\cdot CH_2\cdot S\cdot C(SMe)\colon N\cdot NH\cdot C_6H_4Br$, could only be obtained in one form; it crystallises in slender, monoclinic prisms, capped with clinodomes or pyramids, and has m. p. 119° or 120—121°, according to the method of preparation.

o-*Nitrobenzyl* p-*nitrobenzyl dithiocarbonate* p-*bromophenylhydrazone*, $C_{21}H_{17}O_4N_4BrS_2$, crystallises in clusters of small, stout, golden-yellow needles, m. p. 113—114°; the *isomeride* forms felted, orange-red needles, m. p. 107°. When fused for some time, each modification yields a mixture of the two isomerides in approximately equal proportions.

The *benzoylphenylhydrazone* of *methyl ethyl dithiocarbonate*,

$$SMe\cdot C(SEt)\colon N\cdot NPhBz,$$

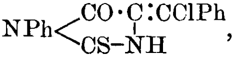
prepared from methyl benzoylphenyldithiocarbazinate and ethyl iodide, crystallises from alcohol in colourless, transparent columns, m. p. 93°, and from light petroleum in pointed needles, m. p. 94°. The isomeric *ethyl methyl dithiocarbonate benzoylphenylhydrazone*, obtained from ethyl benzoylphenyldithiocarbazinate and methyl iodide, separates from alcohol in stout, white needles, m. p. 83—84°, and from light petroleum in hard needles of a diamond lustre, m. p. 85—86°.

F. B.

Hydantoins. IV. Reduction of Aldehyde Condensation Products of 2-Thio-1-phenylhydantoin. TREAT B. JOHNSON and CHARLES A. BRAUTLECHT (*J. Amer. Chem. Soc.*, 1911, **33**, 1531—1538). —Wheeler and Hoffmann (this vol., i, 498) have shown that on condensation of hydantoin with aldehydes, unsaturated compounds are formed, which when warmed with hydriodic acid are reduced at the double bond and transformed quantitatively into alkyl-hydantoins. These are hydrolysed by acids or alkalis to the corresponding α-amino-acids.

2-Thio-1-phenylhydantoin likewise condenses with aldehydes, but its derivatives are not reduced at the double bond by hydriodic acid. Zinc dust and acetic acid, or ammoniacal ferrous sulphate, were also ineffective, but sodium amalgam effected a quantitative transformation into the alkylthiohydantoins. These compounds could not be hydrolysed by sodium or barium hydroxides to α-amino-acids.

2-Thio-1-phenyl-4-benzylidenehydantoin is attacked by chlorine and bromine in glacial acetic acid solution. 2-*Thio*-1-*phenyl*-4-α-*chlorobenzylidenehydantoin*,

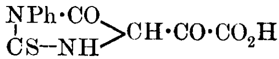


$$NPh<\begin{matrix}CO\cdot C\colon CClPh\\ \vert\\ CS-NH\end{matrix}$$

, crystallises in colourless prisms, m. p. 236—237°. The corresponding α-*bromobenzylidene* compound separates in yellow plates, m. p. 211°.

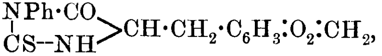
On reduction of 2-thio-1-phenyl-4-benzylidenehydantoin with sodium amalgam, the same 2-thio-1-phenyl-4-benzylhydantoin is obtained as is obtained by the interaction of phenylthiocarbamide and phenylalanine (Brautlecht).

On alkylation of this with ethyl bromide in presence of sodium ethoxide, 2-*ethylthiol*-1-*phenyl*-4-*benzylhydantoin* is formed as an oil, which when digested with hydrochloric acid is converted into 1-phenyl-4-benzylhydantoin.

2-*Thio*-1-*phenylhydantoin*-4-*glyoxylic acid*, 
$\genfrac{}{}{0pt}{}{NPh\cdot CO}{CS{-}NH}\!\!>CH\cdot CO\cdot CO_2H$, prepared by the interaction of ethyl oxalate and 2-thio-1-phenylhydantoin, crystallises in pale yellow needles, m. p. 240° (decomp.).

2-*Thio*-1-*phenyl*-4-p-*methoxybenzylhydantoin* crystallises in slender, colourless prisms, m. p. 171°.

2-*Thio*-1-*phenyl*-4-*piperonylhydantoin*,



$$\genfrac{}{}{0pt}{}{NPh\cdot CO}{CS{-}NH}\!\!>CH\cdot CH_2\cdot C_6H_3\colon O_2\colon CH_2,$$

is obtained in straw-coloured needles, m. p. 172—173°. E. F. A.

Compound of Antipyrine with Ferric Chloride, obtained with Ferrous Chloride.

Charles Astre and J. Vidal (*Bull. Soc. chim.*, 1911, [iv], 9, 836—839. Compare this vol., i, 399).—A solution of ferrous chloride to which antipyrine dissolved in hydrochloric acid has been added develops a gooseberry-red coloration, and on evaporation and treatment of the syrupy residue with ether, deposits yellowish-green crystals of a *substance* having the formula

$$(C_{11}H_{12}ON_2)_9,FeCl_3,9HCl.$$

This becomes pasty at 121—122°, and dissolves in water, forming a gooseberry-red solution, which becomes yellowish-green on addition of an acid, or enough alkali to neutralise it. The solution gives the usual reactions of ferric iron, antipyrine, and chlorides. The ferric iron is reduced to the ferrous state by sodium nitrite, hydrogen sulphide, or sulphur dioxide, but not by zinc and acetic acid. The compound is quite distinct from that with ferric chloride, called ferripyrine, described by Schuyten (Abstr., 1896, i, 575).

T. A. H.

Formation of 1-Nitroso-5-methyl-3-pyrazolidone from Crotonoylhydrazide.

Ernst Muckermann (*J. pr. Chem.*, 1911, [ii], 84, 278—292. Compare this vol., i, 682).—*Crotonoylhydrazide*, $CHMe\colon CH\cdot CO\cdot NH\cdot NH_2$, is obtained as a viscid liquid by the interaction of ethyl crotonate and hydrazine hydrate in alcoholic solution. It possesses the usual reducing properties, and forms a *hydrochloride*, crystallising in snow-white needles, m. p. 173° (decomp.). When treated with benzaldehyde it yields a *benzylidene* derivative,

$$CHMe\colon CH\cdot CO\cdot NH\cdot N\colon CHPh,$$

m. p. 72°; the o-*hydroxybenzylidene* derivative, $C_{11}H_{12}O_2N_2$, has m. p. 190°; the p-*methoxybenzylidene* derivative, $C_{12}H_{14}O_2N_2$, crystallises in yellowish-white needles, m. p. 99°.

Crotonoylsemicarbazide, $CHMe\colon CH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$, prepared by the interaction of crotonoylhydrazide hydrochloride and potassium cyanate in aqueous solution, crystallises in stout prisms, m. p. 171°.

When treated with sodium nitrite, the hydrazide hydrochloride is converted into 1-*nitroso*-5-*methyl*-3-*pyrazolidone*. This crystallises in lustrous, white leaflets, m. p. 131°, and gives a cherry-red coloration with ferric chloride; the *ammonium* salt, $C_4H_{10}O_2N_4,1\frac{1}{2}H_2O$, forms radiating needles, m. p. 144° (decomp.); the *silver* salt, $C_4H_6O_2N_3Ag$, long, lustrous, silky needles, m. p. 148—149° (decomp.); the *copper* salt, $Cu(C_4H_6O_2N_3)_2,2H_2O$, stout, dark blue, monoclinic prisms

[$a:b:c = 1\cdot23:1:0\cdot85$; $\beta = 101°30'$] (Beder). The ammonium salt forms with picric acid a *compound*, $C_4H_{10}O_2N_4,C_6H_3O_7N_3$, which crystallises with one molecule of ethyl alcohol in lustrous, golden-yellow, monoclinic columns, m. p. 162—164°.

1-*Nitroso*-5-*methyl*-2-*ethyl*-3-*pyrazolidone*, $C_6H_{11}O_2N_3$, obtained by the action of ethyl iodide on the above-mentioned silver salt, separates from ether in colourless, monoclinic plates, m. p. 83°.

When 1-nitroso-5-methyl-3-pyrazolidone is treated with bromine in glacial acetic acid solution below 10°, it yields 4-*bromo*-3-*methyl*-5-*pyrazolone*, $C_4H_5ON_2Br$, which crystallises in colourless, hexagonal platelets, m. p. 182°, and may also be obtained by brominating 3-methylpyrazolone (Curtius and Jay, Abstr., 1889, 393). The interaction of 1-nitroso-5-methyl-3-pyrazolidone and excess of bromine in glacial acetic acid solution yields 4 : 4-*dibromo*-3-*methyl*-5-*pyrazolone*, $C_4H_4ON_2Br_2$. This crystallises in short, monoclinic columns, m. p. 132°, and may also be prepared by brominating 3-methylpyrazolone (compare Rothenburg, Abstr., 1895, i, 686). The compound described by Rothenburg as 4 : 4-dibromo-3-methylpyrazolone of m. p. 182° is probably identical with the above-mentioned 4-bromo-3-methylpyrazolone. F. B.

Hydroxyindazoles. V. Constitution. PAUL FREUNDLER (*Bull. Soc. chim.*, 1911, [iv], **9**, 778—784. Compare this vol., i, 577, 753).—Further proof is given of the constitution of the chlorinated hydroxyindazoles obtained from substituted benzeneazo-*o*-benzoic acids. The presence of an indazole nucleus is shown by the fact that 5 : 7-dichloro-3-hydroxy-2-phenylindazole yields, on treatment with phosphorus pentachloride in the presence of phosphoryl chloride, 3 : 5 : 7-*trichloro*-2-*phenylindazole*, needles, m. p. 172·5°. This substance can also be obtained by direct chlorination of 2-phenylindazole of known constitution.

The position of the hydroxyl group is shown in that on oxidation of the hydroxyindazole by moderate oxidising agents it is transformed into 2-*benzeneazo*-3 : 5-*dichlorobenzoic acid*, $N_2Ph\cdot C_6H_2Cl_2\cdot CO_2H$, red prisms, m. p. 142·5—143°, which is also obtained by the oxidation of the above-mentioned trichloro-compound. On reduction, it yields aniline and 3 : 5-dichloroanthranilic acid, thus proving the position of the chlorine atoms.

Further, the hydroxyindazole yields a *benzoyl* derivative, long needles, m. p. 203·5—204°, and a *methyl ether*, tabular prisms, m. p. 144—144·5°. W. G.

Crystallographical Examination of Inactive Ornithine Monopicrate. P. REINER (*Zeitsch. physiol. Chem.*, 1911, **73**, 192—193).—The triclinic crystals of *dl*-ornithine monopicrate, m. p. 170° (compare Kossel and Weiss, Abstr., 1910, ii, 909), have $a:b:c = 0\cdot6962:1:0\cdot6301$; $\alpha = 93°10'$, $\beta = 100°55'$, $\gamma = 81°19'$. E. F. A.

Extractives of Muscles. XII. Constitution of Carnosine. WLADIMIR VON GULEWITSCH (*Zeitsch. physiol. Chem.*, 1911, **73**, 434—446. Compare Skwarzoff, Abstr., 1910, ii, 879).—The author has suggested (Abstr., 1907, i, 337) that the products of hydrolysis of carnosine by barium hydroxide are histidine and a substance $C_3H_7O_2N$, probably alanine.

It is now established that three-quarters of the carnosine-nitrogen belong to histidine and the rest to a substance which is not *dl*-α-alanine, but is proved to be β-alanine, m. p. 230—232°. Carnosine is accordingly β-alanylhistidine or histidyl-β-alanine, and may have been derived from asparagylhistidine or histidyl-lysine by the loss of an amino-group and elimination of a carbon atom, so that the β-alanyl residue is formed. E. F. A.

***N*-Amino-heterocyclic Compounds. III. Properties of α-Acylhydrazines, 1-Amino-2 : 5-diphenyl-1 : 3 : 4-triazole, and 1-Amino-2 : 5-dibenzyl-1 : 3 : 4-triazole.** HARTWIG FRANZEN and F. KRAFT (*J. pr. Chem.*, 1911, [ii], **84**, 122—139. Compare Franzen and Scheuermann, Abstr., 1908, i, 293).—The reactions previously described (*loc. cit.*) as characteristic of *as.-sec.*-hydrazines are also given by α-acylhydrazines, with the exception of the reaction with pyruvic acid. When α-acetyl- or α-benzoyl-phenylhydrazine is boiled with alcohol and precipitated mercuric oxide, the latter rapidly turns black, and dark-coloured oily products are obtained when the alcoholic solutions are evaporated. It has not been settled whether tetrazones are formed as intermediate products. α-Acetylphenylhydrazine forms a quaternary nitrogen derivative, namely, the *ethiodide*,

$$NH_2\cdot NEtPhAcI,$$

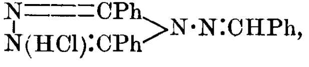
when heated with ethyl iodide at 100° for several hours; this crystallises from alcohol, and has m. p. 201°. α-Benzoylphenylhydrazine under similar conditions gives tarry products.

1-Amino-2 : 5-diphenyl-1 : 3 : 4-triazole (Pinner, Abstr., 1894, i, 386) and 1-amino-2 : 5-dibenzyl-1 : 3 : 4-triazole (Pinner, Abstr., 1897, i, 640) have been examined as further examples of *N*-amino-heterocyclic compounds. Their behaviour resembles that of similar compounds already studied (Abstr., 1906, i, 706; 1908, *loc. cit.*). They are not affected when boiled with alcohol and mercuric oxide, and do not condense with acetophenone, acetone, or pyruvic acid. The diphenyl derivative reacts slowly with aldehydes, for example, with benzaldehyde, it yields the benzylidene derivative, $C_2Ph_2N_3\cdot N\colon CHPh$, which forms salts with most acids.

Tertiary hydrazines can be obtained by reducing the condensation products of aromatic aldehydes and alcohol with *as.-sec.*-hydrazines by means of sodium amalgam; phenylbenzylbenzylidenehydrazine yields α-phenyl-αβ-dibenzylhydrazine, and dibenzylbenzylidenehydrazine yields tribenzylhydrazine. The condensation products of 1-amino-2 : 5-diphenyltriazole with aldehydes can be reduced in a similar manner.

The best yields of 1-amino-2 : 5-diphenyl-1 : 3 : 4-triazole are obtained by the action of an alcoholic solution of hydrogen chloride on diphenyldihydrotetrazine. Its *picrate*, $C_{20}H_{15}O_7N_7$, separates from alcohol in brilliant yellow crystals, m. p. 154°.

The *hydrochloride* of the benzylidene derivative,



$$\begin{array}{l} N{=\!=\!=}CPh \\ | \\ N(HCl){:}CPh \end{array}\!\!>\!N\cdot N{:}CHPh,$$

has m. p. 175° ; it cannot be recrystallised, as it readily loses hydrogen chloride. The *sulphate*, $2C_{12}H_{16}N_4,H_2SO_4$, has m. p. 178° ; the *nitrate*, m. p. 166° ; the *picrate*, $C_{27}H_{19}O_7N_7$, crystallises from alcohol in slender, yellow needles, m. p. 169° ; the *platinichloride* forms an orange-coloured precipitate, m. p. 231°.

aβ-Dibenzyl-a-phenylhydrazine hydrochloride,
$CH_2Ph\cdot NPh\cdot NH\cdot CH_2Ph,HCl$,
crystallises from alcohol, and has m. p. 186° ; the corresponding *base*, $C_{20}H_{20}N_2$, solidifies slowly, crystallises from ether, has m. p. 42°, and decomposes on exposure to the air, giving an odour of benzaldehyde. When boiled with alcohol and mercuric oxide, it is oxidised to phenylbenzylbenzylidenehydrazone, and the same product appears to be formed by the action of dilute nitric acid or of picric acid on the base.

β-Benzoyl-a-phenyl-aβ-dibenzylhydrazine, $CHPh\cdot NPh\cdot NBz\cdot CH_2Ph$, crystallises from alcohol, in which it is readily soluble, and has m. p. 107° ; the corresponding *acetyl* derivative, $C_{22}H_{22}ON_2$, obtained by boiling the hydrochloride of the base with acetic anhydride, has m. p. 78°.

a-Phenyl-aβ-dibenzylhydrazine hydrochloride does not react with potassium cyanate ; when boiled for several hours with 20% hydrochloric acid, it yields benzyl chloride and phenylhydrazine.

Tribenzylhydrazine hydrochloride, $CH_2Ph\cdot NH\cdot N(CH_2Ph)_2,HCl$, obtained by reducing the corresponding benzylidene derivative, or by the action of benzyl chloride on hydrazine hydrate, crystallises from alcohol in compact needles, m. p. 181°. When boiled for fifty-six hours with 20% hydrochloric acid, it yields benzyl chloride and hydrazine hydrochloride.

The product obtained by reducing 1-benzylideneamino-2 : 5-diphenyl-1 : 3 : 4-triazole with sodium amalgam and alcohol is diphenyltriazole (Pinner, *loc. cit.*), the *hydrochloride* of which has m. p. 203°.

The following generalisations with regard to the decomposition of tertiary hydrazines by boiling hydrochloric acid are given : (1) When the substituents are aryl groups, the hydrazine undergoes a benzidine rearrangement if such be possible. Quaternary hydrazines can, in addition, undergo fission at the $\equiv N\cdot N\equiv$ union. (2) When the substituents are partly aromatic and partly aliphatic, several reactions are possible. As a rule, the hydrazine with cold hydrochloric acid is transformed into a primary hydrazine and a hydrazone of the hydrazine. When two aliphatic and one aromatic groups are present, heating with 20% hydrochloric acid leads to the formation of the primary aromatic hydrazine and an alkyl chloride (2 mols.). Quaternary hydrazines with two aromatic and two aliphatic substituents undergo fission at the nitrogen linking. (3) Aliphatic hydrazines, as a rule, yield hydrazine and alkyl chlorides. The decomposition of *as.-sec.*-aliphatic hydrazines and of quaternary aliphatic hydrazines has not been studied. J. J. S.

Structure of the Azoxy-compounds. ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 896—900).—*p*-Nitroazoxybenzene prepared by Zinin's method (*Annalen*, 1860, **114**, 218) has m. p. 152° (Zinin : 153°). p-*Nitroazobenzene*, prepared from nitrosobenzene and *p*-nitroaniline, forms red laminæ, m. p. 135°. Oxidation of this substance with hydrogen peroxide in solution in glacial acetic acid yields a compound, m. p. 148°, which also differs in colour and solubilities from the *p*-nitroazoxybenzene of Zinin. It is suggested that the two substances are isomerides having the formulæ $Ph{\cdot}NO{:}N{\cdot}C_6H_4{\cdot}NO_2$ and $Ph{\cdot}N{:}NO{\cdot}C_6H_4{\cdot}NO_2$ respectively.

R. V. S.

New Synthesis of *o*-Hydroxyazobenzene. N. N. Voroschtsoff (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 787—791).

—Although *p*-nitrophenol and *p*-aminophenol do not combine with diazo-salts, *p*-acetylaminophenol readily yields *m*-acetylamino-*o*-hydroxyazobenzene. When treated with concentrated hydrochloric acid, the latter easily loses the elements of acetic acid, yielding *m*-amino-*o*-hydroxyazobenzene hydrochloride. On diazotising this with amyl nitrite in glacial acetic acid solution (compare Hantzsch and Jochem, Abstr., 1902, i, 62), a solid diazo-compound is obtained, which, on treatment with boiling alcohol, gives *o*-hydroxyazobenzene in more than 50% yield (calculated on the aminohydroxyazobenzene hydrochloride). This method of preparing *o*-hydroxyazobenzene hence gives much better results than that of Bamberger (Abstr., 1900, i, 531).

m-*Acetylamino*-o-*hydroxyazobenzene*, $NHAc{\cdot}C_6H_3(OH){\cdot}N_2Ph$, crystallises from acetic acid in long, straw-yellow needles, m. p. 226°.

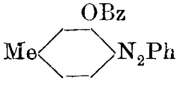
T. H. P.

Action of Substituted Hydrazines on β-Orthotoluquinone. William McPherson and Cecil Boord (*J. Amer. Chem. Soc.*, 1911, 33, 1525—1531).

—In the case of the reaction between *o*-benzoquinone and *as*-acylphenylhydrazines a migration of the acyl group takes place (compare McPherson and Lucas, Abstr., 1909, i, 193), and the conclusion is drawn that the acyl derivatives of the *o*-hydroxyazo-compounds, like those of the *p*-series, have the acyl group attached to oxygen, and are therefore represented by the formula $NPh{:}N{\cdot}R{\cdot}OAcyl$.

3 : 4-Toluquinone is more readily prepared and more stable than *o*-benzoquinone; it reacts with *as*-benzoylphenylhydrazine, forming 4-benzeneazo-*m*-tolyl benzoate. When saponified it yields 4-benzeneazo-*m*-cresol isomeric with the corresponding *p*-cresol described by Nölting and Kohn (Abstr., 1884, 900). The compound undergoes no change when dissolved in ether containing a small amount of fused potassium hydroxide and heated for some hours, a fact which makes it extremely probable that the acyl group is joined to oxygen.

3 : 4-*Toluquinone* is a reddish-brown solid, non-volatile, and odourless; it crystallises in clusters of needles, m. p. 70—75° (decomp.). 4-*Benzeneazo*-m-*tolyl benzoate* (annexed formula) forms orange-yellow needles, m. p. 98°. When saponified with concentrated sulphuric acid, 4-*benzeneazo*-m-*cresol* is obtained in thin, red plates, m. p. 122°.



4-*Tolueneazo*-m-*tolyl benzoate* separates in light orange-coloured needles, m. p. 93°.

4-*Tolueneazo*-m-*cresol* crystallises in thin, lathe-shaped, orange-red crystals, m. p. 148°.

E. F. A.

Bisulphite Compounds of Hydroxyazo-colouring Matters. N. N. Voroschtsoff (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 771—786).—The author has investigated the structure of the compounds formed by sodium hydrogen sulphite with the following hydroxyazo-colouring matters: beneneazo-*p*- and -*o*-cresols and benzeneazo-*α*- and -*β*-naphthols. It is found that all hydroxyazo-compounds do not react in the ordinary manner with sodium hydrogen sulphite; thus, *p*- and *o*-hydroxyazobenzenes and benzeneazo-*o*- and -*p*-cresols undergo no change on prolonged boiling with aqueous-alcoholic sodium hydrogen sulphite solution, whereas the azo-derivatives of *α*- and *β*-naphthol readily react under these conditions, giving crystalline compounds soluble in water. The acetyl derivatives of the two azonaphthols also react with sodium hydrogen sulphite, the compounds obtained yielding, on decomposition with cold dilute ammonia or sodium hydroxide solution, the same hydroxyazo-compounds as are given under similar conditions by the sodium hydrogen sulphite compounds of the non-acetylated azonaphthols; the acetyl groups evidently undergo hydrolysis during the reaction with the sulphite.

The readiness with which these sulphite compounds are decomposed by even dilute alkalis, taken in conjunction with the fact that hydrazobenzene-*N*-sulphonic acid (compare Bucherer and Donnenburg, Abstr., 1910, i, 144) gives azobenzene only when heated with sodium hydroxide, is not in agreement with Spiegel's view (Abstr., 1885, 987) that these compounds are hydrazo-*N*-sulphonic derivatives. Then, too, aminoazo-compounds react with sodium hydrogen sulphite, giving products identical with those formed by the corresponding hydroxyazo-compounds; thus, treatment with sodium hydrogen sulphite and subsequently with ammonia affords a simple means for the quantitative conversion of the aminoazo- to the hydroxyazo-compounds of the naphthalene series.

The author regards the compounds formed by sodium hydrogen sulphite with the hydroxyazophenols of the naphthalene series as salts of sulphurous esters, those formed by the benzeneazonaphthols, for example, having the structure: $NPh:N\cdot C_{10}H_6\cdot O\cdot SO_2Na$.

Although the phenols of the naphthalene series can be readily converted into the corresponding amino-compounds by being heated under pressure with ammonia and ammonium sulphite, thus: $R\cdot OH \longrightarrow R\cdot O\cdot SO_2\cdot NH_4 \longrightarrow R\cdot NH_2$, benzeneazo-*α*-naphthol does not undergo a similar change, the chief product formed under the conditions named being *αα*-dinaphthylamine-bis-azobenzene,

$$NPh:N\cdot C_{10}H_6\cdot NH\cdot C_{10}H_6\cdot N:NPh.$$

Sodium benzeneazo-α-naphthyl sulphite, $NPh:N\cdot C_{10}H_6\cdot O\cdot SO_2Na$, forms dark yellow needles, and is stable towards cold dilute acids. The corresponding *barium* salt, $C_{32}H_{22}O_6N_4S_2Ba$, forms microscopic, yellow prisms. The yellowish-green copper salt gradually turns brown, free benzeneazo-*α*-naphthol being developed. The same sodium salt is also obtained from benzeneazo-*α*-naphthylamine and sodium hydrogen sulphite.

Sodium benzeneazo-β-naphthyl sulphite forms shining, golden-yellow needles. The *barium* salt is yellow, and the characteristic *copper* salt, $C_{32}H_{22}O_6N_4S_2Cu$, forms shining, dark yellow, hexagonal plates.

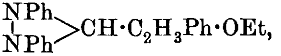
When benzeneazo-β-naphthol is heated with ammonia and ammonium sulphite in a sealed tube at 150—160°, the sulphite compound formed undergoes quantitative conversion into benzeneazo-β-naphthol. At temperatures exceeding 200°, new basic products are formed. In the case of the α-compound, however, change takes place even at 125°, and increases in extent as the temperature is raised; thus, a mixture of sodium benzeneazo-α-naphthyl sulphite, alcohol, and ammonia, heated to 180—200° for twelve hours, yielded a *compound*, $C_{32}H_{23}N_5$, as a violet powder with metallic lustre, m. p. 280°; with concentrated sulphuric acid it forms a dark green solution, which becomes cinnamon-yellow and then reddish-violet on dilution. It dyes wool and cotton violet-red in a faintly acid bath, and thus possesses the properties of a basic, substantive colouring matter. A mixture of benzeneazo-α-naphthol, ammonium sulphite, and ammonia when heated to 130—140° for four hours gave benzeneazo-α-naphthylamine and a violet compound resembling that described above in its general properties, but differing from it in giving with concentrated sulphuric acid a dark violet-blue solution, changing to a reddish-violet colour on dilution. Analogous products are formed at still lower temperatures. T. H. P.

Hydrazo-compounds. V. Reaction of Hydrazobenzene with Mixed Aldehydes.

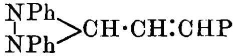
Berthold Rassow and Fritz Burmeister (*J. pr. Chem.*, 1911, [ii], **84**, 249—259).—In continuation of previous work (Abstr., 1901, i, 777; 1910, i, 79) the authors have examined the behaviour of hydrazobenzene towards phenylacetaldehyde, cinnamaldehyde, and salicylaldehyde, and find that whilst phenylacetaldehyde and cinnamaldehyde resemble the aliphatic aldehydes in readily condensing with hydrazobenzene, all attempts to effect a condensation with salicylaldehyde proved fruitless.

β-Phenylethylidenebishydrazobenzene, $CH_2Ph\cdot CH(NPh\cdot NHPh)_2$, prepared by the interaction of hydrazobenzene and phenylacetaldehyde in alcoholic solution at the ordinary temperature, crystallises in pale yellow needles, m. p. 93—95°, and is readily hydrolysed by dilute acids.

When equimolecular quantities of hydrazobenzene and cinnamaldehyde are heated together in ethyl-alcoholic solution, they yield α-(or β)-*ethoxy*-β-1 : 2-*triphenyl*-3-*ethylhydrazimethylene*,



$$\begin{matrix}NPh\\|\\NPh\end{matrix}\!\!>CH\cdot C_2H_3Ph\cdot OEt,$$

which crystallises in white, prismatic needles, m. p. 135°. It is considered probable that the first stage in the reaction consists in the formation of  $\begin{matrix}NPh\\|\\NPh\end{matrix}\!\!>CH\cdot CH{:}CHPh$, addition of alcohol subsequently taking place at the double linking, but experiments undertaken with the object of preparing this compound by the condensation of hydrazobenzene and cinnamaldehyde in ethereal or benzene solution yielded no definite results. Attempts to determine the position of the ethoxy-group by hydrolysing the ethoxy-compound with dilute sulphuric acid were also unsuccessful.

α-(or β)-*Methoxy-β-*1 : 2-*triphenyl-*3-*ethylhydrazimethylene*, $C_{22}H_{22}ON_2$, prepared in a similar manner from hydrazobenzene and cinnamaldehyde in methyl-alcoholic solution, crystallises in lustrous, white, rhombic leaflets, m. p. 163°. F. B.

Hydrazo-compounds. VI. Methylhydrazobenzene and Methylbenzidine. BERTHOLD RASSOW and KURT BERGER (*J. pr. Chem.*, 1911, [ii], **84**, 260—277).—N-*Methylhydrazobenzene*,

$$NMePh\cdot NHPh,$$

is prepared by heating a benzene solution of hydrazobenzene with methyl sulphate for two days in the presence of magnesium oxide ; it crystallises in needles or small, rod-shaped prisms, m. p. 75°, and differs from the parent substance in being very stable. When treated with cold strong hydrochloric acid, it yields an intense, dark green solution, from which N-*methylbenzidine*, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NHMe$, may be isolated in white needles, m. p. 83°. The latter compound is, however, best prepared in the form of its *hydrochloride*,

$$C_{13}H_{14}N_2,2HCl,$$

which crystallises in microscopic leaflets, decomposing at 250—300°, by the action of strong hydrochloric acid on methylhydrazobenzene in alcoholic solution. It yields a *picrate*, $C_{13}H_{14}N_2,C_6H_3O_7N_3$, crystallising in yellow, microscopic needles, which decompose at 167—169°, and a *platinichloride*, $C_{13}H_{16}N_2PtCl_6$. The *diacetyl* derivative,

$$NMeAc\cdot C_6H_4\cdot C_6H_4\cdot NHAc,$$

crystallises from alcohol in white, triangular prisms, m. p. 238° ; the *dibenzoyl* derivative, $C_{27}H_{22}O_2N_2$, in microscopic needles, m. p. 231—233°.

Methylbenzidine condenses with salicylaldehyde, yielding *salicylidene-*N-*methylbenzidine*, $NHMe\cdot C_6H_4\cdot C_6H_4\cdot N{:}CH\cdot C_6H_4\cdot OH$, m. p. 194°, and, when heated with methyl iodide in methyl-alcoholic solution, is converted into tetramethylbenzidine methiodide, m. p. 263° (Michler and Pattinson, Abstr., 1882, 199), from which tetramethylbenzidine is obtained by distillation with soda-lime.

Its hydrochloride reacts with two molecules of nitrous acid to form 4-*methylnitrosoaminodiphenyl-*4′-*diazonium chloride*, which condenses with dimethylaniline, yielding 4-*methylnitrosoaminodiphenyl-*4′-*azo-*p-*dimethylaniline*, $NO\cdot NMe\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$. This crystallises in microscopic leaflets of a golden lustre, decomposing at 243°. It forms a violet *hydrochloride*, and, when boiled with alcoholic hydrogen chloride, is converted into 4-*methylaminodiphenyl-*4′-*azo-*p-*dimethylaniline*, $NHMe\cdot C_6H_4\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NMe_2$, which crystallises in carmine-red needles, m. p. 234°, and forms a *hydrochloride*, $C_{21}H_{24}N_4Cl_2$.

The *azo-dyes* produced by the combination of diazotised *N*-methylbenzidine with β-naphthol-3 : 6-disulphonic acid and α-naphthylamine-5-sulphonic acid are respectively red and brown.

The alcoholic mother liquors from the preparation of *N*-methylbenzidine hydrochloride by the action of hydrochloric acid on *N*-methylhydrazobenzene contain 2-(or 4)*amino-*4′-(or 2′)*methylaminodiphenyl*, $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NHMe$, together with aniline, methylaniline, and dimethylaniline; the formation of the three last-mentioned substances is represented as follows:

$$2NHPh\cdot NMePh = NMe_2Ph + NH_2Ph + NPh\colon NPh.$$
$$2NHPh\cdot NMePh = 2NHMePh + NPh\colon NPh.$$

The base just mentioned is a strongly refractive, viscid, yellow liquid, b. p. 255°/25 mm., which yields a *diacetyl* derivative,

$$NMeAc\cdot C_6H_4\cdot C_6H_4\cdot NHAc,$$

crystallising in rhombic leaflets, m. p. 327°. It condenses with salicylaldehyde in alcoholic solution, yielding the *compound*,

$$OH\cdot C_6H_4\cdot CH(NMe\cdot C_6H_4\cdot C_6H_4\cdot N\colon C_6H_4\cdot OH)_2;$$

this has m. p. 255°, and is hydrolysed by boiling dilute sulphuric acid into its components. F. B.

Heat Coagulation of Proteins. II. The Action of Hot Water on Egg-albumin and the Influence of Acid and Salts on Reaction Velocity. HARRIETTE CHICK and CHARLES JAMES MARTIN (*J. Physiol.*, 1911, 43, 1—27. Compare Abstr., 1910, i, 597).—Heat coagulation consists of (1) the reaction between the protein and hot water (denaturation), and (2) the separation of the altered protein in a particulate form (agglutination); (2) occurs more rapidly than (1), and the experiments mainly are concerned with the latter. Denaturation, if means are taken to prevent change in acidity, is a reaction of the first order. As the protein is precipitated, free acid is progressively removed from the solution. Experiments are described which show that egg-albumin fixes acid in the cold, and give the relative amount of acid fixed to the acidity of the solution; the process is reversible. Determinations of the amount fixed during coagulation and its dependence on (1) total concentration of acid, and (2) on hydrogen-ion concentration are given. Salts (sodium chloride and ammonium sulphate) lower the rate of reaction, and up to a certain concentration the effect varies geometrically as the salt is added arithmetically. For the explanations advanced, the original paper must be consulted. W. D. H.

The Partial Hydrolysis of Proteins. III. Fibrin Proto-albumose. PHŒBUS A. LEVENE, DONALD D. VAN SLYKE, and F. J. BIRCHARD (*J. Biol. Chem.*, 1911, 10, 57—71).—The most striking difference between hetero- and proto-albumose is in the amount of glutamic acid on hydrolysis. The former yields 9·51, and the latter 0·63%. Proto-albumose is also poor in valine as compared with hetero-albumose. Any difference in the yield of hexone bases is insignificant.
W. D. H.

Hæmochromogen and the Spectroscopic Differentiation of Carboxyhæmoglobin and Oxyhæmoglobin. FRANZ MICHEL (*Chem. Zeit.*, 1911, 35, 996).—The author finds that the best reducing agent for changing the colouring matter of the blood into hæmochromogen is an alcoholic, alkaline solution of sodium hyposulphite; a cherry-red coloured solution for the investigation of the absorption spectrum is thus readily obtained at the ordinary temperature, whereas the use of other reducing agents necessitates warming. Heating the red solution so obtained gradually destroys the hæmochromogen spectrum, the solution becoming yellowish-green, but the addition of a few drops of pyridine to the boiling solution restores the spectrum and further heating has no effect. If the solution, after cooling, is then shaken in the air, the spectrum again disappears, but is reproduced on heating once more.

The sodium hyposulphite reagent may also be used to detect small quantities of carboxyhæmoglobin. After the addition of the hyposulphite to the diluted blood, a few drops of pyridine are added. The colour of the solution changes to an intense yellowish-red, and only the oxyhæmoglobin is changed to hæmochromogen in the cold, the spectrum of carboxyhæmoglobin remaining unchanged. On heating, the carboxyhæmoglobin is changed also into hæmochromogen.

T. S. P.

The Cleavage of Nucleins in Relation to Enzymes, with Special Reference to the Formation of Hypoxanthine in the Absence of Adenase. SAMUEL AMBERG and WALTER JONES (*Zeitsch. physiol. Chem.*, 1911, 73, 407—415).—The work of Levene and Jacobs on the intermediate products of hydrolysis of the nucleic acids have led them to consider that the part of the molecule which contains purine substances may be represented by the following shortened formula:

$$C_5H_4N_5{\cdot}C_5H_8O_3{\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}PO(OH){\cdot}O{\cdot}C_5H_8O_3{\cdot}C_5H_4ON_5.$$

By splitting off phosphoric acid, two nucleosides, guanosine and adenosine, are obtained; the former consists of guanine and *a*-ribose, and from it free guanine is obtained by hydrolysis with acids. Adenosine consists of adenine and *d*-ribose, and from it free adenine is obtained on hydrolysis. By the action of nitrous acid these two amino-nucleosides are converted into the hydroxy-nucleosides, xanthosine and inosine (hypoxanthosine). Gland extracts produce the same kind of effect by means of enzymes, but different glands act differently; for example, pig's pancreas decomposes nucleic acid with the formation of guanosine, which is not further changed; adenosine, which is simultaneously formed, is changed to inosine as an end product. Pig's liver extract produces from nucleic acid, xanthosine (by deamidation of guanosine), from which xanthine is then formed. The following list of enzymes is given: (1) phosphonuclease, (2) purine nuclease, (3) guanosine-deamidase, (4) adenosine-deamidase, (5) adenase, (6) guanase, (7) xanthosine-hydrolase, (8) inosine-hydrolase, and (9) xantho-oxydase.

The present experiments show that phosphonuclease and purine-nuclease, which respectively split off phosphoric acid and purine bases, are independent enzymes. Dog's liver can split off phosphoric acid from nucleic acid, but cannot split off adenine from the adenosine so formed; no adenine is found among the products, and it would be if it were formed, since the dog's liver contains no adenase to convert it into hypoxanthine. Nevertheless, dog's liver extract splits off hypoxanthine quantitatively from thymus-nucleic acid; this is because the adenosine formed is deamidised to inosine, and this is hydrolytically split so as to yield hypoxanthine. W. D. H.

The Application of the Optical Method to a Study of the Enzymatic Decomposition of Nucleic Acids. Samuel Amberg and Walter Jones (*J. Biol. Chem.*, 1911, **10**, 81—87. Compare Pighini, this vol., ii, 236).—Extracts of organs freed from blood produce the same results as those containing blood; their varying activities on nucleic acids are therefore not due to blood or blood-serum. By the optical method no change was observed in the rotation of thymus-nucleic acid under the influence of serum. Yeast-nucleic acid, however, does suffer a diminution in rotatory power, as Pighini stated, but this does not mean liberation of either phosphoric acid or purine bases. Rotation is also lowered as the temperature rises, and returns to its previous value on cooling. Pighini's results must therefore be accepted with caution. W. D. H.

A Method for the Study of Proteoclastic Enzymes. Philip Adolph Kober (*J. Biol. Chem.*, 1911, **10**, 9—14).—Amino-acids (six were tested) form copper salts that yield their copper as hydroxide when boiled with a slight excess of alkali. The polypeptides and peptones tested which form copper salts do not yield their copper as hydroxide when treated in the same way. The method is suggested as one for distinguishing the two classes of substances in digests.
W. D. H.

The Mechanism of Proteoclastic Enzymes. Auguste Fernbach and Marcel Schoen (*Compt. rend.*, 1911, **153**, 133—136).—A greater proteoclastic action is produced in the presence of monopotassium phosphate than in that of the dipotassium salt by papayotin, pancreatin, and the proteoclastic enzyme of *Tyrothrix tenius*, acting on fibrin, caseinogen, and other proteins. This difference is due mainly to the reactions of the media. When pancreatin is incubated with a solution of potassium or sodium phosphate, an increase in activity is produced. W. J. Y.

The Behaviour of Phenolase towards Acids. Alexis Bach and B. Sbarsky (*Biochem. Zeitsch.*, 1911, **34**, 473—480).—The phenolase was prepared from *Lactarius vellerius*, and its action on pyrogallol was determined by estimating quantitatively the purpurogallin formed. This was done by filtering it off from the solution, dissolving it in concentrated sulphuric acid, and titrating the solution thus obtained, after dilution with water, with $0{\cdot}01N$-permanganate solution. In addition to this, the amount of pigment formed, which remains in solution after removing the purpurogallin, was estimated colorimetrically. It was found that the presence of small quantities of acid accelerated the action of phenolase. With increasing quantities of acid, the amount of purpurogallin diminishes, but that of the soluble pigment increases. At the limit at which the purpurogallin formation ceases, however, the amount of soluble pigment commences to diminish. The amount of the toxic dose of acid, however, is so great in comparison with the amount of ferment that there can be no question of the acid merely acting on a manganese or other metallic compound. By varying phenolase concentrations on the same substrate, the toxic action of the acid is proportional, not to the absolute phenolase content, but to its activity under the given conditions. The authors draw the conclusion that their results do not accord with Bertrand's theory of phenolase action. S. B. S.

Preparation of Pure Invertase. HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, **73**, 335—344).—Invertase prepared by autolysis (O'Sullivan and Tompson, Trans., 1890, **57**, 834) was purified by solution in water and precipitation with an equal volume of alcohol. Invertase is precipitated with colloidal iron only when other impurities, particularly electrolytes, are also present. The most active preparations were obtained by precipitation of the autolysed liquor with lead acetate, removal of the lead as sulphide, and of the protein by rubbing the filtrate with much kaolin; a final precipitation with alcohol gave an invertase of great activity. This contained 4·7% of nitrogen, which was lessened by diffusion to 1·85%. Molecular-weight determinations based on the rate of diffusion gave a value of 27,000. During diffusion about 25% of impurities of lower molecular weight are separated, and the activity of the invertase correspondingly increased. The activity of the purified invertase was directly proportional to the weight used. E. F. A.

Yeast-Gum. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, **73**, 314—316. Compare Euler and Fodor, this vol., i, 607).—Polemical. Invertase is perhaps the magnesium salt of an acid containing nitrogen and phosphorus; it is not a protein. A plea is made for the continuance of the term invertin instead of invertase. The suggestion of Euler and Fodor that invertase is a complex carbohydrate related to yeast-gum is negatived; active preparations containing no trace of yeast-gum have been obtained frequently. E. F. A.

Influence of the Reaction of the Medium on the Activity of Cellase. New Character Distinguishing it from Emulsin. GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1911, **153**, 360—363. Compare Abstr., 1910, i, 212, 290, 800; this vol., i, 592). —The diastase from sweet almonds capable of hydrolysing cellose functions best in a medium having almost the same reaction as that of the natural preparation, namely, alkaline to methyl-orange and acid to phenolphthalein, corresponding with a concentration in hydrogen ions of $10^{-6\cdot3}$. Addition of more that a trace of acid inhibits the diastatic activity. Cellase in this respect differs from emulsin, which shows maximum activity only in solutions alkaline to phenolphthalein. W. O. W.

Heat Resistant Lipase. N. L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 166—170).—The lipase produced by *Bacterium fluorescens liquefaciens*, *B. pyocyaneum*, *B. punctatum*, and *B. liquefaciens albus* is capable of withstanding a temperature of 100° for five minutes without being rendered inactive, whilst that formed by *Bacterium lypolyticum*, *B. Stutzeri*, *B. fluorescens non-liquefaciens*, *Oidium lactis*, *Aspergillus niger*, *Penicillium glaucum*, and *Cladosporium butyri* is destroyed at 80°.

The two enzymes also differ in their relation to small quantities of acid; ordinary lipase is inhibited only when the reaction of the medium is *N*/50-acid, whereas the heat resisting lipase is rendered inactive at *N*/100-acid. H. B. H.

The Chemical Occurrences in Milk Curdling by Rennet. IVAR BANG (*Skand. Archiv. Physiol.*, 1911, **25**, 105—144).—Rennet converts the caseinogen of milk into casein, and the latter is then united to calcium phosphate to form the curd. In the thirty or forty years since this was established by Hammarsten little or nothing has been added, especially in relation to the intermediate stages in the reaction. After the addition of rennet, milk remains apparently unaltered for minutes or hours, and then, suddenly, coagulation takes place. It is the object of the present research to ascertain what is occurring before the last step, the actual curdling, is seen. Some of the experiments were performed with milk, and some with solutions of caseinogen prepared by Hammarsten's method. Rennet is destroyed by momentary heating to 65°, and milk is not changed at this temperature. By adding rennet fractionally, summation is noted; for example, the coagulation time on adding 0·1 c.c. of rennet to 10 c.c. of milk was eight minutes, and on adding 0·2 c.c. four minutes; if, however, 0·1 c.c. is added, and four minutes later another 0·1 c.c., then clotting occurs two minutes after the second addition. If, however, the milk after the first addition is heated to 65°, no such summation is seen; and if the second dose of rennet is not added until four minutes after the heating and subsequent cooling, the coagulation time is lengthened. Although the milk had not curdled in the interval, it had undergone certain changes, due to the first addition of rennet and to the heating of the mixture. If a caseinogen solution is boiled, cooled, and then rennet and calcium chloride added, the coagulation time is also shortened, especially in experiments in which any suspended calcium carbonate (used in the preparation of the solution) is removed by centrifugalising. The so-called solution of caseinogen prepared by Hammarsten's method is really a solution of caseinogen united to calcium carbonate; rennet alone does not curdle it; the addition of calcium chloride or phosphate is also necessary; the original solution is opalescent, but clears on the addition of a little sodium chloride; but heating after the addition of this salt restores the opalescence, and this is reversible on alternate heating and cooling. At a high temperature caseinogen has therefore a greater affinity for calcium carbonate than for alkali; at a low temperature this is reversed. The actual curdling is due to the formation of a compound between the caseinogen–calcium carbonate and other calcium salts, such as the chloride or phosphate, and the numerous experiments, both with caseinogen solution and milk, show differences in action between the chloride and the phosphate. The suggestion that these latter salts act as activators of the enzyme was examined and negatived. The longer the enzyme has acted previous to the addition of the calcium chloride, the more rapidly does curdling occur after the addition. Rennet does not produce only a change in the caseinogen of the milk, but has also something to do with the mobilisation of the calcium salts. Further experiments, which are difficult to summarise shortly, lead to the conclusion that calcium chloride by its osmotic pressure inhibits the dissociation of the caseinogen–calcium carbonate–calcium chloride compound, and the undissociated compound is precipitated; an excess of phosphate, on the other hand, inhibits precipitation; calcium phosphate is insoluble in water, and so cannot affect osmotic pressure; it forms an insoluble compound with the caseinogen; the avidity of caseinogen for calcium salts rises with temperature.

Milk itself contains, in addition to caseinogen, other proteins and salts; the lactose is indifferent to curdling phenomena. The salts are alkali chloride, phosphate and carbonate, and calcium citrate. The influence of the salts is discussed at length with numerous experiments. Calcium citrate favours, alkali citrate inhibits, curdling; the former gives up calcium, the latter removes it from the milk. The effect of milk-serum on the process did not give constant results. Crystalline egg-albumin (and serum-albumin to a less degree) inhibits the process, but this is in part due to the alkali used in neutralising the solution. Egg-white and serum act in the same way. Lact-albumin acts similarly, and colostrum, which is very rich in lact-albumin, has a very strong inhibitory action. This action in all cases is not on the activity of the enzyme in changing caseinogen, but on the final act of curdling. Rennet action is thus very complex; the calcium salts of the milk are partitioned between organic and inorganic acids and the various milk proteins; the caseinogen takes up more and more calcium phosphate long before it is united, sufficient to cause precipitation to occur. There are probably several phases in the formation of casein, and several more in the combination of casein with calcium phosphate. It is doubtful whether rennet should be classed with coagulating enzymes, for rennet does not in itself produce curdling, and the final act of curdling is not true coagulation, but is more akin to the precipitation of protein by neutral salts. Casein itself is capable of re-solution, and can be re-curdled with rennet under appropriate conditions.

The nomenclature adopted in the preceding abstract is that usually adopted in this country. In the original German, caseinogen and casein are spoken of respectively as casein and paracasein. W. D. H.

Further Observations on Rennin and Pepsin in the Gastric Juice of the Calf. A. Rakoczy (*Zeitsch. physiol. Chem.*, 1911, **73**, 453—458).—This is a continuation of the author's previous work (Abstr., 1910, i, 801), in which he found that milk curdling is produced by two enzymes in the calf's gastric juice, namely, by pepsin, and by a special milk-curdling enzyme, rennin (chymosin). With increase of age, the latter disappears, but there is no ground for believing that there is any difference in the pepsin of animals of varying ages. W. D. H.

Amylases. III. Preparation and Properties of Pancreatic Amylase. Henry C. Sherman and M. D. Schlesinger (*J. Amer. Chem. Soc.*, 1911, **33**, 1195—1204. Compare Abstr., 1910, ii, 1012; i, 799).—Having been much hampered in previous work by the deterioration of amyloclastic power in pancreatin solutions, the authors have examined the influence of different solvents and precipitants on the amyloclastic activity of commercial pancreatin, and find that it is fairly permanent in 50% alcohol, the pancreatic amylase being recovered in active form from the solution by precipitation with strong alcohol or a mixture of alcohol and ether. By a process involving extraction of dry pancreas powder with 50% alcohol, repeated precipitation, and purification by dialysis in 50% alcohol, preparations having diastatic powers up to 3480 on the new scale (Abstr., 1910, i, 799) have been obtained, corresponding with over 5000 on Lintner's scale, and with $D_{30}^{38} = 500,000$ on Wohlgemuth's scale. Six independent preparations showed in the dry substance activities of 3310, 3670, 3540, 3570, 3720, and 3320. This agreement indicates that these preparations are substantially alike, and that the process yields a fairly definite result. The product has a composition and the characteristic reactions of a protein closely resembling Osborne's malt diastase.

The pancreatic amylase thus prepared, acting at 40° on soluble starch made by Lintner's method, formed 6000 times its weight of maltose in twenty minutes, and 211,000 times its weight in thirty hours. It digested 400,000 times its weight of starch to the "erythrodextrin stage" in less than twenty-two hours, and to products giving no reaction with iodine in forty-eight hours. C. S.

Catalase. Oskar Loew (*Biochem. Zeitsch.*, 1911, **34**, 354).—A claim for priority in reference to the action of nitrates on, and the detection of, catalase. S. B. S.

Extraction of Zymase. Alexandre Lebedeff (*Bull. Soc. chim.*, 1911, [iv], **9**, 744—750).—Reply to Kayser (compare this vol., ii, 640). The author has systematically studied the factors influencing the activity of the zymase preparation, namely, the temperature and the time of fermentation, the condition and kind of yeast, the method of preservation of the juice, etc. The top yeast, called "parisienne," does not give an active juice either by the process of Lebedeff or by that of Buchner. W. G.

Is Zymase a Diastase? Alexandre Lebedeff (*Bull. Soc. chim.*, 1911, [iv], **9**, 672—682; *Ann. Inst. Pasteur*, 1911, **25**, 682—684).—From experiments with an extract made by macerating dried yeast for two hours with three volumes of water, the author finds that the zymase contained in it is a typical diastase. The quantity of sugar fermented, however, is nearly proportional to the amount of co-enzyme present, provided that this is not less than 20%. The unusual activity of the extract prepared by the author's method is due to the amount of co-enzyme contained in it. It is suggested that yeast is more active than any of its extracts, not because it contains more zymase, but because as fast as co-enzyme is destroyed during the fermentation, it is produced again by cellular activity. R. V. S.

Organic Chemistry.

Absorption of Hydrocarbon Gases by Non-aqueous Liquids. ALONZO SIMPSON MCDANIEL (*J. Physical Chem.*, 1911, **15**, 587—610).—The absorption of methane, ethane, and ethylene in ten organic liquids has been determined at a series of temperatures lying between 20° and 60°.

The gas burette and Ostwald absorption pipette were water-jacketed, and the temperatures were maintained approximately equal by means of a suitably proportioned resistance coil in each jacket, the two coils being in series. The gas in the burette was saturated with the solvent vapour and measured at the temperature of each absorption experiment, so that no correction for vapour pressure of solvent was necessary. The solvents were boiled under diminished pressure, and precautions were adopted to remove dissolved air, the presence of which introduces considerable errors.

The solvents, in order of increasing absorptive power at 25° for methane, are methyl, amyl, ethyl, *iso*propyl alcohols, benzene, toluene, *m*-xylene, hexane, heptane. With ethane and ethylene the solvents fall into a similar series, which, however, is quite unlike the order of the same solvents for the less soluble gases nitrogen, carbon monoxide, hydrogen, and carbon dioxide.

It is suggested that the solubilities of the hydrocarbon gases are largely influenced by specific chemical relations with the solvents.

The absorption coefficient decreases in all cases as the temperature rises. R. J. C.

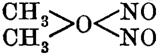
Preparation of $\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 235311).—A 70% yield of $\beta\gamma$-dimethyl-$\Delta^{\alpha\gamma}$-butadiene can be obtained by heating pinacone or pinacolin at 400° with a dehydrating agent followed by fractional distillation of the products. F. M. G. M.

Action of Di-iodoacetylene on Organic Bases. WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1911, **33**, 1598—1601).—Di-iodoacetylene can be prepared in a yield of 80—90% of the theoretical by passing acetylene into a solution of potassium iodide and adding sodium hypochlorite solution drop by drop. On mixing solutions of di-iodoacetylene and triethylamine in ether, the *compound*, $NEt_3,2C_2I_2$, m. p. 115°, separates in feathery needles. Dipropylamine when treated in the same way yields the *compound*, $NHPr_2,2C_2I_2$, m. p. 160°, which forms long needles. By the action of acetylene di-iodide on phenylhydrazine, nitrogen is evolved and iodophenylacetylene is produced, together with two phenylhydrazine *hydriodides*, $2NHPh{\cdot}NH_2,HI$, m. p. 128° (decomp.), and $NHPh{\cdot}NH_2,HI$, which does not melt below 300°. E. G.

Action of Alkaline Solutions on Trichlorinated Organic Compounds. G. BRESSANIN and E. SEGRÈ (*Gazzetta*, 1911, **41**, i, 671—674).—Trichloro*iso*propyl alcohol (Mossler, Abstr., 1908, i, 751), phenyltrichloromethylcarbinol (Jocitsch, *Chem. Zentr.*, 1897, i, 1013), and chloroform (Mossler, *loc. cit.*) yield carbon monoxide when treated with alkalis. The authors find that acetonechloroform behaves similarly, and the amount of carbon monoxide evolved indicates that the substance decomposes chiefly according to the equation

$$CCl_3{\cdot}CMe_2{\cdot}OH = COMe_2 + CHCl_3.$$

R. V. S.

Fusibility Curves of Gaseous Mixtures: Oxonium Systems Formed by Acetylene, Ethylene, Nitric Oxide, and Methyl Ether. GEORGES BAUME and ALBERT F. O. GERMANN (*Compt. rend.*, 1911, **153**, 569—572. Compare this vol., i, 414; ii, 696).—The fusibility curve for methyl ether and acetylene shows a very sharp maximum at −117·4°, corresponding with the compound $Me_2O{:}C_2H_2$. The existence of an analogous compound with ethylene is evident from the occurrence of a maximum at −163·2°, but this is unstable in the liquid phase. The curve for methyl ether and nitric oxide shows a maximum at −166·3°, corresponding with an oxonium compound, to which the constitution  $\begin{matrix}CH_3\\CH_3\end{matrix}{>}O{<}\begin{matrix}NO\\NO\end{matrix}$ is ascribed.

Methyl ether has m. p. −138·4°.

W. O. W.

Primary Aliphatic Dinitro-, Nitro-nitrite, and Dialdoxime Compounds. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, **44**, 2526—2534).—It has been shown to be possible to apply V. Meyer's method of preparing nitro-compounds from alkyl halides to dihalogen compounds which contain the halogen atoms at some distance from one another in the molecule. αδ-Dinitrobutane, αε-dinitropentane, and ακ-dinitrodecane have been isolated and found to be stable substances. The nitro-nitrite compounds are considerably less stable.

On cautious reduction, the dinitro-compounds are converted into dioximes, hence affording a useful method of preparing aliphatic dialdehydes.

αδ-Di-iodobutane was allowed to react in ethereal solution with silver nitrite. From the product three fractions were isolated by distillation.

1. A small quantity of *butyl dinitrite*, $NO{\cdot}O{\cdot}[CH_2]_4{\cdot}O{\cdot}NO$, b. p. −105°/15 mm.

2. *Nitrobutyl nitrite*, $NO_2{\cdot}[CH_2]_4{\cdot}O{\cdot}NO$, b. p. about 110°/14 mm., a liquid of ethereal odour, which soon began to decompose. On treatment with stannous chloride in hydrochloric acid solution, this liquid yielded δ-hydroxybutylamine, b. p. 100°/15 mm. The dibenzoyl derivative of the latter was found to melt at 75°, whereas Henry found 58°.

3. *αδ-Dinitrobutane* is an almost colourless, practically odourless liquid of b. p. 176—178°/13 mm.; the *sodium* salt was analysed. Bromine transformed it into *ααδδ-tetrabromo-αδ-dinitrobutane*, $NO_2{\cdot}CBr_2{\cdot}CH_2{\cdot}CH_2{\cdot}CBr_2{\cdot}NO_2$, m. p. 100°.

αε-Di-iodopentane and silver nitrite gave a similar series of products. *Nitroamyl nitrite*, b. p. 130—133°/15 mm., was found to be somewhat unstable. Reduction transformed it into *ε-hydroxyamylamine*,

$$OH\cdot[CH_2]_5\cdot NH_2,$$

a colourless liquid, b. p. 122°/16 mm., which forms an oily *benzoyl* derivative and a *gold* salt. The constitution of this compound was proved by its reduction to piperidine by means of fuming hydriodic acid.

αε-Dinitropentane is an almost colourless liquid, b. p. 194—196°/16 mm. Its salts resemble those of αδ-dinitrobutane. The *sodium* salt when treated with benzenediazonium sulphate yields the *compound*, $N_2Ph\cdot CH(NO_2)\cdot[CH_2]_3\cdot CH(NO_2)\cdot N_2Ph$, m. p. 169°. *ααεε-Tetrabromo-αε-dinitropentane* has m. p. 39°.

ακ-Dinitrodecane, $C_{10}H_{20}O_4N_2$, m. p. 49°, was obtained by similar methods. The *tetrabromo*-derivative is an oil.

On reduction with stannous chloride in hydrochloric acid solution, dinitropentane gives glutardialdoxime, m. p. 178° (Harries, Abstr., 1910, i, 361, gives 171°); dinitrobutane gives succindialdoxime, and dinitrodecane furnishes *ακ-dioximinodecane*, m. p. 137—141°.

H. W.

Anhydrous Formic Acid. James B. Garner, Blair Sexton, and H. O. Parker (*Amer. Chem. J.*, 1911, **46**, 236—240).—Attention is drawn to the lack of agreement in the values given by previous investigators for the physical constants of formic acid. The methods of dehydration hitherto employed yield only a 97—98% acid.

The anhydrous acid is best prepared by distilling the ordinary acid over anhydrous copper sulphate under a pressure of 120 mm. It has m. p. 8·35°, b. p. 50°/120 mm., 99·7°/741 mm.

The density and viscosity of the pure acid have been determined at temperatures varying from 10° to 40°: D^{15} 1·2260, D^{20} 1 2200.

F. B.

Soy Bean Oil. Hermann Matthes and A. Dahle (*Arch. Pharm.*, 1911, **249**, 424—435. Compare this vol., i, 858).—The oil contains about 94% of fatty acids in the form of glycerides. The fatty acids comprise palmitic 15%, oleic 56%, linoleic 19%, and linolenic 4·8% approximately (compare Lewkowitsch, *Oils, Fats, and Waxes*, 1909, **2**, 124, and Keimatsu, this vol., i, 766).

The two oils examined were "refined" and "unrefined," and gave the following constants respectively: D^{15} 0·9260 and 0·9265; solidifying point $-11·5°$, $-12°$; n_D^{40} 1·468, 1·468; $[\alpha]_D$ 0°, 0°; acid number 5·711, 1·713; saponification value 192·3, 194·3; Hehner number 94·07, 95·52; iodine value 131·3, 132·6; Reichert-Meissl value 0·7549, 0·7549; Polensky number 0·7843, 1·0784. Both oils gave the elaidin reaction. The two oils were exposed to (1) damp air, (2) dry air, (3) oxygen, (4) damp oxygen during six months, and then re-examined. The results indicated that (1) moisture raised the acid number; (2) oxygen alone or in presence of moisture did not lower the iodine value, whilst (3) damp air reduced the iodine value from 131·3 to 122·5 and from 132·6 to 105·4 for the refined and unrefined oils respectively.

Farnsteiner's process applied to the mixed fatty acids gave a good separation of palmitic acid, but the mixed unsaturated acids thus obtained still contained some saturated acid. Bremer's method gave a bad separation of saturated acid, but the mixed unsaturated acids obtained contained less palmitic acid than the product obtained by Farnsteiner's method. No separation of components of the mixed unsaturated acids could be effected by fractional distillation, and recourse was had to bromination, and a method is described for the successive separation of linolenic acid hexabromide, linoleic acid tetrabromide, and oleic acid dibromide from the mixture. T. A. H

Preparation and Properties of α-Linolenic Acid from Linseed Oil. Ernst Erdmann (*Zeitsch. physiol. Chem.*, 1911, **74**, 179—197).—The acids obtained by the hydrolysis of linseed oil are freed from the solid acids at −18° in the presence of petroleum, and the residual liquid acids are converted into their zinc salts by trituration with freshly precipitated basic zinc carbonate. By extracting the salts with alcohol, the easily soluble zinc α-linolenate can be removed, and from it pure α-linolenic acid obtained in 16—18% yield, calculated on the liquid acids. The acid, the purity of which is controlled by its iodine number, 269—278, and by its quantitative conversion into the hexabromide, m. p. 179°, is an unstable, somewhat mobile liquid, D_4^{20} 0·9046 (after a few days, D_4^{21} 0·9248); the *zinc* salt, $(C_{18}H_{29}O_2)_2Zn,\frac{1}{2}ZnO$, m.p. 72—73°, *ammonium*, *barium*, *sodium*, and basic *copper* salts are described. The acid yields *trichlorotri-iodostearic acid*, $C_{18}H_{30}O_2Cl_3I_3$, m. p. 146°, with iodine chloride, and *tribromotri-iodostearic acid*, m. p. 124—126°, with iodine bromide, and is converted by ozone into an *ozonide peroxide*, $C_{18}H_{30}O_{12}$, which is decomposed by cold water, yielding hydrogen peroxide and a semi-solid mass consisting probably of the semialdehyde of azelaic acid and malondialdehyde.

The paper concludes with a reply to Rollett (this vol., i, 175). It is very questionable whether β-linolenic acid is present in linseed oil, although there is no doubt that it constitutes the chief ingredient of the mixture of acids obtained by the debromination of α-linolenic acid hexabromide. C. S.

Keto-enolic Tautomerism. III. Tautomerism of Ethyl Acetoacetate. Kurt H. Meyer and Paul Kappelmeier (*Ber.*, 1911, **44**, 2718—2724).—Knorr, Rothe, and Averbeck's general results on the desmotropy of ethyl acetoacetate (this vol., i, 516) confirm those obtained by K. H. Meyer (this vol., i, 350), but these authors found that, in a state of equilibrium, the ester contains 2% of the enolic form, whilst Meyer's results indicated 7·71%.

The authors have therefore investigated the sources of error in Meyer's method, namely, the necessity of adding a slight excess of bromine before a recognisable yellow colour is obtained, the conversion of ketonic into enolic form during the titration, and the possible presence in the alcoholic bromine solution of substances which liberate iodine from potassium iodide (such are really present in old, but not in fresh, solutions); but when allowance is made for all these errors, the proportion of the enolic form is still found to exceed 7%.

The principal errors may be eliminated by adding to the solution, immediately after the bromine, alcoholic β-naphthol solution, which does not react with iodine, but does so very rapidly with bromine, giving a product unacted on by hydrogen iodide; the solution of the ester in alcohol at $-7°$, and the addition of the alcoholic bromine and β-naphthol solutions need not occupy more than fifteen seconds. The bromide of the ethyl acetate is then estimated by addition of potassium iodide and titration of the separated iodine with thiosulphate. By this method the presence of 7·4% of the enolic form is indicated. The difference between this and Knorr, Rothe, and Averbeck's value hence remains unexplained.

This titration method can only be employed where the bromine is added instantaneously to the ester, and where the transformation of the one form of the ester into the other is not too rapid.

The publication of Piccard's results (this vol., ii, 561) has led the author to apply the above method to the equilibrium of solutions of widely varying concentrations of ethyl acetoacetate in alcohol, benzene, carbon disulphide, and *n*-hexane. The surprising result was obtained that up to dilutions which can still be accurately investigated by the titration method, namely, $N/5$—$N/10$, the proportion of the enolic form present continues to increase with the dilution, the equilibrium hence depending on the concentration. This is explained on the assumption that the solvent itself does not remain constant on dilution, but consists of a variable mixture of alcohol, etc., and the ester. Also, Dimroth (this vol., ii, 31) has shown that the equilibrium is dependent on the solubilities of the two components, and it may be that addition of the ester increases the solubility of the ketonic form and so increases its proportion.

For the four solvents named above, the curves connecting the logarithm of the concentration with the percentage of enolic compound in the ester apparently become perpendicular to the enolic axis at high dilutions, as though the equilibrium were then independent of the concentration, but the errors of the method are too great with dilute solution to permit of this relation being definitely established.

T. H. P.

Keto-enolic Tautomerism. IV. Ferric Chloride Reaction of Enols. KURT H. MEYER (*Ber.*, 1911, 44, 2725—2729).—No quantitative measurements have been made of the velocity of enol-formation with ethyl acetoacetate, or of the quantity of enol-iron-compound formed with ferric chloride, but from their conductivity measurements Hantzsch and Desch (Abstr., 1902, i, 708) drew the conclusion that only very little enolate is present in an iron enolate solution of ethyl acetoacetate, in spite of the intensity of the colour. This conclusion is not confirmed by the author's results.

The estimation of enol in ethyl acetoacetate by titration with bromine (this vol., i, 350; preceding abstract) can be effected also in presence of ferric chloride, the titration being continued until the violet colour of the enolate disappears. As the colour soon returns again, owing to further enolisation, and can then be destroyed again by further addition of bromine water, and so on, the reaction serves as a striking lecture experiment. In order to avoid enolisation during the titration, this must be carried out as rapidly as possible and at 0°.

Varying proportions of aqueous ethyl acetoacetate and ferric chloride solution were mixed, left at 0° for an hour so that equilibrium might be established, and titrated with $N/10$-bromine water. The results show that the ferric chloride exerts a direct enolising action, the quantity of enol formed varying with, but not proportionally to, the amount of ferric chloride added. The law of mass action leads to, the equation: $C_{\text{enolate}} = K.C_{\text{enol}'}.C_{\text{Fe}^{\cdots}} = K.C_{\text{Fe}^{\cdots}}.C_{\text{ketone}}/C_{\text{H}^{\cdot}}$, the quantity of enolate formed being dependent on the number of hydrogen ions present; indeed, the complex salt can be decomposed and the solution decolorised by addition of acid. With low concentrations of the ferric chloride, its hydrolysis, and hence the free acid present in it, may be neglected, so that it can be assumed that, in a state of equilibrium, the hydrogen ions correspond with the hydrochloric acid liberated from the ferric chloride by the enol. Hence $C_{\text{enolate}} = K\sqrt{C_{\text{FeCl}_3}.C_{\text{ketone}}}$. The values of this expression agree fairly well for low concentrations of ferric chloride, but vary considerably for the higher concentrations. It may be that in the latter case the free acid in the ferric chloride influences the equilibrium, and that with higher enol-concentrations which require larger amounts of bromine solution, the liberated hydrogen bromide destroys some of the enolate.

In alcoholic solution the quantity of enolate cannot be estimated so accurately, owing to the change of colour on titration being less distinct, but the colour of the enolate quickly re-appears, so that the velocity of conversion of keto- to enol-form is apparently catalytically accelerated to a considerable extent.

That the slow formation of enolate is in reality due to the slowness of enolisation is shown by the fact that enolate formation is a unimolecular reaction, its course being quite analogous with that of enolisation by halogens (compare Lapworth, Trans., 1904, **85**, 30). The velocity constant, $K = 0{\cdot}017$ at 0°, shows that the catalytic action of ferric chloride is almost exactly as weak as that of free hydrochloric acid (this vol., i, 350). In alcoholic solution ferric chloride exerts a much more marked catalytic effect on enolisation. T. H. P.

Formation of Lævulic Acid from Glucosamine, Chitin, and Chitose. HEDWIG HAMBURGER (*Biochem. Zeitsch.*, 1911, **36**, 1—4).—Lævulic and formic acids are produced when *d*-glucosamine and chitin are heated for four or five days with 25—30 per cent. sulphuric acid.

By treatment with sodium nitrite, glucosamine hydrochloride may be converted into chitose, and this when heated with hydrochloric acid also forms lævulic acid. These substances must therefore be included in those groups contained in the protein molecule which yield lævulic acid when hydrolysed with strong mineral acids. W. J. Y.

The Walden Inversion. VII. Optically Active Leucic (*a*-Hydroxy*iso*hexoic) Acid and its Transformation into *a*-Bromo*iso*hexoic Acid. HELMUTH SCHEIBLER and ALVIN S. WHEELER (*Ber.*, 1911, **44**, 2684—2690. Compare Abstr., 1911, i).—The resolution of *a*-hydroxy*iso*hexoic acid into its optically active components has been accomplished by the crystallisation of its quinidine salt.

l-Leucine on treatment with nitrous acid yields *l*-hydroxy*iso*hexoic acid, the ethyl ester of which is converted by the action of bromine and phosphorus into ethyl *d*-*a*-bromo*iso*hexoate. Since it has been shown by Fischer (Abstr., 1907, i, 194) that the *l*-bromo-ester may be obtained from the *l*-bromo-acid formed by the action of nitrosyl bromide on *l*-leucine, it is, therefore, possible to convert the latter into the ethyl ester of either *d*- or *l*-*a*-bromo*iso*hexoic acid.

dl-*a*-Hydroxy*iso*hexoic acid, prepared by the action of aqueous sodium hydroxide on *a*-bromo*iso*hexoyl bromide, first at the ordinary temperature and then at 100°, crystallises in rhombic plates, m. p. 76—77° (compare Röhmann, Abstr., 1908, i, 56; Gmelin, Abstr., 1893, i, 501); the *ethyl* ester has b. p. 80—81°/16 mm., and yields *ethyl* dl-*a*-*bromo*iso*hexoate*, b. p. 86—87°/11 mm., when treated with phosphorus and bromine

The resolution of the acid into its optically active components may be effected by means of the quinine or brucine salts, but most readily by crystallisation of the quinidine salt.

l-*a*-*Hydroxy*iso*hexoic acid* crystallises in thin prisms, m. p. 81—82°, with previous sintering at 78°, and has, in *N*-sodium hydroxide $[a]_D^{20}$ $-27·8°$ ($\pm 0·2°$), in water $[a]_D^{20}$ $-10·4°$ ($\pm 0·2°$). It may also be obtained by the action of nitrous acid on *l*-leucine, no appreciable racemisation taking place during the transformation; the *barium* salt was analysed. The d-*isomeride* could not be obtained pure by the crystallisation of its alkaloidal salts, and is, therefore, best prepared from *d*-leucine and nitrous acid; in *N*-sodium hydroxide it has $[a]_D^{20}$ $+2·63°$ ($\pm 0·2°$).

Ethyl l-*a*-*hydroxy*iso*hexoate*, prepared by esterifying the *l*-acid with alcohol and hydrogen chloride, has b. p. 79—80°/12 mm., $[a]_D^{20}$ $-11·07°$ ($\pm 0·02°$), D^{20} 0·965, and is converted by treatment with phosphorus and bromine into ethyl *d*-*a*-bromo*iso*hexoate, considerable racemisation accompanying the action. F. B.

Lactarinic Acid and Ketostearic Acid Isolated from Fungi of the genus Lactarius. J. BOUGAULT and C. CHARAUX (*Compt. rend.*, 1911, **153**, 572—573*).—Thörner's lactarinic acid has been isolated from *Lactarius theiogalus*, *L. plumbeus*, etc., but does not occur in all species. It is extracted by alcohol, and obtained as spangles, m. p. 87°, having the composition $C_{18}H_{34}O_3$. The substance appears to be a ketonic acid, since it yields an *oxime*, m. p. 59—61°, which undergoes the Beckmann transformation, giving a *compound*, m. p. 104°; the *ethyl* ester has m. p. 41°. Reduction of the acid by means of sodium and alcohol leads to the formation of an *hydroxy-acid*, $C_{18}H_{36}O_3$; this substance yields an *acetyl* derivative, m. p. 52—53°, and furnishes stearic acid when its iodo-derivative is reduced with zinc and acetic acid. W. O. W.

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* and *J. Pharm. Chim.*, 1911, [vii], **4**, 337–343.

β-Butanolglycuronic Acid. SUMIO SANEYOSHI (*Biochem. Zeitsch.* 1911, **36**, 22—24).—Methyl ethyl ketone when given to rabbits by the mouth undergoes reduction in the body, and is excreted in the urine as a β-butanol derivative of glycuronic acid. This compound was isolated as the barium salt, $C_{10}H_{17}O_7Ba$, and from the fact that it did not reduce Fehling's solution directly, a glucoside formula is attributed to it. W. J. Y.

Action of the Chlorides of Dibasic Fatty Acids on Ethyl Sodioacetoacetate. JOHANNES SCHEIBER [with P. LUNGWITZ] (*Ber.*, 1911, **44**, 2422—2429).—Chlorides of succinic, glutaric, and adipic acids react with ethyl sodioacetoacetate to form compounds of the type $[CH_2]_n[CO\cdot CH(COMe)\cdot CO_2Et]_2$. In addition, succinyl chloride reacts with 1 mol. of ethyl sodium acetoacetate, yielding *ethyl succinylacetoacetate*, $CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot CH(COMe)\cdot CO_2Et$. The corresponding malonic ester derivative (Scheiber, Abstr., 1909, i, 363) has a cyclic structure, but the succinyl ester shows no tendency either to form a γ-lactone or other cyclic derivative.

Ethyl succinylacetoacetate crystallises in prisms, m. p. 82°; it gives a red coloration with alcoholic ferric chloride. With phenylhydrazine four products are obtained:

(*a*) The *phenylhydrazine* salt of *ethyl-β-carboxypropionylacetoacetate*-bis-*phenylhydrazone*, m. p. 138°, forming colourless, unstable needles.

(*b*) A *pyrazole*, $C_{16}H_{18}O_4N_2$, the colourless crystals of which have m. p. 43°.

(*c*) A *base*, $C_{14}H_{14}O_2N_2$ or $C_{28}H_{28}O_4N_4$, m. p. 157°.

(*d*) A *product*, m. p. 214—215°, soluble in alcohol.

With hydroxylamine an iso*oxazole*, m. p. 81°, is obtained. With hydrazine the products are a *hydrazone*, m. p. 188°, and a *substance*, m. p. 118°.

Ethyl succinyldiacetoacetate was obtained as an oil; it showed a cornflower-blue coloration with sulphuric acid changing to green.

Ethyl glutaryldiacetoacetate, $CH_2[CH_2\cdot CO\cdot CH(COMe)\cdot CO_2Et]_2$, is an oil of acid properties; with phenylhydrazine it gives *glutaric acid*-bis-*phenylhydrazide*, $CH_2[CH_2\cdot CO\cdot NH\cdot NHPh]_2$, which crystallises in plates, m. p. 217—218°.

Ethyl adipyldiacetoacetate is also an oil; with phenylhydrazine, *adipic acid*-bis-*phenylhydrazide*, $C_2H_4(CH_2\cdot CO\cdot NH\cdot NHPh)_2$, is formed; it crystallises in nacreous, lustrous plates, m. p. 206—207°. E. F. A.

Preparation of Additive Compounds of Chloral with Amides. CHEMISCHE FABRIK GEDEON RICHTER (D.R.-P. 234741).—When chloral is fused with a molecular proportion of an acid amide an additive compound is produced.

*Bromo*iso*valeramide - chloral*, $CHMe_2\cdot CHBr\cdot CO\cdot NH_2,CCl_3\cdot CHO$, forms small, colourless, odourless crystals with an intensely bitter taste and m. p. 116—118° (decomp.); it is insoluble in petroleum and in water, but dissolves readily in other organic solvents, and is of therapeutic value. F. M. G. M.

Hexose Phosphoric Acid Ester. A. von Lebedeff (*Biochem. Zeitsch.*, 1911, 36, 248—260. Compare Abstr., 1910, i, 716; Young, *ibid.*, 12).—The author gives a short historical sketch of the rôle of phosphoric acid in alcoholic fermentation. A further investigation of the phenyl- and *p*-bromophenyl-hydrazones showed that the derivatives contain one molecule of hexose to two molecules of phosphoric acid, corresponding with Young's suggested formula for the phosphoric acid ester, $C_6H_{10}O_4(RPO_4)_2$. The sodium and lead salts of the osazone of the ester were prepared and analysed, the full experimental method being given, and the formulæ given by the author two years ago were confirmed. The author claims that the possibility of ascribing the correct formula given by Young is due to his own investigations, and the isolation by him of osazones and hydrazones. The paper is very controversial. S. B. S.

Preparation of Phosphoric Acid Esters of Carbohydrates and of Glycerol. Carl Neuberg and E. Kretschmer (*Biochem. Zeitsch.*, 1911, 36, 5—14).—*Calcium* d-*galactophosphate*, $C_6H_{11}O_9PCa,H_2O$, is obtained by slowly adding a solution of phosphoryl chloride in chloroform to a suspension of calcium carbonate in water containing *d*-galactose, which is stirred continuously and cooled in a freezing mixture; it is a white powder, which in solution in water reduces Fehling's solution and is fermented by beer-yeast.

Lævulose, when treated in the same manner, gave a product which consisted of a double salt of *calcium laevulosephosphate* and calcium chloride, from which the latter could not be removed. The compound was obtained, however, by partly hydrolysing calcium sucrose-phosphate by heating for fifteen minutes with dilute hydrochloric acid. It is a white powder, which gives Seliwanoff's reaction for lævulose, reduces Fehling's solution, and is readily fermented by yeast, thus differing from calcium dextrose-phosphate and sucrose-phosphate. It has the composition $C_6H_{11}O_9PCa,H_2O$.

Calcium glycerolphosphate was obtained in a similar manner to the galactophosphate. W. J. Y.

Nature of the So-called Gallisin in Commercial Starch-Syrup. Jos. Gatterbauer (*Zeitsch. Nahr. Genussm.*, 1911, 22, 265—290).—That portion of commercial starch-syrup which ferments with difficulty and to which the name gallisin has been applied consists of a new carbohydrate, together with a small quantity of maltose; dextrins are not present. This carbohydrate is termed *glucosin* provisionally, and is an isomeride of maltose, yielding only dextrose on hydrolysis. It may be separated from fermented starch-syrup as a viscous syrup, which, by treatment with a mixture of anhydrous alcohol and ether, is converted into a white or yellowish-white powder. Beer-yeast ferments glucosin slowly, whilst yeast-maltase and emulsin convert it into dextrose. Mineral acids and oxalic acid also convert glucosin into dextrose, but with high concentrations of mineral acids the reaction is reversible. The *phenylosazone*, m. p. 97—100°, is soluble in hot water and in alcohol; the p-*nitrophenylosazone*, m. p. 240°, is a red powder, which yields a blue coloration when treated with sodium hydroxide. Glucosin also yields amorphous esters with benzoyl chloride, *p*-chlorobenzoyl chloride, *m*-nitrobenzoyl chloride, and benzenesulphonyl chloride. Glucosin is formed by the action of acids on dextrose in the manufacture of starch-syrup (compare Abstr., 1905, i, 684). W. P. S.

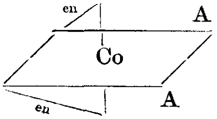
Viscosity of Cellulose Solutions. HERMANN OST (*Zeitsch. angew. Chem.*, 1911, **24**, 1892—1896).—A number of determinations of the viscosity of cuprammonium solutions of various forms of cellulose, such as cotton, wood-pulp, cotton-wool, filter paper, &c., have led the author to the conclusion that these viscosity determinations supply useful information on the nature and technical value of celluloses.

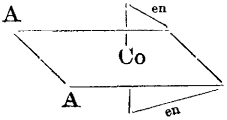
The cuprammonium solution employed was prepared by treating a solution containing 59 grams of copper sulphate with ammonium hydroxide and dissolving the basic copper sulphate thus obtained in ammonium hydroxide (D 0·900) to form one litre of solution. A quantity of cellulose was dissolved in this solution in each case so as to give a solution containing one gram of the anhydrous cellulose in 50 c.c. The viscosity was determined by means of a special form of Ostwald's capillary viscometer.

It is found that previous treatment of the cellulose with bleaching agents produces a marked decrease in the viscosity of the cuprammonium cellulose solution; the same result is brought about also by heating the cellulose for about fifteen hours at 120—125°. On the other hand, treatment of the cellulose with a cold 5% solution of sodium hydroxide for about twenty-four hours, or with a cold 20% solution for one hour, does not affect the viscosity of the solution, from which observation the conclusion is drawn that cotton does not undergo a chemical change during mercerisation. Sodium hydroxide, however, does act on cotton chemically, although very slowly, for cotton which has been soaked in a 20% solution of sodium hydroxide, pressed, and kept in a stoppered bottle for several months, dissolves very readily in a cuprammonium solution and forms a solution having a low viscosity.

Cuprammonium solutions of hydrocellulose, obtained by the action of dilute mineral acids on cellulose, are far less viscid than equivalent solutions of cellulose which have been acted on by bleaching agents. W. H. G.

The Asymmetric Cobalt Atom. II. ALFRED WERNER (*Ber.*, 1911, **44**, 2445—2455).—The author finds that compounds with complex radicles $[A_2\,Co\,en_2]$, in which the two groups A are in the *cis*-position with respect to each other, can be resolved into their optically active isomerides, which is in accordance with the space formulæ of such compounds:





This case is quite different from that reported in the previous communication (this vol., i, 613). Compounds of the type $\left[\begin{matrix}\mathrm{A}\\\mathrm{B}\end{matrix}\,\mathrm{Co\ en_2}\right]$ contain two tetrahedra, with four different groups (Co, A, B, and en), which are not mirror images of each other, since the ethylenediamine groups possess a different orientation in space in the two tetrahedra, the one being in the same plane as A, and the other in the same plane as B. This is no longer the case with compounds of the type $[\mathrm{A_2\,Co\,en_2}]$, so that they cannot be said to contain an asymmetric cobalt atom; the image and mirror image do not contain a plane of symmetry, but there occurs a kind of molecular asymmetry which the author denotes as *Molecular Asymmetry I.* It is of a simpler character than that occurring with carbon compounds, since there are only two groups, ethylenediamine and A, attached to the cobalt atom.

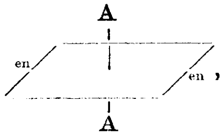
The compounds which have been resolved belong to the 1 : 2-dinitrodiethylenediamine series (the flavo-series), $\left[\begin{matrix}(1)\ \mathrm{O_2N}\\(2)\ \mathrm{O_2N}\end{matrix}\,\mathrm{Co\ en_2}\right]$, and in the course of their resolution, interesting analogies have been found with carbon compounds. When *d*-camphorsulphonic acid is used, the salt of the *l*-dinitrodiethylenediamine cobalt radicle is difficultly soluble, whilst that of the *d*-radicle is easily soluble. When *d*-bromocamphorsulphonic acid is used, the least soluble salt is that formed with the *d*-radicle. These relations are just the reverse of those which occur in the resolution of optically active carbon compounds, as, for example, in the resolution of tetrahydroquinaldine.

The active 1 : 2-dinitrodiethylenediaminecobalti-salts show a very pronounced anomalous rotation dispersion, the *D*-line being strongly rotated, whereas the *C*-line is rotated to a very small extent or not at all. In 1% solutions the following rotations were observed:

	$[\alpha]_D$.	$[M]_D$.		$[\alpha]_D$.	$[M]_D$.
Chloride	+49° −50	±153°	Bromide	+42·5° −44·0	±151°
Iodide	+34 −35	±139	Nitrate	+41·5 −41·5	±136
Perchlorate	+39 −39·5	±144	Sulphate	+45 −45	±143
d-Flavo-*d* bromocamphorsulphonate	+66	+383·5	*l*-Flavo-*d*-camphorsulphonate ...	−16	−80·32

Very great differences exist in the solubilities of the active and inactive salts, as shown by the following table, where the solubilities are expressed in terms of grams of salt in 100 c.c. of water:

Salt.	Temperature.	*d*-Isomeride.	*l*-Isomeride.	Racemate.	1 : 6-Dinitro-salts.
Nitrate	22°	4·36	4·17	1·2	2·202
Iodide	22	0·49	0·46	0·56	2·652
Sulphate	28	1·63	1·71	2·55	—

Compounds of the formula $[\mathrm{A_2\,Co\,en_2}]$, in which the A-radicles are in the *trans*-position, , should not show optical isomerism, and in proof of this it was not found possible to resolve the salts of the 1 : 6-dinitrodiethylenediaminecobalti-series (croceo-series).

The cases of isomerism which have been proved to exist in the diacido-diethylenediaminecobalti-salts may be summarised as follows :

(1) *Cis-trans*-isomerism :

$$\left[\begin{matrix}(1)\ \mathrm{O_2N}\\(2)\ \mathrm{O_2N}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{X} \quad \text{and} \quad \left[\begin{matrix}(1)\ \mathrm{O_2N}\\(6)\ \mathrm{O_2N}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{X}.$$

Flavo-salts. Croceo-salts.

(2) Salt isomerism :

$$\left[\begin{matrix}(1)\ \mathrm{ON{\cdot}O}\\(2)\ \mathrm{ON{\cdot}O}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{X} \quad \text{and} \quad \left[\begin{matrix}(1)\ \mathrm{O_2N}\\(2)\ \mathrm{O_2N}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{X},$$

1 : 2-Dinitritodiethylenediaminecobalt salts. Flavo-salts.

and also the 1 : 6-dinitritodiethylenediaminecobalt salts and the croceo-salts.

(3) Ionisation metamerism :

$$\left[\begin{matrix}\mathrm{O_2N}\\\mathrm{O_2N}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{X} \quad \text{and} \quad \left[\begin{matrix}\mathrm{O_2N}\\\mathrm{X}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{NO_2}.$$

X can be either Cl, Br, or SCN, etc.

(4) Co-ordination polymerism :

$$\left[\begin{matrix}\mathrm{O_2N}\\\mathrm{O_2N}\end{matrix}\ \mathrm{Co\,en_2}\right]_3\left[\mathrm{Co(NO_2)_6}\right] \quad \text{and} \quad \left[\mathrm{Co\,en_3}\right]\left[\mathrm{Co(NO_2)_6}\right].$$

(5) Mirror image isomerism :

$$d\text{- and } l\text{-}\left[\begin{matrix}(1)\mathrm{O_2N}\\(2)\mathrm{O_2N}\end{matrix}\ \mathrm{Co\,en_2}\right]\mathrm{X}.$$

The inactive 1 : 2-dinitrodiethylenediaminecobalt salts (compare Abstr., 1901, i, 511) are best obtained by heating together 20 grams of potassium cobaltinitrite and 48 grams of 10% ethylenediamine until the mixture begins to froth. The dark brown solution is filtered from unchanged cobaltinitrite, and on keeping deposits brownish-yellow crystals of the 1 : 2-dinitronitrite. The mother liquor, on evaporating, gives at first a further quantity of the salt, and then a mixture of the 1 : 2- and 1 : 6-dinitro-salts which can be separated by fractional crystallisation. The iodide is obtained by heating the hot solution with sodium iodide.

In the resolution of the iodide by means of silver *d*-camphorsulphonate, a precipitate of a mixture of silver iodide and *l*-1 : 2-dinitrodiethylenediaminecobalt *d*-camphorsulphonate is first obtained from the hot solution, from which mixture the camphorsulphonate may be extracted with hot water. The mother liquor from the mixture deposits a partial racemate on cooling, from which further quantities of the *l*-salt can be obtained by appropriate treatment (recrystallisation, etc.). When about 20 grams of the *l*-salt have been obtained, the mother liquors are united, the iodide precipitated, and then treated with silver *d*-bromocamphorsulphonate. After collecting the silver iodide, the hot solution, on cooling, deposits brown needles of *d*-dinitrodiethylenediaminecobalt *d*-bromocamphorsulphonate.

To prepare the various active salts, the camphor- and bromocamphor-sulphonates were precipitated with excess of sodium iodide, the aqueous suspension of the iodide transformed into the base by shaking with silver oxide, and the salts then obtained by neutralisation of the base with the respective acids.

1 : 2-d- and l-*Dinitrodiethylenediaminecobalt chlorides*, YCl, where $Y = \left[\begin{matrix}(1)\ O_2N \\ (2)\ O_2N\end{matrix}\ Co\ en_2\right]$, form brownish-yellow, columnar crystals. The racemate is deep brown in colour, and crystallises in broad, thick plates. The *bromides*, YBr, are similar in colour and shape to the chlorides. The *active iodides*, YI, give well-developed octahedral crystals, whereas the inactive salt is microcrystalline and of prismatic habit. The *active nitrates*, YNO_3, form stout, prismatic or columnar crystals, as distinguished from the long prisms of the inactive compound. The *active sulphates*, Y_2SO_4, give flat prisms or tablets, whilst the inactive salt forms long, silky, light yellow crystals. The *active perchlorates*, $YClO_4$, crystallise in aggregates of short, stout prisms or tablets, whilst the *inactive* salt gives rhombic leaflets of amber-yellow colour.

l-1 : 2-*Dinitrodiethylenediaminecobalt* d-*camphorsulphonate*,

$$Y(O_3S{\cdot}C_{10}H_{15}O),$$

forms long, flat, pointed, golden-yellow crystals. d-1 : 2-*Dinitrodiethylenediaminecobalt* d-*bromocamphorsulphonate*, $Y(O_3S{\cdot}C_{10}H_{14}OBr)$, gives flat, centimetre-long, brownish-yellow prisms. 1 : 6-*Dinitrodiethylenediaminecobalt* d-*camphorsulphonate*,

$$\left[\begin{matrix}(1)\ O_2N \\ (6)\ O_2N\end{matrix}\ Co\ en_2\right][O_3S{\cdot}C_{10}H_{15}O],$$

forms stout, amber-yellow or brownish-yellow prisms, which are often a centimetre long; $[M]_D + 45{\cdot}2$—$47{\cdot}7°$. T. S. P.

Preparation of Mercury Derivatives of Alkali Alkyldithiocarbamic Acetates.

Les Etablissements Poulenc Frères and Ernest Fourneau (D.R.-P. 235356. Compare Abstr., 1907, i, 594).—*Ethyldithiocarbaminoacetate*,

$$CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S{\cdot}NHMe{\cdot}CH_2{\cdot}CO_2Et,$$

leaflets, m. p. 70—71°, is prepared by slowly treating a cooled solution of ethyl methylaminoacetate, $CO_2Et{\cdot}CH_2{\cdot}NHMe$ (60 parts), in anhydrous ether with carbon disulphide (25 parts) in the same solvent. An energetic reaction takes place; an oil separates which rapidly solidifies, and is purified by crystallisation from ether or acetone. The *mercury* salt, $(CO_2Et{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S)_2Hg$, a pale yellow powder, is obtained when the foregoing compound is treated with a saturated solution of mercuric chloride, and this, when slowly treated with a 30% solution of sodium hydroxide (containing 2 mols. NaOH), yields a bulky, yellow precipitate of the *mercury sodium* double salt,

$$(CO_2Na{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S)_2Hg,$$

which is isolated in the form of a yellow powder. If the solution of the mercury sodium salt be heated until it darkens, a *compound*, $CO_2Na{\cdot}CH_2{\cdot}NMe{\cdot}CS{\cdot}S{\cdot}Hg{\cdot}S{\cdot}CH_2{\cdot}CO_2Na$, is obtained as a green powder. F. M. G. M.

Preparation of Optically Active Polypeptides from Racemic Compounds. EMIL ABDERHALDEN and HEINRICH GEDDERT (*Zeitsch. physiol. Chem.*, 1911, **74**, 394—408).—As a general rule, digestive ferments only hydrolyse those polypeptides which are built up from amino-acids which occur naturally. An exception is afforded by *d*-leucyl-*l*-tryptophan, which, according to Hans Fischer (Abstr., 1910, i, 22, 599), is hydrolysed by the liver and by pancreatin. Abderhalden and Schuler (Abstr., 1910, i, 304) have pointed out the possibility of racemisation in the preparation of an optically active dipeptide, and consider the hydrolysis observed by Fischer to be due to *l*-leucyl-*l*-tryptophan. The action of pressed yeast juice towards *d*-, *l*-, and *dl*-leucyl-*l*-tryptophan indicates that only *l*-leucyl-*l*-tryptophan is hydrolysed by the enzyme; the racemic compound yields a mixture of *l*-leucine, *l*-tryptophan, and *d*-leucyltryptophan; *d*-leucyl-*l*-tryptophan when pure is not attacked.

It is possible by means of enzymes to obtain optically pure polypeptides from racemic compounds; these are the opposite of the natural compounds, but a comparison of the magnitude of the rotatory power is possible.

Prepared by the action of yeast juice in this manner, *d*-leucylglycine has $[\alpha]_D^{20}$ $-87·87°$ to $-88·5°$, and glycyl-*d*-leucine, $[\alpha]_D^{20}$ $+37·62°$ to $+37·1°$, in both cases somewhat higher values than those obtained by Fischer for the optical antipodes. E. F. A.

Remarks on Henze's Paper on the History of Iodogorgonic Acid. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **74**, 290—300. Compare this vol., i, 617).—Certain misstatements contained in Henze's paper are corrected. W. D. H.

Methylated Guanidines. MARTIN SCHENCK (*Arch. Pharm.*, 1911, **249**, 463—480. Compare Abstr., 1910, i, 99, 545, 546).—The first part of this paper describes attempts to prepare *a*-methylguanidine, $NMe:C(NH_2)_2$, the second, efforts to obtain *aβ*-dimethylguanidine, $NMe:C(NH_2)·NHMe$, and the third gives an account of the preparation of some new methylated guanidines and substances related thereto. The failure to obtain *a*-methyl- and *aβ*-dimethyl-guanidines is due to the tendency these substances have to transform immediately into *β*-methyl- and *s*-dimethyl-guanidines respectively.

By the interaction of thiocarbamide and methylamine in presence of mercuric oxide, *β*-methylguanidine and dicyanodiamide are formed, the first probably by the action of cyanamide, first formed on methylamine. Ethyl iminocarbonate furnishes with methylamine, *ββ'*-dimethylguanidine; with dimethylamine, *as*-dimethylthiocarbamide (*aurichloride*, $B_2,HAuCl_4$, m. p. 105°; platinichloride, $B_2,H_2PtCl_6,2H_2O$, m. p. 115°, anhydrous), and with ammonia, guanidine. Ethyl iminocarbonate appears to undergo methylation when left fourteen days in the cold with methyl iodide and potassium hydroxide solution, since the product reacts with methylamine to form *aββ'*-trimethylguanidine, with dimethylamine to form a substance giving a crystalline aurichloride, $C_{15}H_{30}O_2N_{10}Au_2Cl_8$, m. p. 250—252°, and with ammonia in alcohol to form *β*-methylguanidine (?). With ammonia in one case a small amount of guanidine was obtained, indicating the presence of unmethylated ester in the material used. Ethyl methyliminodithiocarbonate, NMe:C(SMe)$_2$, gives with methylamine in alcohol, *αββ'*-trimethylguanidine, with ammonia in alcohol, *β*-methylguanidine, and with dimethylamine a substance yielding a crystalline aurichloride, which melted below 100°.

For the preparation of *αβ*-dimethylguanidine, NMe:C(NHMe)·NH$_2$, the following methods were tried unsuccessfully: Dimethylthiocarbamide treated with ammonia in alcohol in presence of mercuric oxide gave chiefly *αββ'*-trimethylguanidine with some *ββ'*-dimethylguanidine (compare Chancel, Abstr., 1893, i, 297). *Dimethylethyl-ψ-thiocarbamide*, NMe:C(NHMe)·SEt, in the form of its *ethiodide*, m. p. 100° (approx.), gives with ammonia in alcohol *ββ'*-dimethylguanidine (compare Noah, Abstr., 1890, 1241), and the same substance was obtained by the action of ammonia on *αββ'*-trimethyl-*ψ*-thiocarbamide.

βββ'-Trimethylguanidine aurichloride, NH:C(NHMe)·NMe$_2$,HAuCl$_4$, m. p. 153°, obtained by the addition of gold chloride to the product resulting from the interaction of methylthiocarbamide methiodide (m. p. 135—136°) and dimethylamine in alcohol, forms small needles, and is easily soluble in water.

ββ'-Dimethylthiocarbamide methiodide, m. p. 210—212°, obtained by direct combination of its two components in alcohol, gives an *aurichloride*, CS(NHMe)$_2$,CH$_3$Cl,AuCl$_3$, m. p. 122° (approx.), on treatment first with silver chloride and then with gold chloride. The similarly constituted *platinichloride* has m. p. 192—194°. The methiodide reacts with methylamine in alcohol to form *αββ'*-trimethylguanidine, which is also obtained by the action of methylamine on the corresponding ethiodide. The free trimethyl-*ψ*-thiocarbamide regenerated from the methiodide gives with ammonia in alcohol, as stated above, *ββ'*-dimethylguanidine, and with dimethylamine, *αββ'*-tetramethylguanidine, of which the *aurichloride* has m.p. 117° (approx.). T. A. H.

Melamazine from Hydrazine Salt and Dicyanodiamide.

KARL A. HOFMANN and OSKAR EHRHART (*Ber.*, 1911, **44**, 2713—2717).—Aminoguanidine nitrate may be easily and cheaply prepared from "Nitrolime" (50% calcium cyanamide) and hydrazine sulphate.

When heated with hydrazine or one of its salts, dicyanodiamide (cyanoguanidine) yields a series of hydrazine derivatives, among them a *melamazine*, (C$_3$N$_3$NH$_2$)$_2$(NH·NH)$_2$,H$_2$O, distinguished by its ability to take up oxygen in alkaline solution, giving an intensely bluish-violet colouring matter. The *hydrochloride*, C$_6$H$_8$N$_{12}$,HCl, dissolves in hot water, giving a colloidal solution. The azine exhibits only slight salt-forming capacity, as water effects partial hydrolysis and ammonia liberates the base. It is very stable towards strong acids; when heated with fuming hydrochloric acid for twenty-four hours at 170°, it is largely converted into carbon dioxide, ammonium chloride, and hydrazine hydrochloride, whilst with fuming sulphuric acid at 190° it is slowly decomposed, giving principally ammelide (melanurenic acid). Nitro-hydrochloric acid also attacks it slowly, giving ammeline nitrate. With excess of alkaline permanganate solution, it yields four atoms of nitrogen per molecule, and, if the reaction is carried to an end on the water-bath, the hydrazine groups are burnt away, whilst the cyanamide part of the molecule loses part of its ammonia and yields substances of the ammeline-ammelide group.

The bluish-violet coloration formed when an alkaline solution of the azine is left exposed to the air is visible even after dilution with 100,000 parts of water. Reducing agents, such as hydroxylamine, hydrazine, hyposulphite, and zinc dust, decolorise the solution instantly, but the colour soon returns in the air. On acidification, the violet alkaline solution becomes wine-red and then colourless, with separation of transparent, flocculent matter.

The colouring matter can be fixed on unmordanted cotton by soaking the tissue with the alkaline solution and then adding calcium chloride solution; the violet colour is changed to red by acids, even by acetic acid. The colouring matter was isolated as *barium* salt, $(C_6HO_2N_{10})_2Ba$, in the form of an opaque, violet-black powder with bronzy lustre; the *thallium* salt, $(C_6O_2N_{10})Tl_3H$, was also prepared.

In concentrated sulphuric acid melamazine gives with a nitrite or nitrate an intense yellowish-red coloration, which resembles the brucine reaction, and on warming turns to blue and then disappears with evolution of gas. Hydrogen peroxide in concentrated sulphuric acid also gives a transitory reddish-yellow coloration, whilst chromic acid yields a deep reddish-brown colour, changing to green, with evolution of gas, on heating. T. H. P.

Prussian Blue and Turnbull's Blue. III. ERICH MÜLLER [and, in part, G. WEGELIN, FREDERICK P. TREADWELL, and OTTO DIEFENTHALER] (*J. pr. Chem.*, 1911, [ii], 84, 353—369. Compare Abstr., 1909, i, 142, 705).—The composition of the precipitates obtained by mixing (0·1 molar) solutions of hydroferrocyanic acid and ferric chloride and of hydroferricyanic acid and ferrous chloride has been investigated by methods similar to those already described. The experiments on the composition of the precipitates formed from potassium ferrocyanide and ferric chloride and from potassium ferricyanide and ferrous chloride have been repeated, with results differing somewhat from those previously given.

The precipitates obtained by mixing potassium ferrocyanide and ferric chloride consist of $Fe_4'''[Fe(CN)_6]_3''''$ only when the ratio $K_4[Fe(CN)_6]/FeCl_3(=x)<0·75$. When x lies between 0·75 and 0·92 the precipitate consists of a mixture of $Fe_4'''[Fe(CN)_6]_3''''$ and $KFe'''[Fe(CN)_6]''''$, whilst as x becomes greater than 0·92, a mixture of these compounds with gradually increasing amounts of $K_2Fe''[Fe(CN)_6]''''$ is produced.

With hydroferrocyanic acid and ferric chloride, when the ratio $H_4[Fe(CN)_6]''''/FeCl_3(=y)<0·75$, the precipitate has the composition $Fe_4'''[Fe(CN)_6]_3''''$. For values of y between 0·75 and 0·85, the precipitate consists of the latter compound mixed with $HFe'''[Fe(CN)_6]''''$. When $y >0·85$ the precipitate consists of a mixture of these two compounds with $Fe_2''[Fe(CN)_6]''''$.

In the case of potassium ferricyanide and ferrous chloride, when the ratio $H_3[Fe(CN)_6]'''/FeCl_2(=z)<0·714$, $KFe_2''Fe_5'''[Fe(CN)_6]_5''''$ is produced. For values of z lying between 0·714 and 0·75, this is accompanied by $KFe''Fe_3'''[Fe(CN)_6]_3''''$. When z varies from 0·75 to 0·9, the precipitate consists of a mixture of $KFeFe_3'''[Fe(CN)_6]_3''''$ and $KFe'''[Fe(CN)_6]''''$, whilst for values of $z > 0·9$, the two latter compounds are accompanied by $Fe_4'''[Fe(CN)_6]''''$, produced according to the equation: $4KFe'''[Fe(CN)_6]'''' = Fe_4'''[Fe(CN)_6]'''' + K_4[Fe(CN)_6]''''$.

Similar results were obtained in the case of ferrous chloride and hydroferricyanic acid. When the ratio $H_3[Fe(CN)_6]'''/FeCl_2 < 0·75$, the precipitate consists of a mixture of $HFe_2''Fe_5'''[Fe(CN)_6]_5''''$ and $HFe''Fe_3'''[Fe(CN)_6]_3''''$; if the ratio $> 0·78$, a mixture of the latter compound with $HFe'''[Fe(CN)_6]''''$ and $Fe_4'''[Fe(CN)_6]_3''''$ is produced.

F. B.

Oxidation of Hydrazine. VI. Reaction between Mercuric Oxide and Hydrazine Hydrate in Alcoholic Solution. C. F. HALE and V. E. NUNEZ (*J. Amer. Chem. Soc.*, 1911, **33**, 1555—1563).—Browne and Shetterly (Abstr., 1909, ii, 658) have shown that when an aqueous solution of hydrazine sulphate is heated with either yellow or red mercuric oxide, neither ammonia nor azoimide is produced, but that if the yellow oxide is added gradually to a slightly alkaline solution of the salt at 0°, both ammonia and azoimide are formed in appreciable quantities.

A study has now been made of the action of mercuric oxide on an alcoholic solution of hydrazine hydrate, and it has been found that at the ordinary temperature the reaction proceeds in accordance with the equation $N_2H_4,H_2O + 2HgO = N_2 + 2Hg + 3H_2O$. The amount of nitrogen actually obtained was slightly less than that required by this equation. Neither ammonia nor azoimide was produced, but indications were obtained of the formation of ethylideneazine. Mercury diethyl was also found to be a product of the reaction, together with a white, waxy, solid compound containing carbon, hydrogen, and about 55% of mercury. The latter substance has a strong odour, resembling that of garlic, does not show a definite m. p., and when applied to the skin produces painful and slow-healing burns. The same compound is slowly produced by the action of diffused daylight on mercury diethyl.

E. G.

The Constitution of Aliphatic Diazo-compounds and of Azoimide. JOHANNES THIELE (*Ber.*, 1911, **44**, 2522—2525).—A theoretical paper in which arguments are brought forward in favour of a hydrazone formula for certain products of the action of hydrazine on ketones and of the formula $HN{:}N{:}N$ for azoimide.

H. W.

Tetra-alkylsilicanes. ARTUR BYGDÉN (*Ber.*, 1911, **44**, 2640—2652).—A thorough examination of the action of magnesium alkyl halides on silicon tetrachloride shows that the mono-alkyl derivatives, $SiRCl_3$ (where R is ethyl, propyl, butyl, *iso*butyl, or *iso*amyl), and tetra-alkylsilicanes are obtained with comparative ease, but the separation of the dialkyl and trialkyl derivatives presents great difficulties, and these substances have not been obtained pure. Magnesium methyl bromide is a more efficient reagent than the iodide, and by its means tetramethylsilicane, b. p. 26—27°, is easily obtained.

The following substances have been prepared by the usual Grignard reaction; the desired product is finally separated from its ethereal solution by treatment with concentrated sulphuric acid, in which the ether (and usually a small quantity of unexamined silicon derivatives) dissolves, leaving the desired product, which is removed by distillation. *Trimethylpropylsilicane*, $SiMe_3Pr$, b. p. 89·5° (corr.), D_4^{15} 0·7063, from trichloropropylsilicane and magnesium methyl bromide (3·3 mols.); *dimethyldiethylsilicane*, $SiMe_2Et_2$, b. p. 95·8° (corr.), D_4^{15} 0·7214, from dichlorodiethylsilicane and magnesium methyl iodide (2·5 mols.); *trimethylbutylsilicane*, b. p. 115·1° (corr.), D_4^{15} 0·7227, from trichlorobutylsilicane and magnesium methyl bromide (3·2 mols.); *dimethylethylpropylsilicane*, b. p. 121·0° (corr.), D_4^{15} 0·7347, from dichloroethylpropylsilicane and magnesium methyl bromide (2·3 mols.); *trimethyl*iso*amylsilicane*, b. p. 131·5° (corr.), D_4^{15} 0·7322, from trichloro*iso*amylsilicane and magnesium methyl bromide (3·2 mols.); *dimethylethyl*iso*butylsilicane*, b. p. 138·0° (corr.), D_4^{15} 0·7463, from dichloroethyl*iso*butylsilicane and magnesium methyl bromide (2·3 mols.).

Tetra-ethylsilicane has b. p. 153·0° (corr.), and D_4^{15} 0·7694.

The preceding tetra-alkylsilicanes have an odour of petroleum, are almost unattacked by concentrated sulphuric acid or alkalis, are oxidised by concentrated nitric acid at a high temperature, react with chlorine in the cold and with bromine by warming, and explode when their mixture with air or oxygen is heated. The b. p. is lower and the molecular volume (of isomerides) is greater, the larger is the number of methyl groups directly attached to the silicon atom.

The new chlorosilicanes required in the preceding syntheses are: *trichlorobutylsilicane*, $C_4H_9·SiCl_3$, b. p. 148·5—149·5°, D_4^{15} 1·169, from magnesium butyl bromide and silicon tetrachloride; *trichloro*iso*butylsilicane*, b. p. 138—143°, D_4^{15} 1·161, prepared like the preceding compound; *dichloroethylpropylsilicane*, b. p. 152—158°, D_4^{15} 1·048, from trichloropropylsilicane and magnesium ethyl bromide; *dichloroethyl*iso*butylsilicane*, b. p. 165—174°, from trichloro*iso*butylsilicane and magnesium ethyl bromide. C. S.

Organo-metallic Ester Compounds. I. Iodostanni-ester Compounds. Bruno Emmert and Wilhelm Eller (*Ber.*, 1911, **44**, 2328—2330).—Tin reacts with ethyl iodoacetate in presence of iodine to form ethyl di-iodostanni-diacetate, $SnI_2(CH_2·CO_2Et)_2$. Compounds of this type differ from the alkyl compounds of the metals in being completely decomposed by water and alkalis, thus:

$$SnI_2(CH_2·CO_2Et)_2 + 2H_2O = 2CH_3·CO_2Et + SnO_2 + 2HI.$$

They appear to yield salts when treated with silver nitrate or sulphate, but so far these have not been separated from their decomposition products. Treated with the Grignard reagent they give the corresponding tin tetra-alkyls.

Ethyl di-iodostanni-diacetate, m. p. 101·5° (corr.), crystallises from carbon tetrachloride on addition of ether in colourless, odourless needles. It is decomposed by baryta into ethyl acetate, stannic oxide, and hydriodic acid. With magnesium phenyl bromide and magnesium ethyl bromide, it gives tin tetraphenyl and tin tetraethyl respectively.

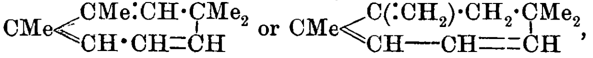
*Ethyl di-iodostanni-di-*o*-benzoate*, obtained by heating ethyl *o*-iodobenzoate (5 grams), tin foil (1·2 grams), and a little iodine, in a closed tube during five days at 150°, crystallises in greyish-yellow, microscopic needles, and is practically insoluble in all solvents. T. A. H.

$\Delta^{1:3}$-Dihydrobenzene [$\Delta^{1:3}$-*cyclo*Hexadiene]. NICOLAI ZELINSKY and ALEXANDER GORSKY (*Ber.*, 1911, **44**, 2312—2316[*]).—Doubts have been expressed by Brühl (Abstr., 1908, ii, 1002) and by Harries and von Splawa-Neyman (Abstr., 1909, i, 218) as to the accuracy of the data published by the authors regarding $\Delta^{1:3}$-*cyclo*hexadiene (Abstr., 1908, i, 619, 722), the latter suggesting that the apparent absence of optical exaltation in this hydrocarbon, in spite of the presence of conjugated double linkings, was due to the occurrence of *cyclo*hexene in the material examined. The authors find that when quinoline reacts with 1 : 2-dibromo*cyclo*hexane, the products obtained depend on the relative quantities used and the method of mixing. When the dibromo-derivative is added drop by drop to quinoline in excess, the product is a mixture of *cyclo*hexadiene and *cyclo*hexene, but the material they originally worked with could not have contained more than a trace of *cyclo*hexene. Further, determinations of the molecular refractions of mixtures of $\Delta^{1:3}$-dihydro-*m*-xylene (Klages, Abstr., 1907, i, 597) with 1 : 3-dimethyl*cyclo*hexene (Abstr., 1902, i, 2) show that the latter does not mask the optical exaltation of the former to any considerable extent. Moreover, the ultra-violet absorption spectra of the two *cyclo*hexadienes examined by the authors (*loc. cit.*) are normal and similar, indicating that the hydrocarbon now under discussion is homogeneous.

Bromo-Δ^1-cyclo*hexene*, b. p. 164—166°, or 69°/35 mm., D_4^{20} 1·3901, n_D^{20} 1·5134, obtained as a by-product in the action of quinoline on 1 : 2-dibromo*cyclo*hexane, combines with bromine to form a *dibromide*, b. p. 138—140°/16 mm., and is oxidised by permanganate to adipic acid.

$\Delta^{1:3}$-*cyclo*Hexadiene combines with hydrogen bromide to form a hydrobromide, b. p. 80—85°/39 mm. This combines with bromine to form a *tribromide*, b. p. 150°/15 mm., and is oxidised by permanganate to a dibasic hydroxy-acid, $C_6H_{10}O_5$, m. p. 93—94°, which distils almost unchanged at 240°/20 mm. The formation of this dibasic hydroxy-acid on oxidation renders improbable the constitution assigned to this hydrobromide by Crossley (Trans., 1904, **85**, 1422). T. A. H.

Tetramethyl*cyclo*heptatriene. HANS RUPE and W. KERKOVIUS (*Ber.*, 1911, **44**, 2702—2713).—The action of magnesium methyl iodide on eucarvone yields a tetramethyl*cyclo*heptatriene,



$$CMe{<}\begin{matrix}CMe{:}CH{\cdot}CMe_2\\ CH{\cdot}CH{=}CH\end{matrix} \text{ or } CMe{<}\begin{matrix}C({:}CH_2){\cdot}CH_2{\cdot}CMe_2\\ CH{-}CH{=}CH\end{matrix},$$

which is a tetramethyl derivative of the *cyclo*heptatriene prepared by Ladenburg (Abstr., 1883, 670) and Willstätter (Abstr., 1901, i, 223, 649). In one instance the corresponding *tertiary alcohol*, b. p. 96—97°/11 mm., was also obtained, but this could not be obtained pure, as it undergoes partial decomposition on distillation with formation of the tetramethyl*cyclo*heptatriene. Further, a slight variation in the method of preparing the latter results in its admixture with two dimeric, isomeric methyl derivatives of dihydroeucarvone $(C_{11}H_{18}O)_2$.

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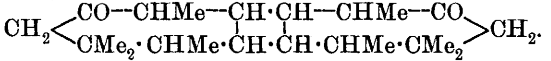
[*] and *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1102—1107.

*Tetramethyl*cyclo*heptatriene*, $C_{11}H_{16}$, is a colourless, mobile oil, b. p. 67—68°/11 mm., D^{20} 0·8687, n_D^{20} 1·50660. The optical exaltation (compare Auwers and Eisenlohr, Abstr., 1910, ii, 365, 367), +0·9, is exactly what is observed for a pair of conjugated ethylene linkings with a side-chain at one of the end carbon atoms; the fact that the three conjugated double linkings of the above formulæ do not give a considerably higher exaltation than 0·9 seems to be a new proof for the assumption made by Auwers and Eisenlohr (*loc. cit.*) that central disturbances (side-chains) may partly or completely annul the optical anomaly of a conjugated linking. It is more stable than methylmenthatriene (compare Rupe and Liechtenhan, Abstr., 1906, i, 374), and yields a *dihydrobromide*, $C_{11}H_{18}Br_2$. When reduced by sodium in amyl alcohol solution, it yields a mixture of di- and tetra-hydro-derivatives, whilst in ethyl alcohol, it gives the pure dihydro-compound, *tetramethyl*cyclo*heptadiene*, $C_{11}H_{18}$, b. p. 64·5—65·5°/12 mm., D^{20} 0·8491, n_D^{20} 1·47643. Which pair of conjugated double linkings is thus easily reduced is not known.

The two methyl derivatives of dihydroeucarvone have the following properties: (*A*) The less readily soluble form gives shining, white, monosymmetric leaflets, m. p. 177—178°. That its *oxime*, $C_{11}H_{19}ON$, decomposing at 265°, and its *semicarbazone*, decomposing at 259°, and also those of compound *B*, are likewise dimeric is indicated by the high melting points. (*B*) This modification forms four-sided, prismatic crystals, m. p. 142—143°; its *oxime* is found to be a mixture of two compounds, m. p.'s 204—205° and 265° respectively, the latter being identical with the oxime of *A*. Unlike eucarvone, the compounds *A* and *B* decolorise permanganate in acetic acid solution only after some minutes; the conclusion is hence drawn that these compounds contain no ethylene linking, and that they are probably stereoisomerides of the structure:



$$CH_2{<}\begin{matrix}CO{-}CHMe{-}CH\cdot CH{-}CHMe{-}CO\\ CMe_2\cdot CHMe\cdot CH\cdot CH\cdot CHMe\cdot CMe_2\end{matrix}{>}CH_2.$$

These results render it highly probable that methylmenthatriene contains two conjugated double linkings. T. H. P.

Δ^3-Butenylbenzene. C. N. Riiber (*Ber.*, 1911, 44, 2391—2393).—Attempts to prepare Δ^3-butenylbenzene, $C_6H_5\cdot CH_2\cdot CH_2\cdot CH{:}CH_2$, have previously given only Δ^2-butenylbenzene. On condensing allyl bromide and benzyl chloride by means of sodium, it is now shown that, in addition to diallyl and dibenzyl, a hydrocarbon, b. p. 64°/10 mm., is formed. This is proved to be Δ^3-*butenylbenzene*, since it yields phenylpropionic acid when oxidised by permanganate in acetone.

The hydrocarbon is a mobile, strongly refractive and dispersive liquid, with an odour similar to that of cress leaves; it has D_4^{20} 0·8831, n_D^{20} 1·5059. E. F. A.

Preparation of 2:4:6-Trinitrobenzene from Halogenated Trinitrobenzenes. Jacob. Meyer (D.R.-P. 234726).—When 1-chloro-2:4:6-trinitrobenzene is vigorously boiled during two hours with finely divided copper in a neutral solvent (such as alcohol), the chlorine is eliminated and pure 2 : 4 : 6-trinitrobenzene separates from the cooled solution. The metals capable of reacting in this manner are copper, zinc, magnesium, brass, iron, or aluminium, whilst methyl, ethyl, or amyl alcohols, benzene, acetone, or ether can be employed as solvent. F. M. G. M.

Barium Oxide as a Reducing Agent. Reduction of Nitrobenzene to Nitroso- and Azo-benzene, Aniline, Phenazine, and Ammonia. TH. ZEREWITINOFF and IWAN VON OSTROMISSLENSKY (*Ber.*, 1911, **44**, 2402—2409).—When nitrobenzene vapour is passed over a layer of barium oxide heated in a tube at 230°, nitrosobenzene is at first formed, but the reduction goes further, and, in addition to the chief product, azobenzene, considerable quantities of phenazine and aniline and traces of ammonia are formed. Nitrobenzene is unchanged when passed over heated coal or pumice, and also when calcium or strontium oxide is substituted for barium oxide.

p-Nitrotoluene under similar conditions gives *p*-toluidine and a crystalline, yellowish-red azotoluene, m. p. 139°. *o*-Nitrotoluene gives exclusively *o*-toluidine. *m*-Dinitrobenzene is not altered by barium oxide.

With barium hydroxide and nitrobenzene only aniline and phenazine are formed.

The formation of nitroso- and azo-benzene is due to the tendency of barium to form peroxide.

The following new double compounds of phenazine are described: *phenazine-quinol*, $C_6H_4(OH)_2,2C_{12}H_8N_2$, forms orange-yellow needles, m. p. 232° (decomp.); *phenazine-resorcinol*, $C_6H_4(OH)_2,2C_{12}H_8N_2$, forms bright yellow needles, m. p. 213·5°; *phenazine-catechol* crystallises in stellate aggregates of bright yellow needles m. p. 184°. E. F. A.

Quantitative Investigation of the Sulphonation of Toluene. ARNOLD F. HOLLEMAN and P. CALAND [with T. VAN DER LINDEN and J. P. WIBAUT] (*Ber.*, 1911, **44**, 2504—2522).—The quantities of *o*-, *m*-, and *p*-toluenemonosulphonic acids formed by the action of sulphuric acid on toluene under various conditions have been investigated. The method consisted in sulphonation of the toluene and transformation of the mixture of sulphonic acids into the corresponding sulphonyl chlorides. The composition of the latter mixture was deduced from its first and second melting points.

The influence of temperature, concentration of acid, and amount of acid was investigated. Increase of temperature favoured the production of para- and meta-acid at the expense of ortho-acid. Concentration of acid, between the limits of 96% and 100%, appeared to be without influence. Increase in the amount of acid favoured the production of ortho-acid at low temperatures, but this influence was masked at higher temperatures by the effect due to rise of the latter.

The presence of *m*-toluenesulphonic acid among the products of the sulphonation of toluene has been definitely proved by the isolation of *m*-toluenesulphonamide (m. p. 107°).

The addition of potassium sulphate, mercurous sulphate, and silver sulphate has been shown to have no influence on the course of sulphonation.

The action of chlorosulphonic acid on toluene has also been studied. *p*-Toluenesulphonic acid is again the main product.

The possible interconversion of the isomeric toluene monosulphonic acids has been investigated. *m*-Toluenesulphonic acid was found unaltered after being heated with sulphuric acid during six hours at 100°. At 35° and at 75°, the transformation of ortho- and para-acids into one another occurs very slowly. At 100° this action has a certain influence on the relative proportion of acids formed during sulphonation. H. W.

Preparation of Chloroalkylarylsulphonyl Chlorides. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234913).—When derivatives of *p*-toluenesulphonyl chloride are treated with phosphorus pentachloride and chlorine introduced at a temperature of 120—140°, chlorination takes place in the side-chain, yielding the corresponding chlorobenzyl derivatives.

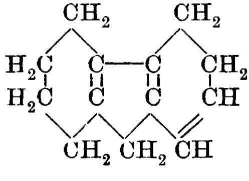
*ω-Chlorotoluene-*p*-sulphonyl chloride*, $C_7H_6O_2Cl_2S$, colourless needles, m. p. 64—65°, b. p. 183—185°/15 mm., was obtained from *p*-toluenesulphonyl chloride; and *m*-toluenesulphonyl chloride furnished *ω-chlorotoluene-*m*-sulphonyl chloride*, colourless crystals, m. p. 65°, b. p. about 190°/21 mm.

*ω-2-Dichlorotoluene-*p*-sulphonyl chloride*, a colourless oil, b. p. 185—190°/15·5 mm., was obtained from *o*-chlorotoluene-*p*-sulphonyl chloride, whilst 6-chlorotoluene-3-sulphonyl chloride furnished *ω-6-dichlorotoluene-3-sulphonyl chloride*, colourless crystals, b. p. 182—186°/14 mm. F. M. G. M.

Preparation of a Mixture of 1 : 4- and 1 : 5-Dichloronaphthalenes. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234912).—The preparation of dichloronaphthalenes has not in the past been technically satisfactory; it is now found that by working at low temperatures and in the presence of a halogen carrier that a mixture containing over 80% of 1 : 4- and 1 : 5-dichloronaphthalenes is obtained, the remainder consisting of the 1 : 2- and 1 : 7-isomerides. The naphthalene, accompanied by some freshly sublimed ferric chloride, is treated in carbon tetrachloride solution with chlorine at – 10° to 0°; on fractional distillation the greater part distils at 170—190°/40 mm., and when crystallised from alcohol furnishes a colourless, crystalline powder (m. p. 50—60°) consisting of the 1 : 4- and 1 : 5-dichloronaphthalenes.

An alternative separation is to treat the crude mixture with sulphuric acid at the ordinary temperature during twenty hours, when the 1 : 4- and 1 : 5-derivatives remain unchanged, whereas the isomerides are converted into soluble sulphonic acids. F. M. G. M.

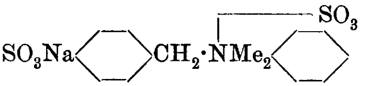
A Constituent of Coal. AMÉ PICTET and LOUIS RAMSEYER (*Ber.*, 1911, **44**, 2486—2497).—A French gas coal from Montrambert was extracted with boiling benzene and also submitted to distillation under diminished pressure. The extract and distillate were fractionated and shown to contain hexahydrofluorene. On fractionating the extract it was found impossible to obtain fractions of constant boiling point, since the lower boiling fractions readily polymerise. In all fractions, analysis showed the ratio C : H to be the same. For investigation, a fraction was used having a b. p. 110—120°/10 mm., 240—250°/ordinary pressure, and D^{20} 0·920. This, when passed through a red-hot tube, yielded fluorene, m. p. 112—113°. When treated with bromine in carbon disulphide solution, dibromofluorene, m. p. 166—167°, was formed, whilst when placed in a desiccator with bromine, it became converted into monobromofluorene, m. p. 101—102°. On oxidation with potassium permanganate, acetic, adipic, and oxalic acids were formed. Nitration yielded a mixture of products from which, on reduction and benzoylation, a dibenzoyldiaminotetrahydrofluorenol, m. p. 150°, was obtained. From the above experiments the annexed formula is proposed for hexahydrofluorene. When distilled under diminished pressure at a temperature not exceeding 450°, the same coal yielded a series of more complex fractions in which the ratio C : H was not constant. H. W.



Triphenylmethyl Peroxide. The Chemistry of Free Radicles. Heinrich Wieland (*Ber.*, 1911, **44**, 2550—2556).—Elaborating his conception, already applied to ·NPh_2 and ·CPh_3 (this vol., i, 569), that a free radicle R, containing hydrogen, reacts by intermolecular autoreduction and autoxidation in accordance with the scheme $4(R^{-H})H \longrightarrow 2RH + (R^{-H})_2$, the author suggests that peroxides may dissociate thus: $R·O·O·R \longrightarrow 2R·O·$; the resulting radicle may or may not react further, as in the preceding scheme; thus the spontaneous decomposition of triphenylmethyl peroxide in boiling xylene is assumed to result in the formation of the radicle $CPh_3·O·$. A small portion of this is converted into triphenylcarbinol, but the bulk of it, 60—70%, undergoes rearrangement to phenoxydiphenylmethyl, $OPh·CPh_2·$, by the polymerisation of which diphenylbenzpinacone, the chief product of the decomposition of the peroxide, is formed. *Benzpinaconediphenyl ether*, $OPh·CPh_2·CPh_2·OPh$, forms colourless plates, and has m. p. about 196°, darkening at 135°, by the usual process, but when heated in carbon dioxide, it becomes yellow at 150° and melts at 215° to a garnet-red liquid. When reduced by zinc and boiling acetic acid, it is converted into phenol and benzhydryl acetate, together with a little *substance*, m. p. 198°, which probably has the constitution $OPh·CPh_2·C_6H_4·CHPh·OPh$.

When heated at 230—240° in the absence of air, benzpinaconediphenyl ether undergoes the reverse change to phenoxydiphenylmethyl, which, in accordance with the preceding scheme (except that the phenoxy-group wanders instead of a hydrogen atom), is converted into tetraphenylethylene and *diphenoxydiphenylmethane*, $CPh_2(OPh)_2$, m. p. 132°; the latter is readily hydrolysed to phenol and benzophenone by boiling acetic and concentrated hydrobromic acids. Since a little phenol and benzophenone are obtained by the depolymerisation of benzpinaconediphenyl ether by heat, especially in boiling xylene, it is probable that a portion of the phenoxydiphenylmethyl suffers the normal autoreduction and autoxidation, yielding substances from which the phenol and benzophenone are produced. C. S.

Preparation of Phenylbenzyldimethylammoniumdisulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 234915 and 234916).—*Sodium phenylbenzyldimethylammoniumdisulphonate* (annexed formula), a yellow, hygroscopic powder, is prepared by heating sodium benzylmethylanilinedisulphonate with methyl sulphate at 50°, and subsequently evaporating under reduced pressure; when heated with aqueous ethylaniline, it furnishes benzylethylanilinesulphonic acid and dimethylaniline-3-sulphonic acid (dimethylmetanilic acid). The second patent states that the methyl sulphate can be replaced by methyl *p*-toluenesulphonate (or other methyl esters), in which case calcium benzylmethylanilinedisulphonate in the presence of calcium carbonate (or hydroxide) is employed, and the mixture heated at 60°; after separation of the toluenesulphonic acid by known methods, *calcium phenylbenzyldimethylammoniumdisulphonate* is obtained as a yellow powder, which is readily soluble in water. F. M. G. M.



Kinetics of Ammonium Salts. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1911, **77**, 719—734).—Polemical against Wedekind and Paschke (compare Abstr., 1909, ii, 722; Wedekind and Paschke, Abstr., 1908, i, 723; this vol., i, 628). The contention of these investigators that the rate of decomposition of dissolved quaternary ammonium salts is related to the dissociating power of the solvent is not valid. As already pointed out (*loc. cit.*), the reactions are relatively slow in solvents containing hydroxyl groups. The influence of the corresponding nitrate on the rate of decomposition of *d*-phenylbenzylmethylpropylammonium iodide is much smaller than Wedekind and Paschke state, and an alternative explanation of this effect is given. The very small temperature-coefficient (1·02 for a rise of temperature of 10°) given by these authors for the rate of formation of a quaternary ammonium salt is due to experimental error; the true value is 1·7.

Phenylbenzyldiethylammonium iodide forms a crystalline compound with chloroform, and *p*-bromophenylbenzyldimethylammonium iodide a similar compound with bromoform, which contains a molecule of the solvent. In contrast to solutions in chloroform, quaternary ammonium salts are only slightly polymerised in tetrachloroethane. G. S.

The Metallic Salts of Trinitrophenols and Trinitrocresols. HERMANN KAST (*Zeitsch. ges Schiess-sprengstoffwesen*, 1911, **6**, 7—9, 31—34, 67—70. Compare *Annalen*, 1843, **48**, 336; *Zeitsch. Chem.*, 1865, 189).—A description of the preparation of the following compounds in crystalline form, with special details as to their explosive qualities.

Salts of picric acid.—Potassium, ammonium, and sodium: reddish-yellow needles, the latter containing one molecule of water of crystallisation.

Calcium, $(C_6H_2O_7N_3)_2Ca,3H_2O$ (also 5 or $10H_2O$); barium, $(C_6H_2O_7N_3)_2Ba,3$ or $5H_2O$; magnesium, $(C_6H_2O_7N_3)_2Mg,3H_2O$ (also 5 or $8H_2O$), two mols. of which persist until 130°, and zinc, $(C_6H_2O_7N_3)_2Zn,8H_2O$ (also 2, 6 or $9H_2O$), two mols. of which persist until 130°, all form reddish-yellow needles. Ferrous,

$$(C_6H_2O_7N_3)_2Fe,7 \text{ or } 8H_2O,$$

transparent, green leaflets. *Ferric*, $(C_6H_2O_7N_3)_3Fe,11H_2O$, reddish-yellow crystals. *Cuprous*, $(C_6H_2O_7N_3)_2Cu,5H_2O$ (also 4 or $11H_2O$), two mols. of which persist until 130°, forms small, greenish-yellow needles. *Silver*, reddish-yellow, glistening needles unstable in light. *Aluminium*, $(C_6H_2O_7N_3)_2Al(OH),7H_2O$, small, reddish-yellow needles. *Lead*, $(C_6H_2O_7N_3)_2Pb,1$ or $4H_2O$, a yellow, crystalline powder.

Salts of trinitrocresol.—Potassium, $C_7H_4O_7N_3K$. *Sodium*,

$$C_7H_4O_7N_3Na,2H_2O,$$

small, yellow needles. *Ammonium* and *calcium*, $(C_7H_4O_7N_3)_2Ca,4H_2O$, reddish-yellow needles. *Barium*, $(C_7H_4O_7N_3)_2Ba,H_2O$, small, sulphur-yellow leaflets. *Magnesium* and *zinc*, reddish-yellow powders, with $6H_2O$, three of which in the zinc salt persist until 130°. *Cuprous*, $(C_7H_4O_7N_3)_2Cu,2H_2O$, small, greenish-yellow needles, is stable until 130°. Silver, reddish-yellow needles (compare Abstr., 1885, 531). *Aluminium*, $(C_7H_4O_7N_3)_2Al(OH),5H_2O$, reddish-yellow needles, darkening in sunlight. *Lead*, $(C_7H_4O_7N_3)_2Pb,H_2O$, sulphur-yellow leaflets. *Ferrous*, $(C_7H_4O_7N_3)_2Fe,2H_2O$, glistening, greenish-yellow needles, and *ferric*, brown crystals, decomposed by boiling water. F. M. G. M.

Preparation of 4-Chloro-6-nitro-2-aminophenol. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234742).—When 4-chloro-2-acetylaminophenol is treated with dilute nitric acid, 4-*chloro*-6-*nitro*-2-*acetylaminophenol*, m. p. 150—160°, is produced, which when hydrolysed by alkali hydroxides yields 4-chloro-6-nitro-2-aminophenol as a yellowish-brown powder. F. M. G. M.

Derivatives of 1:2-Dimethylbenzene [*o*-Xylene]. II. EMIL DIEPOLDER (*Ber.*, 1911, **44**, 2498—2503. Compare Abstr., 1909, i, 786).—The phenylhydrazone of the *o*-4:5-xyloquinone described previously, when treated with sodium hyposulphite in alcoholic solution, yields 5-amino-*o*-4-xylenol; the *acetyl* derivative crystallises in thin plates, which sinter at 184°, m. p. 190·5—191°, and when heated gives 5-*vinylideneamino*-o-4-*xylenol*, white needles, m. p. 93—94°.

5-*Acetylamino*-o-4-*xylenyl acetate* forms fine, white, silky needles, m. p. 156—157°, and 5-*diacetylamino*-o-4-*xylenyl acetate* crystallises in hexagonal plates, m. p. 100·5—101·5°.

o-Aminophenol when treated with acetic anhydride and sodium acetate yields o-*diacetylaminophenyl acetate* in long, colourless needles, m. p. 78—79°.

4:5-*Dihydroxy*-m-*xylene*, obtained by the reduction of *o*-4:5-xyloquinone with aqueous sulphurous acid or sodium hyposulphite, forms colourless, slender prisms sintering at 85°, m. p. 87—88°.

Attempts to prepare a colourless modification of *o*-4:5-xyloquinone were fruitless. H. W.

Chloroguaiacols. TEMISTOCLE JONA and G. B. POZZI (*Gazzetta*, 1911, **41**, i, 722—737).—5-*Aminoguaiacol hydrochloride*, $C_7H_{10}O_2NCl$, from 5-nitro-1-acetylguaiacol (compare Cousin, Abstr., 1899, i, 200) forms pale greenish-white crystals. 5-*Aminoguaiacol*, $C_7H_9O_2N$, was obtained in grey crystals, m. p. 125—127°, which were not quite pure; it gives a reddish-brown coloration with ferric chloride. 5-*Benzoylaminoguaiacol benzoate*, $C_{21}H_{17}O_4N$, forms colourless crystals, m. p. 162—164°, and does not give a coloration with ferric chloride. 5-*Acetylaminoguaiacol*, $C_9H_{11}O_3N$, forms colourless crystals, m. p. 116—119°, and gives the phenol reaction with ferric chloride. 5-*Chloroguaiacol*, $C_7H_7O_2Cl$, obtained by the Sandmeyer reaction from aminoguaiacol, has b. p. 237—239°/760 mm. (corr.), m. p. 161—163·5°. It gives a yellow coloration with ferric chloride. 5-*Chloroguaiacol benzoate*, $C_{14}H_{11}O_3Cl$, crystallises in long, colourless needles, m. p. 56—58°. 5-*Chloroguaiacol acetate*, $C_9H_9O_3Cl$, crystallises in colourless leaflets, m. p. 42—44°. 5-*Chloroguaiacolethyl ether*, $C_9H_{11}O_2Cl$ (prepared with ethyl iodide), forms colourless crystals, m. p. 49—51°.

4-Aminoguaiacol acetate is obtained by reducing with phenylhydrazine the acetyl derivative of benzeneazoguaiacol.

4-*Acetylaminoguaiacol*, $C_9H_{11}O_3N$ (from 4-aminoguaiacol), forms colourless crystals, m. p. 111—113°, and gives the phenol reaction with ferric chloride. 4-*Chloroguaiacol*, $C_7H_7O_2Cl$ (prepared by the Sandmeyer reaction from 4-aminoguaiacol acetate), is a colourless, crystalline substance, m. p. 158—161°, b. p. 241—243°/760 mm. (corr.). Its *benzoyl* derivative, $C_{14}H_{11}O_3Cl$, crystallises in colourless scales having a mother-of-pearl lustre, m. p. 79—80°.

The benzoyl derivative of chloroguaiacol obtained by Peratoner and Ortoleva (Abstr., 1898, i, 641) had m. p. 76—77°, and was probably identical with the derivative just described. R. V. S.

Preparation of 1:4-Dihydroxynaphthalene Monoalkyl Ethers. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P 234411).—A satisfactory yield of 1:4-dihydroxynaphthalene monoalkyl ethers can be obtained by heating 4-amino-α-naphthol hydrochloride with alcohol during twelve hours at 170—180°. When methyl alcohol is employed under these conditions, 200 parts of the aminonaphthol yield 120—130 parts of the *monomethyl ether*, reddish-white crystals, m. p. 131°. F. M. G. M.

Some Derivatives of Hydroxyquinol. IV. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 18—25. Compare this vol., i, 68, 305).—In the course of attempts to demonstrate the structure of 2:4:5-trimethoxypropiophenone and of its dimethyl ether, previously described, the authors have prepared some new derivatives of these substances. Trimethoxypropiophenone is not acted on by bromine and sodium hydroxide (compare Störmer and Wehln, Abstr., 1903, i, 40).

Hydroxyquinol trimethyl ether may be prepared with good yield by the action of methyl sulphate on triacetylhydroxyquinol, a concentrated solution of sodium hydroxide being added in small portions. Hexamethoxydiphenyl is not formed when the reaction is carried out in this way.

The 2-hydroxy-4 : 5-dimethoxypropiophenone previously mentioned crystallises in small, colourless needles, m. p. 124—126° (softening at 120°). The *acetyl* derivative, $C_{13}H_{16}O_5$, also crystallises in needles, m. p. 117—118°. The *benzoyl* derivative, $C_{18}H_{18}O_5$, forms long needles, m. p. 110—111°

2 : 4 : 5-*Trimethoxypropiophenonephenylhydrazone* has m. p. 113°. 2 : 4 : 5-*Trimethoxypropiophenonemonoxime* (prepared with amyl nitrite), $C_{12}H_{15}O_5N$, crystallises in scales having a slight yellowish-green colour, and has m. p. 146—148°. It gives a deep reddish-brown coloration with an alcoholic solution of nickel acetate. When it is treated with hydroxylamine hydrochloride the *dioxime*, $C_{12}H_{16}O_5N_2$, is formed, which crystallises in prismatic needles, m. p. 206—207°. An alcoholic solution of the substance yields with an alcoholic solution of nickel acetate a bright red precipitate; with ammonium palladichloride it gives a pale yellow substance; with ferrous sulphate in the presence of pyridine an intense red coloration and a red precipitate are produced. The substance seems, therefore, to be a *syn*dioxime (compare Tschugaeff, Abstr., 1908, i, 554). When the above monoxime is treated with phenylhydrazine, the *oxime-phenylhydrazone*, $C_{18}H_{21}O_4N_3$, is obtained as a white, crystalline powder, m. p. 246—248°. By boiling the monoxime, dioxime, or oxime-phenylhydrazone with dilute acids, small quantities of a crystalline *substance*, m. p. 133°, are obtained.

R. V. S.

Some Derivatives of Hydroxyquinol. V. Guido Bargellini and S. Aureli (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 118—124. Compare this vol., i, 305).—Hydroxy-ketones related to hydroxyquinol have been prepared by the action of persulphates on less highly oxygenated phenols in alkaline solution (compare Kumagai and Wolffenstein, Abstr., 1908, i, 159). It is further found that the saponification of 2 : 4 : 5-trimethoxyacetophenone by means of hydrobromic acid (compare Stoermer, Abstr., 1908, i, 190) yields 2 : 4-dihydroxy-5-methoxyacetophenone.

The action of potassium persulphate or of ammonium persulphate on 2-hydroxy-4-methoxyacetophenone (paeonol) in alkaline solution under diverse conditions yields 2 : 5-*dihydroxy*-4-*methoxyacetophenone*, $C_9H_{10}O_4$, which crystallises in white scales having a yellow tinge, m. p. 164°. When dissolved in concentrated sulphuric acid, it gives a yellowish-green coloration. Its aqueous solution gives with ferric chloride a red coloration. The *acetyl* derivative, $C_{13}H_{14}O_6$, forms small, colourless needles, m. p. 118—119°. The *benzoyl* derivative is a yellowish-white, crystalline powder, m. p. 215°. When sodium peroxide is used instead of a persulphate in the above oxidation, the paeonol remains unchanged, whilst when hydrogen peroxide is employed a mixture of products is obtained. Esterification of 2 : 5-dihydroxy-4-methoxyacetophenone with methyl sulphate yields both the trimethoxy- and dimethoxy- derivatives. The former can be extracted with ether from the alkaline solution, and is identical with the 2 : 4 : 5-trimethoxyacetophenone, m. p. 101—102°, previously described (Bargellini and Avrutin, this vol., i, 68). From the alkaline liquid after acidification, 2-*hydroxy*-4 : 5-*dimethoxyacetophenone*, $C_{10}H_{12}O_4$, can be extracted with ether; it crystallises in yellowish-white needles, m. p. 114—115°. Its aqueous solution gives a green coloration with ferric chloride. The *acetyl* derivative, $C_{12}H_{14}O_5$, forms small, colourless needles, m. p. 146—147°. With anisaldehyde, 2-hydroxy-4 : 5-dimethoxyacetophenone yields *2'-hydroxy 4 : 4' : 5'-trimethoxychalkone*, which crystallises in small, red needles, m. p. 130°. It dissolves in concentrated sulphuric acid, giving an intense orange-yellow coloration.

When trimethoxyacetophenone in acetic acid solution is boiled for two hours with hydrobromic acid (D 1·47), *2 : 4-dihydroxy-5-methoxyacetophenone*, $C_9H_{10}O_4$, is produced; it forms yellowish-white needles, m. p. 166°. Its aqueous solution gives a red coloration with ferric chloride. The *acetyl* derivative, $C_{13}H_{14}O_6$, crystallises in long, colourless needles, m. p. 127—128°. R. V. S.

A Nitroso-compound of Dimethoxyphenol, and its Derivatives.

RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1911, **44**, 2293—2298).—The substance obtained by boiling asaronic acid in aqueous solution with sodium nitrite, and formerly supposed to be 4 : 5-dimethoxy-*o*-benzoquinoneoxime or its tautomeride (Abstr., 1907, i, 45), is now shown to be 2 : 5-dimethoxy-1 : 4-benzoquinoneoxime or the tautomeric 4-nitroso-2 : 5-dimethoxyphenol, and a number of its derivatives are described. The substance on repeated crystallisation from hot acetic acid forms transparent, lustrous citron-yellow needles identical in composition with the red form described previously.

On methylation with methyl sulphate, it gives *4-nitroso-1 : 2 : 5-trimethoxybenzene*, m. p. 191°, which crystallises in long, reddish-yellow needles from alcohol. The reduction to 4-amino-2 : 5-dimethoxyphenol, m. p. 157° (*loc. cit.*), is best effected by ammonia and hydrogen sulphide; the *acetylamino*-compound, m. p. 180°, crystallises from boiling water, and the *diacetyl* derivative, m. p. 190°, from either water or boiling alcohol; the *dipropionyl* derivative, m. p. 131°, also crystallises from alcohol. On oxidation with 50% nitric acid the aminodimethoxyphenol yields 2 : 5-dimethoxy-1 : 4-benzoquinone (compare Schüler, Abstr., 1907, i, 700), and on treatment with ethyl chlorocarbonate in alcohol gives *ethyl 4-hydroxy-2 : 5-dimethoxyphenylaminoformate*, m. p. 143°, which crystallises from benzene in glancing leaflets, and is readily soluble in alcohol, chloroform, or acetic acid; the *acetyl* derivative of this, m. p. 135°, crystallises from hot alcohol, and the *carboxymethyl ether*, $CO_2H\cdot CH_2\cdot O\cdot C_6H_2(OMe)_2\cdot NH\cdot CO_2Et$, m. p. 108°, obtained by condensation with ethyl bromoacetate in presence of sodium and alcohol, crystallises from alcohol.

4-Acetylamino-2 : 5-dimethoxyphenoxyacetic acid,

$$NHAc\cdot C_6H_2(OMe)_2\cdot O\cdot CH_2\cdot CO_2H,$$

m. p. 172°, obtained by condensing ethyl bromoacetate with 4-hydroxy-2 : 5-dimethoxyacetanilide, forms colourless crystals from alcohol.

Several of the substances described exert an antipyretic action, which is, however, less marked than that due to phenacetin.

T. A. H.

Aromatic Tellurinium Compounds with the same Hydrocarbon Residue. CHARLES LEDERER (*Ber.*, 1911, **44**, 2287—2292).—Tellurium tetrachloride reacts with the Grignard reagent to form telluronium compounds containing three aromatic hydrocarbon residues. These react in part with the Grignard reagent present to form the corresponding diaryl tellurides and diaryl hydrocarbons, thus: $R_3TeCl + R\cdot MgBr = R_2Te + R_2 + MgClBr$. In addition, the diaryltelluride so formed reacts with hydrochloric acid subsequently added, in presence of air, to form some diaryltellurinium dichloride, which in turn is decomposed on addition of water, forming a basic chloride, thus:

$$TeR_2 + 2HCl + O = TeR_2Cl_2 + H_2O = TeR_2Cl\cdot OH + HCl.$$

In these equations R represents an aromatic hydrocarbon residue. In certain cases irregularities were observed. With magnesium *o*-tolyl iodide, no di-*o*-tolyl was formed, but, instead, an unidentified high-boiling hydrocarbon. With magnesium *p*-tolyl bromide, the di-*p*-tolyl obtained was not identical with that of Weiler (Abstr., 1899, i, 490). A description is given of the method used for the separation of all the substances formed.

Triphenyltellurinium iodide, $TePh_3I$, sinters at 245°, has m. p. 247—249°, and crystallises from hot water in small needles. The corresponding *bromide*, m. p. 259—260°, separates from hot water in small prisms. The *chloride*, m. p. 244—245°, crystallises from dry alcohol on addition of ether in long, slender needles.

Tri-p-*tolyltellurinium iodide*, m. p. 232—233° (decomp.), crystallises from alcohol in six-sided tablets. The *bromide*, m. p. 265—266° (decomp.), crystallises from water or from alcohol on addition of ether. The *chloride*, m. p. 260—261°, crystallises in small prisms from dry alcohol on addition of ether.

Tri-o-*tolyltellurinium iodide*, m. p. 195—196°, forms small, four-sided columns from water or alcohol on addition of ether. Its aqueous solution is precipitated by picric acid. T. A. H.

Preparation of ω-*p*-Alkylhydroxyphenylethylamines and their *N*-Alkyl Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234795).—It is found that ω-*p*-alkylhydroxyphenylethylamines can be readily prepared by treating primary *p*-alkylhydroxyphenylethyl alcohols with phosphorus pentahalides and subsequently heating the ω-*p*-alkylhydroxyphenylethyl halide so obtained with ammonium hydroxide (or the required alkylamine) in a closed vessel at 100°.

p-*Methoxyphenylethyl alcohol*, m. p. 22°, b. p. 143°/13 mm. (prepared from ethylene chloride and magnesium *p*-anisyl bromide), furnished under these conditions a 50—60% yield of ω-*p*-methoxyphenylethylamine, and when dimethylamine was employed, an 80% yield of ω-*p*-methoxyphenylethyldimethylamine; the intermediate *chloride* has b. p. 100—105°/7 mm.

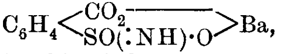
p-*Ethoxyphenylethyl alcohol*, prepared from ethylene chlorohydrin and magnesium *p*-phenetyl bromide, can also be employed in the foregoing reaction; it has m. p. 40° and b. p. 135—140°/7 mm.; the intermediate *chloride* has b. p. 125—130°/7 mm. F. M. G. M.

Phytosterols of Soy Bean. Hermann Matthes and A. Dahle (*Arch. Pharm.*, 1911, **249**, 436—444. Compare this vol., i, 831; Klobb and Block, Abstr., 1907, i, 521; Keimatsu, this vol., i, 766).—Soy bean oil contains 0·7% of unsaponifiable matter, of which 55% is solid and crystalline, and is composed of stigmasterol 2·4%, and a new phytosterol 97%, and 45% is liquid.

The crude unsaponifiable matter was mixed with light petroleum and the mixture strongly cooled, when it separated into (1) a solid, crystalline product; (2) a solution in light petroleum of a viscous, brown material. The solid product was acetylated and the acetylated product brominated in ether solution, when stigmasterol acetate tetrabromide, m. p. 205—206° (compare Windaus and Hauth, Abstr., 1907, i, 129), separated. The portion of the brominated product soluble in ether was recovered in crystalline form by gradual addition of water to its solutions in alcohol. It proved to be *phytosterol acetate dibromide*, $C_{29}H_{46(\text{or }48)}O_2Br_2$, m. p. 125°, and on reduction and subsequent hydrolysis gave the corresponding *phytosterol*, $C_{27}H_{44(\text{or }46)}O,H_2O$, m. p. 139°, $[\alpha]_D^{15} - 22\cdot83°$.

The liquid product had iodine number 124·4, $n_D^{50} - 1\cdot4835$, $[\alpha]_D$ 0°, and gave the colour reactions of the phytosterols. On treatment with digitonin (compare Windaus, Abstr., 1909, i, 172) a small amount of the material separated as a *crystalline additive product*, $[\alpha]_D^{15} - 44\cdot66°$ in methyl alcohol, but no separation of the liquid into its components was thereby effected. The liquid has the same empirical composition as the phytosterol referred to above. T. A. H.

Action of Chlorine on "Saccharin." Pasquale Bertolo (*Gazzetta*, 1911, **41**, i, 698—705).—When "saccharin" is subjected to the prolonged action of nascent chlorine (from hydrochloric acid and potassium chlorate), *o*-chlorobenzoic acid is obtained. When the duration of the action is more limited, however, a substance is obtained to which the constitution of *potassium* o-*iminosulphobenzoic acid*, $NH\colon SO(OK)\cdot C_6H_4\cdot CO_2H$, is ascribed. In this case "saccharin" is boiled with dilute hydrochloric acid, and potassium chlorate is added from time to time until the "saccharin" is completely dissolved, and the boiling is then continued for a few minutes to expel excess of chlorine. The above-mentioned substance, $C_7H_6O_4NSK$, crystallises from the solution, after concentration, in the form of transparent, colourless, tabular, rhombic crystals [S. Di Franco: $a:b:c = 1\cdot46335:1:1\cdot79093$], m. p. 285—286°. The *barium* salt,



$$C_6H_4<\begin{matrix}CO_2\text{————}\\SO(\colon NH)\cdot O\end{matrix}>Ba,$$

crystallises with 1½HO, which it loses at 110°. From it the free *acid* may be obtained. When the potassium salt is boiled with 50% potassium hydroxide, ammonia is evolved, and *potassium* o-*sulphobenzoate* is obtained. *Barium sulphobenzoate*, $C_7H_4O_5SBa,2H_2O$, was also prepared. R. V. S.

Preparation of Esters of Cinnamic Acid. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 235357).—*Ethylene cinnamate*, a colourless, odourless oil, b. p. 190—195°/11 mm., is prepared by heating together equal quantities of ethylene glycol and cinnamic acid during thirty hours at 140° in the presence of concentrated sulphuric acid. *Glycerol monocinnamate*, a yellow, oily liquid, and *ethylene chlorohydrin ethoxycinnamate*, a yellow liquid, and other substances allied to the constituents of Peru balsam are discussed in the original. F. M. G. M.

Refraction of Light by *allo*- and *iso*-Cinnamic Acids. Hans Stobbe and Fritz Reuss (*Ber.*, 1911, **44**, 2735—2739).—Two specimens of *allo*cinnamic acid were examined : (1) m. p. 68°, prepared by the action of hydrogen on phenylpropiolic acid in presence of colloidal palladium, and (2) m. p. 67—68°, prepared from an aniline salt.

With acid (1) the following refractometric measurements were made on the melted acids: (*a*) of *allo*cinnamic acid from 71·7° to 52·0°; (*b*) of *iso*cinnamic acid, m. p. 58°, from 70·7° to 55·8°, and (*c*) of *iso*cinnamic acid, m. p. 42°, from 45·8° to 51·1°. The results, plotted against the temperature, all fell on a straight line, so that the refraction of all three acids is continuous and diminishes proportionally with the temperature, as happens with compounds known to be chemical individuals. The results obtained with *allo*cinnamic acid (2) from 77·3° to 22·6° also fell on a straight line with the same slope as, and only very slightly distant from, that of the (1) acids. Fused *allo*- and *iso*-cinnamic acids are hence to be regarded as optically identical. T. H. P.

Transformations of *allo*- and *iso*-Cinnamic Acids in the Fused and Crystalline States. Hans Stobbe (*Ber.*, 1911, **44**, 2739—2754. Compare preceding abstract).—The author has confirmed and extended the observations of Liebermann (Abstr., 1903, i, 255; 1909, i, 303; 1910, i, 36, 175), Biilmann (Abstr., 1909, i, 155, 382; 1910, i, 346), Erlenmeyer (Abstr., 1891, 200; 1896, i, 46), Erlenmeyer, jun. (Abstr., 1906, i, 429; 1907, i, 318; 1909, i, 156, 647, 648), Paal and Hartmann (Abstr., 1909, i, 926), and Stoermer (Abstr., 1910, i, 114) on *allo*- and the two *iso*-cinnamic acids. In the experiments described, extreme care was taken to avoid accidental seeding of the fused or crystalline masses under examination.

By crystal-seeding, the crystalline acid m. p. 42° can be converted into that with m. p. 68° (with development of considerable heat) or 58°, and the latter into that with m. p. 68°.

When the crystalline 42°-acid is heated in a sealed tube for eighty hours at 37°, or the 58°-acid for thirty hours at 52°, no change occurs; but the 42°-acid is transformed completely into the 68°-acid in five minutes at −80° and almost instantaneously at −180°; with the 58°-acid similar conversion takes place in three hours at −80° and in ten minutes at −180°. The 68°-acid undergoes no change at either −80° or −180°, so that, in all cases, the most labile acid (42°) is converted, by grinding (Liebermann, *loc. cit.*) or cooling, into the stable *allo*-acid more rapidly than is the less labile form (58°). The two labile acids appear to be only metastable forms of a single chemical compound, trimorphous *cis*-cinnamic acid.

If a few milligrams of the fused 68°-acid, heated for 0·5—5 minutes to 72—80°, are cooled to the ordinary temperature or to $-14°$, the result was almost always the 42°-acid, but occasionally the 68°-acid; but 0·05—1·0 gram of the 68°-acid, on heating to 80—105° for ten minutes or for several hours, and then cooling to the ordinary temperature or to $-14°$, solidifies to the 68°-acid more frequently than to the 42°-acid.

The observation of Liebermann and of Biilmann, that the fused 42°- and 58°-acids always solidify to the 42°-acid on cooling to the ordinary temperature or to 0°, is confirmed, but if the cooling is effected in a mixture of ice and salt, sometimes the 42°-acid and sometimes the 58°-acid separates; separation of the former can always be recognised by the slowness with which crystallisation occurs. Further, if the fusion from the 42°- or 58°-acid is immersed in a mixture of ether and carbon dioxide or in liquid air, it forms an amorphous, glassy mass with a concave, funnel-shaped surface, and shows no tendency to crystallise, even after some hours; but if the mass is removed from the cooling mixture so that its temperature rises, the concavity of the surface gradually disappears, and it undergoes a usually sudden and always rapid crystallisation, the 58°-acid invariably separating, so that these two labile acids, which in the fused condition are optically identical, can be mutually interconverted without any seeding being necessary.

Results similar to the above were obtained on cooling the fused 68°-acid in ice and salt, ether and carbon dioxide, or liquid air, the only divergence being that occasionally, in additton to the 42°- or 58°-acid, the 68°-acid also separated.

Optical identity (compare preceding abstract) of these three acids does not, therefore, always present itself, and the conclusion is drawn that there are in reality two chemically different isomeric acids: (1) monomorphous *allo*cinnamic acid, m. p. 68°, and (2) dimorphous *iso*cinnamic acid, m. p. 42° and 58°. T. H. P.

Oxidation of *allo*-Cinnamylideneacetic Acid. C. N. Riiber (*Ber.*, 1911, **44**, 2389—2391).—Doebner (Abstr., 1890, 1274) has shown that cinnamylideneacetic acid, when cautiously oxidised with potassium permanganate, is converted into benzoic acid and racemic acid. It is now shown that *allo*-cinnamylideneacetic acid,

$$\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2H},$$

under similar conditions is converted into benzoic acid and mesotartaric acid. The two cinnamylideneacetic acids are accordingly related in the same manner as fumaric and maleic acids, the isomerism being due to the double linking 1 : 2. The double linking 3 : 4 is hardly concerned, since both isomerides when distilled with quinoline give the same stable phenylbutadiene. E. F. A.

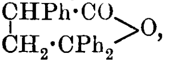
Reaction between Organomagnesium Compounds and Cinnamylidene Esters. III. Reactions with the Isomeric Methyl Esters of Cinnamylideneacetic Acid. Grace P. Reynolds (*Amer. Chem. J.*, 1911, **46**, 198—211. Compare Abstr., 1907, i, 852; 1908, i, 988).—The action of magnesium alkyl or aryl bromides on the isomeric methyl cinnamylideneacetates may give rise to three different classes of compounds: (i) tertiary alcohols,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CR_2{\cdot}OH,$$

formed by replacement of the methoxy-group and addition of the magnesium compound to the carbonyl group; (ii) unsaturated ketones, $CHPh{:}CH{\cdot}CHR{\cdot}CH_2{\cdot}COR$, produced by 1:4-addition and simultaneous replacement of the methoxy-group; (iii) unsaturated esters of the type $CHPh{:}CH{\cdot}CHR{\cdot}CH_2{\cdot}CO_2Me$, formed by 1:4-addition only. It is found that the nature of the product depends on the magnesium compound employed. Whilst magnesium phenyl bromide forms only an unsaturated ketone and magnesium ethyl bromide a tertiary alcohol, the action of magnesium benzyl bromide yields a mixture of compounds belonging to all three classes.

Methyl allo*cinnamylideneacetate*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2Me$, obtained by the action of methyl alcohol and hydrogen chloride on the corresponding acid, is a liquid, which solidifies at $-15°$ to a white, crystalline mass, and is partly converted into the isomeric ester by distillation under diminished pressure. Both esters react with magnesium phenyl bromide, yielding β-phenyl-β-styrylpropiophenone (Kohler, Abstr., 1905, i, 258), which is converted by the further action of magnesium phenyl bromide into *αγεε-tetraphenyl-Δ^{α}-penten-ε-ol*,

$$CHPh{:}CH{\cdot}CHPh{\cdot}CH_2{\cdot}CPh_2{\cdot}OH.$$

The latter compound forms slender, white needles, m. p. 134°, and is oxidised by potassium permanganate to benzoic acid and *αγγ-triphenyl-γ-butyrolactone*,  $\left.\begin{array}{l}CHPh{\cdot}CO\\ \,|\\ CH_2{\cdot}CPh_2\end{array}\right>O$, which crystallises in long, iridescent needles, m. p. 157°. Experiments carried out with the isomeric methyl cinnamylideneacetates under similar conditions showed that the *allo*-ester reacts with magnesium phenyl bromide more readily than the isomeride.

The interaction of magnesium benzyl bromide and methyl cinnamylideneacetate yields (1) *αζ-diphenyl-γ-benzyl-Δ^{α}-hexen-ε-one*,

$$CHPh{:}CH{\cdot}CH(C_7H_7){\cdot}CH_2{\cdot}CO{\cdot}CH_2Ph,$$

which is a viscid, lemon-yellow liquid, b. p. 265°/15 mm., and yields a *dibromide*, $C_{26}H_{24}OBr_2$, m. p. 165·5°; (2) *αζ-diphenyl-ε-benzyl-Δ^{αγ}-hexadien-ε-ol*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}C(CH_2Ph)_2{\cdot}OH$, a mobile, lemon-yellow liquid, b. p. 200°/10 mm.; the *tetrabromide* forms slender needles, m. p. 227° (decomp.); (3) *β-benzyl-γ-benzylidenebutyric acid*,

$$CHPh{:}CH{\cdot}CH(C_7H_7){\cdot}CH_2{\cdot}CO_2H,$$

which crystallises in heavy, iridescent plates, m. p. 144°, yields a crystalline *methyl* ester, m. p. 66°, and is oxidised by potassium permanganate in aqueous sodium carbonate solution to benzoic and benzylsuccinic acids.

α-Phenyl-ε-ethyl-Δ^{αγ}-heptadien-ε-ol, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CEt_2{\cdot}OH$, obtained by the action of magnesium ethyl bromide on methyl cinnamylideneacetate, is a pale yellow, mobile liquid, b. p. 169°/10 mm. It is accompanied by a viscid liquid, b. p. 278—285°/10 mm., which deposits an *ester*, crystallising in needles, m. p. 136°, when kept. Hydrolysis of the latter substance with alcoholic potassium hydroxide yields an acid, m. p. 230°. The constitution of the last-mentioned substances has not been determined. F. B.

Reaction between Unsaturated Compounds and Organic Zinc Compounds. II. Elmer P. Kohler, Gertrude L. Heritage, and A. L. Macleod (*Amer. Chem. J.*, 1911, **46**, 217—236).—It has been shown previously (Abstr., 1910, i, 484) that the zinc compounds of esters of bromoacetic acid react with $\alpha\beta$-unsaturated ketones, yielding unsaturated hydroxy-acids, and from this the conclusion was drawn that the addition of organo-zinc compounds occurs only in the 1 : 2-position. The present paper deals with the interaction of phenyl styryl ketone and the zinc derivatives of the methyl or ethyl esters of α-bromopropionic, α-bromobutyric, α-bromo*iso*butyric, and bromomalonic acids. It is found that both 1 : 2- and 1 : 4-addition may take place with the formation of the compounds :

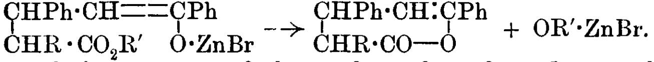
$$\text{(I) } CHPh\colon CH\cdot CPh(O\cdot ZnBr)\cdot CHR\cdot CO_2R' \text{ and}$$
$$\text{(II) } ZnBr\cdot O\cdot CPh\colon CH\cdot CHPh\cdot CHR\cdot CO_2R',$$

the relative proportions of the two products depending on the nature of the bromo-ester, $CHRBr\cdot CO_2R'$, employed.

When decomposed with acids, the zinc compounds of the first type yield esters of unsaturated hydroxy-acids,

$$CHPh\colon CH\cdot CPh(OH)\cdot CHR\cdot CO_2R',$$

whilst those belonging to the second type give rise to esters of ketonic acids of the formula : $COPh\cdot CH_2\cdot CHPh\cdot CHR\cdot CO_2R'$. The zinc compounds produced by 1 : 4-addition may also yield unsaturated lactones, according to the scheme :



$$\begin{array}{ll} CHPh\cdot CH\!=\!=\!CPh & \\ | \qquad\qquad\quad | & \\ CHR\cdot CO_2R' \quad O\cdot ZnBr & \end{array} \longrightarrow \begin{array}{l} CHPh\cdot CH\colon CPh \\ | \qquad\qquad | \\ CHR\cdot CO\!-\!O \end{array} + OR'\cdot ZnBr.$$

The relative amounts of the products formed by 1 : 2- and 1 : 4-addition were determined by heating the mixtures with aqueous sodium carbonate, whereby the lactones and ketonic esters are converted into the sodium salts of the corresponding ketonic acids, whilst the unsaturated hydroxy-esters remain practically unchanged. The results thus obtained were as follows, the value first given being the percentage of the product formed by 1 : 2-addition : methyl α-bromoacetate, 100%, 0%; methyl α-bromopropionate, 55%, 45%; methyl α-bromobutyrate, 50%, 50%; methyl α-bromo*iso*butyrate and methyl bromomalonate, 0%, 100%.

In several cases no reaction occurred when the bromo-esters were heated with zinc and the unsaturated ketone in benzene solution. The reaction is, however, readily induced by the addition of a small quantity of the copper salt of ethyl acetoacetate, or of other copper compounds which are soluble in benzene.

The action of zinc on methyl bromoacetate and phenyl styryl ketone has been re-investigated, and the product, after removal of methyl β-hydroxy-β-phenyl-α-benzylidenebutyrate, carefully examined for methyl benzoylphenylbutyrate, which would be formed by a 1 : 4-addition, but no evidence of its presence could be obtained. Methyl β-hydroxy-β-phenyl-γ-benzylidenebutyrate decomposes below 180° into methyl acetate and phenyl styryl ketone ; a similar decomposition into potassium acetate and phenyl styryl ketone takes place on treating the ester with alcoholic potassium hydroxide. When hydrolysed with aqueous sodium carbonate, it yields the corresponding *acid*, $CHPh\colon CH\cdot CPh(OH)\cdot CH_2\cdot CO_2H$, which crystallises in colourless needles,

m. p. 147° (decomp.). When warmed with a small quantity of hydrochloric acid, the hydroxy-ester is converted into a viscid oil, which is hydrolysed by alcoholic potassium hydroxide to *β-phenylcinnamylideneacetic acid*, $CHPh{:}CH{\cdot}CPh{:}CH{\cdot}CO_2H$; this forms pale yellow, slender needles, m. p. 145—146°.

The product obtained by the interaction of zinc, ethyl α-bromopropionate, and phenyl styryl ketone in benzene solution, when decomposed with hydrochloric acid and heated with aqueous sodium carbonate, yields a mixture of two stereoisomeric *ethyl β-hydroxy-β-phenyl-γ-benzylidene-α-methylbutyrates*,

$$CHPh{:}CH{\cdot}CPh(OH){\cdot}CHMe{\cdot}CO_2H,$$

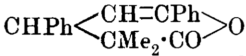
which may be separated by repeated crystallisation from methyl alcohol. The less soluble isomeride crystallises in slender needles, m. p. 107°, instantly decolorises bromine at the ordinary temperature, and decomposes above its m. p. into ethyl propionate and phenyl styryl ketone. When warmed with alcoholic potassium hydroxide, it yields phenyl styryl ketone and potassium propionate. The stereoisomeride, which is produced only in small quantity, separates from alcohol in large, transparent prisms, m. p. 81°, and resembles the preceding compound in its chemical properties.

The alkaline solution from which the above esters were separated yields on acidification two stereoisomeric *γ-benzoyl-β-phenyl-α-methyl butyric acids*, $CH_2Bz{\cdot}CHPh{\cdot}CHMe{\cdot}CO_2H$, which are separated by crystallisation from ether and light petroleum. Of these isomerides, the one obtained in larger quantity crystallises in slender, feathery needles, m. p. 149°, and yield a *methyl* ester crystallising in needles, m. p. 68°; the *ethyl* ester has m. p. 41°. The stereoisomeric acid forms slender needles, m. p. 105°.

The product obtained by the action of zinc on methyl α-bromobutyrate and phenyl styryl ketone in benzene solution when decomposed with acids yields *methyl β-hydroxy-β-phenyl-γ-benzylidene-α ethylbutyrate*,

$$CHPh{:}CH{\cdot}CPh(OH){\cdot}CHEt{\cdot}CO_2Me,$$

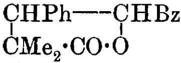
which crystallises in needles, m. p. 117°, and, when heated above its m. p., is resolved into methyl butyrate and phenyl styryl ketone. Decomposition of the product with aqueous sodium carbonate yields *γ-benzoyl-β-phenyl-α-ethylbutyric acid*, $CH_2Bz{\cdot}CHPh{\cdot}CHEt{\cdot}CO_2H$, which crystallises in needles, m. p. 181°, and yields a *methyl* ester, m. p. 95°.

The *lactone*,  $CHPh<\begin{matrix}CH{=}CPh\\ CMe_2{\cdot}CO\end{matrix}>O$, obtained by the action of zinc on ethyl α-bromo*iso*butyrate and phenyl styryl ketone, forms long, colourless needles, m. p. 97°, and is readily hydrolysed by alcoholic potassium hydroxide to *γ-benzoyl-β-phenyl-αα-dimethylbutyric acid*, $CH_2Bz{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2H$, which crystallises in slender, white needles, m. p. 159—160°. The lactone is accompanied by the *ethyl* ester of the last-mentioned acid; this has m. p. 83°, and has also been prepared from the lactone and corresponding acid; the *methyl* ester has m. p. 92°.

γ-Bromo-γ-benzoyl-β-phenyl-αα-dimethylbutyric acid,

$$CHBzBr{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2H,$$

prepared by brominating the preceding ketonic acid in chloroform or carbon tetrachloride solution, forms colourless needles, m. p. 186° (decomp.); the *methyl* ester, m. p. 125°, and *ethyl* ester, m. p. 131°, were prepared in a similar manner. When treated with aqueous sodium carbonate the bromo-acid yields two stereoisomeric *γ-benzoyl-β-phenyl-αα-dimethyl-γ-butyrolactones*,



$$\begin{array}{ll}\mathrm{CHPh} & \!\!\!-\!\!-\mathrm{CHBz} \\ | & \quad\;\; | \\ \mathrm{CMe_2{\cdot}CO{\cdot}O} & \end{array}$$

, which may be separated by extraction with methyl alcohol. The more soluble modification forms needles, m. p. 113°; the stereoisomeride separates from acetone in needles, having m. p. 173°. When dissolved in cold alcoholic potassium hydroxide and the resulting solution immediately acidified, both isomerides yield a mixture of two stereoisomeric *γ-hydroxy-γ-benzoyl-β-phenyl-αα-dimethylbutyric acids*,

$$\mathrm{OH{\cdot}CHBz{\cdot}CHPh{\cdot}CMe_2{\cdot}CO_2H}.$$

The less fusible of these acids loses water so readily that it could not be obtained free from the lactone of m. p. 173°. The stereoisomeric acid, which forms the major portion of the mixture. separates from ether in needles, m. p. 126° (decomp.); when heated for several hours at 120°, it loses water and is converted into the lactone of m. p. 113°.

Methyl bromomalonate, prepared by the addition of the calculated amount of bromine to methyl malonate, is a colourless, mobile liquid, b. p. 145°/22 mm. It reacts with zinc and phenyl styryl ketone in benzene solution, yielding *methyl β-benzoyl-α-phenylethylmalonate*, $\mathrm{CH_2Bz{\cdot}CHPh{\cdot}CH(CO_2Me_2)_2}$. The latter compound crystallises in large, colourless needles, m. p. 107°, and is hydrolysed by alcoholic potassium hydroxide to the corresponding acid (Vorländer, Abstr., 1897, i, 286), which loses carbon dioxide at 170°, yielding γ-benzoyl-β-phenylbutyric acid, m. p. 156°. The preceding ester is accompanied by a viscid liquid, which appears to be a lactonic ester; when hydrolysed with alcoholic potassium hydroxide, this yields the same acid as that obtained by the hydrolysis of methyl β-benzoyl-α-phenylethylmalonate. F. B.

Crystallographic Study of Potassium *p*-Hydroxybenzoate. Aristide Rosati (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 53—54).—This substance, prepared by Comanducci and Marcello (Abstr., 1903, i, 485), forms transparent, colourless crystals belonging to the triclinic system [$a:b:c = 0{\cdot}6471 : 1 : 1{\cdot}7936$]. R. V. S.

***o*-Nitrophenylglyoxylic Acid.** Gustav Heller [with Friedrich Frantz and Heinrich Jürgens] (*Ber.*, 1911, **44**, 2418—2421).—*o*-Nitrophenylglyoxylic acid (compare Claisen and Shadwell, *Ber.*, 1879, **12**, 350) is conveniently prepared by oxidation of *o*-nitromandelic acid (Heller and Amberger, Abstr., 1904, i, 416) with alkaline permanganate. It crystallises in colourless, obliquely cut prisms, m. p. 156—157°.

The *ethyl* ester forms crystals, m. p. 43—44·5°.

The acid is reduced by zinc dust and ammonia to anthroxanic acid; the ester when reduced by stannous chloride and hydrochloric acid is converted into *ethyl anthroxanate*; this crystallises in long, bushy needles, m. p. 64—65°.

Methyl anthroxanate forms crystalline bunches, m. p. 70°. E. F. A.

Keto-enolic Tautomerism. V. Desmotropy of Methyl Benzoylacetate. Kurt H. Meyer (*Ber.*, 1911, **44**, 2729—2732).—Methyl and ethyl benzoylacetate contain respectively 16·7% and 29·2% of enolic modification at the ordinary temperature.

If the methyl ester is dissolved in sodium hydroxide solution and precipitated by dilute sulphuric acid, both strongly cooled, the free enol separates as an oil which solidifies when vigorously shaken; the solid can be dried in an absolute vacuum, but it is soon converted into an oily mixture of enol and ketone. This behaviour is similar to that of *iso*phenylnitromethane. The enolic form or methyl β-hydroxycinnamate melts indefinitely at 30—40°, and solidifies again when rapidly cooled. The alcoholic solution is coloured intensely reddish-violet by ferric chloride, and also reacts quickly with *anti*-*p*-nitrobenzenediazonium hydroxide. The crystalline enol, after two hours' drying, contained 89·1% of the enolic form. In a state of equilibrium at 20°, the ester contained 14% of enol in acetic acid, 21% in alcohol, 56% in carbon disulphide, and 69% in hexane. These numbers are similar to those obtained with ethyl acetoacetate.

The values of the velocity constants at 0° in absolute alcohol are k_1 (ketonisation) = 0·10 and k_2 (enolisation) = 0·04. At the boiling point the alcoholic solution contains only about one-half as much enol as at 0°.

Unlike the equilibrium of ethyl acetoacetate, that of methyl benzoylacetate exhibits a distinct temperature-coefficient, the equilibrium being displaced towards the ketone by rise of temperature; the same is the case with acetylacetone, so that the independence of the equilibrium on the temperature is a constitutive property of ethyl acetoacetate. T. H. P.

Preparation of *m*-Hydroxy-β-phenylpropionic Acid Alkyl Ethers and their Salts. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P 234852).—*m-Ethoxy-β-phenylpropionic acid*, m. p. 52—53°, b. p. 205°/20 mm., can be prepared (1) by heating *m*-hydroxy-β-phenylpropionic acid with ethyl bromide and sodium hydroxide in alcoholic solution at 120°; (2) by reducing *m*-ethoxycinnamic acid with sodium amalgam; or (3) by diazotising *m*-amino-β-phenylpropionic acid in an anhydrous solvent, isolating the diazonium sulphate with ether, and subsequently boiling it with absolute alcohol; the *sodium* salt forms a colourless powder.

m-*Propoxy-β-phenylpropionic acid* has m. p. 56—57° and b. p. 203—204°/15 mm. These compounds have antipyretic and antirheumatic properties. F. M. G. M.

New Reactions of Cyanogen and Acyl Cyanides. Daniel Vorländer [and, in part, A. Friedberg, Ch. van der Merve, L. Rosenthal, M. E. Huth, and M. von Bodecker] (*Ber.*, 1911, **44**, 2455—2476).—The interaction of cyanogen with benzene and its homologues, or with phenolic ethers, yields acyl cyanides, R·CO·CN, nitriles, R·CN, and diketones, R·CO·CO·R, together with more complex substances, the constitution of which has not been determined.

When cyanogen is passed into a mixture of benzene and aluminium chloride for one hour at the ordinary temperature, and the product decomposed with cold dilute hydrochloric acid, benzoyl cyanide is produced. If the mixture is boiled and the passage of cyanogen continued for four hours, the benzoyl cyanide is accompanied by benzonitrile (compare Desgrez, Abstr., 1896, i, 419). The product of the reaction always contains a certain amount of a tarry substance, which, on decomposition with acids, yields benzil. The latter compound forms the main product when a mixture of benzene and aluminium chloride is saturated with cyanogen and allowed to remain at the ordinary temperature for three days. In addition to the above compounds, several other substances are formed in the reaction, one of these being a blue dye, m. p. 145—148°.

With respect to the mechanism of the reaction, it is considered that the first stage consists in the formation of an imino-nitrile (I), which decomposes into benzonitrile and hydrogen cyanide, and on treatment with acids yields benzoyl cyanide, thus:

$$C_6H_6 + C_2N_2 \longrightarrow (I)\ CN{\cdot}CPh{:}NH \longrightarrow CN{\cdot}COPh\ ;$$

the formation of benzil is due to the decomposition of a di-imino-compound (II), produced by the further condensation of the imino-nitrile with benzene:

$$CN{\cdot}CPh{:}NH + C_6H_6 = (II)\ NH{:}CPh{\cdot}CPh{:}NH.$$

The interaction of cyanogen, toluene, and aluminium chloride, under conditions similar to those given in the case of benzene, results in the formation of *p*-toluonitrile, *p*-toluic acid, *pp'*-dimethylbenzil, and *p*-methylbenzoyl cyanide (Söderbaum, Abstr., 1893, i, 159).

With ethylbenzene the product consists of p-*ethylbenzonitrile* and *p*-ethylbenzoic acid, together with p-*ethylbenzoyl cyanide*, which could not be isolated, and was therefore identified by conversion into *p*-ethylbenzanilide, m. p. 121°.

The only substance which could be identified in the product obtained from cyanogen and diphenyl was p-*phenylbenzoyl cyanide.*

The action of cyanogen and hydrogen chloride on a solution of phenetole in carbon disulphide in the presence of aluminium chloride yields p-*ethoxybenzoyl cyanide*, which has m. p. 43°, and is more readily prepared by heating *p*-ethoxybenzoyl chloride with mercuric cyanide at 125—130°; it gives a green, and finally blue, solution with strong sulphuric acid, and is decomposed by boiling with dilute hydrochloric acid into *p*-ethoxybenzoic acid and hydrogen cyanide; with aniline it yields *p*-ethoxybenzanilide (Leuckart, Abstr., 1890, 759).

p-*Ethoxyphenylglyoxylic acid*, obtained by the action of fuming hydrochloric acid on the preceding nitrile, crystallises with water in colourless prisms, m. p. 52°; the anhydrous acid is obtained by crystallisation from benzene, and has m. p. 125° (decomp.); it yields a *phenylhydrazone*, $C_{16}H_{16}O_3N_2$, long, yellow needles, m. p. 153° (decomp.), and an *azine*, crystallising in light yellow needles, which have m. p. 173—176°, and simultaneously lose carbon dioxide with the formation of *pp'*-diethoxybenzalazine; the *oxime* has m. p. 152—154° (decomp.).

pp'-*Diethoxybenzil*, $C_{18}H_{18}O_4$, prepared by the action of cyanogen and hydrogen chloride on a carbon disulphide solution of phenetole in the presence of aluminium chloride for three to four days, crystallises in silvery-white, microscopic prisms, m. p. 149°, and gives a red coloration with concentrated sulphuric acid. It yields an *osazone*, crystallising in small, yellow plates, m. p. 171°, and is converted by alcoholic potassium hydroxide into pp'-*diethoxybenzilic acid*, which forms narrow prisms, m. p. 202°, with previous darkening.

p-Methoxybenzoyl cyanide, obtained from anisole in the usual manner, crystallises in colourless needles, m. p. 60°; Mauthner (Abstr., 1909, i, 160) gives 63—64°. It may also be prepared by the interaction of anisoyl chloride and mercuric cyanide; when warmed with acids or alkalis it yields anisic acid.

In view of the above-mentioned formation of benzil from the intermediate product, $NH:CPh\cdot CN$, it was anticipated that the closely related benzoyl cyanide would condense with benzene to form benzil in a similar manner.

It was, however, found that benzoyl cyanide and benzene react at the ordinary temperature in the presence of aluminium chloride and hydrogen chloride, yielding 9-cyanofluorene (Wislicenus and Russ, Abstr., 1910, i, 839), which is converted by heating with fuming hydrochloric or hydriodic acid into 9-fluorenecarboxylic acid. On the other hand, when a mixture of benzene, benzoyl cyanide, and aluminium chloride is heated in carbon disulphide solution, triphenylacetonitrile (E. and O. Fischer, Abstr., 1879, 326, 385) is produced, thus: $CN\cdot COPh + 2C_6H_6 \longrightarrow CPh_3\cdot CN + H_2O$.

A number of substituted derivatives of triphenylacetonitrile has been prepared in a similar manner.

Phenyldi-p-*tolylacetonitrile*, $C_{22}H_{19}N$, obtained from benzoyl cyanide and toluene, crystallises in apparently monoclinic prisms, m. p. 132—133°, and is converted by the action of sodium on its alcoholic solution into phenyldi-*p*-tolylmethane (Kliegl, Abstr., 1905, i, 186); it may also be prepared by heating ω-chlorophenyldi-*p*-tolylmethane (Gomberg, Abstr., 1904, i, 489) with mercuric cyanide.

4 : 4'-*Diethyltriphenylacetonitrile*, $C_{24}H_{23}N$, prepared from ethylbenzene and benzoylcyanide, crystallises in colourless plates, m. p. 111—112°.

4 : 4'-*Dimethoxytriphenylacetonitrile*, $C_{22}H_{19}O_2N$, obtained from anisole, crystallises in short, colourless, rods, m. p. 98°; it is also obtained in small yield by the interaction of ω-chloro-4 : 4'-dimethoxytriphenylmethane and mercuric cyanide. When reduced with sodium in alcoholic solution, it yields 4 : 4'-dimethoxytriphenylmethane (Baeyer and Villiger, Abstr., 1902, i, 380).

4 : 4'-*Dihydroxytriphenylacetonitrile*, $C_{20}H_{15}O_2N$, prepared by boiling the preceding nitrile with hydriodic acid, forms colourless, hexagonal leaflets, m. p. 202°; it is converted by the action of methyl sulphate in alkaline solution into the original nitrile; the *diacetyl* derivative crystallises in colourless leaflets, m. p. 130°. When boiled with phosphorus and hydriodic acid, 4 : 4'-dimethoxytriphenylacetonitrile yields 4-hydroxydiphenylacetic acid (Bistrzycki and Flatau, Abstr., 1897, i, 190), which forms an *ethyl* ester, crystallising in stellar aggregates of prisms, m. p. 92°; the *methyl* ester is an oil.

4-*Methoxytriphenylacetonitrile*, prepared from anisoyl cyanide and benzene, crystallises in colourless plates or white needles, m. p. 137°.

4 : 4′-*Diethoxytriphenylacetonitrile*, obtained from benzoyl cyanide and phenetole, forms short, pointed prisms, m. p. 120°; it is converted by heating with hydriodic acid into 4 : 4′-dihydroxytriphenylacetonitrile and 4-hydroxydiphenylacetic acid.

Cyanogen and sulphurous acid react slowly in aqueous solution, yielding hydrogen cyanide and sulphuric acid :

$$C_2N_2 + H_2SO_3 + H_2O = 2HCN + H_2SO_4.$$

F. B.

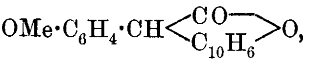
Condensation of *p*- and *o*-Methoxymandelonitriles with Phenols and Phenolic Ethers. AUGUSTIN BISTRZYCKI, J. PAULUS, and R. PERRIN (*Ber.*, 1911, **44**, 2596—2617).—The paper contains merely a description of the following substances, and has been published in consequence of Stoermer and Hildebrandt's recent work (this vol., i, 664).

o- and *p*-Methoxymandelonitriles condense like the corresponding acids with phenols or phenolic ethers in the presence of 73% sulphuric acid, yielding nitriles of the type $OMe\cdot C_6H_4\cdot CHAr\cdot CN$; thus anisaldehydecyanohydrin (1 mol.) and phenol ($2\frac{1}{3}$ mols.) yield 4-*hydroxy*-4′-*methoxydiphenylacetonitrile*, $OMe\cdot C_6H_4\cdot CH(CN)\cdot C_6H_4\cdot OH$, prismatic needles, m. p. 175—176° (erroneously described by Stoermer and Hildebrandt as the lactone of *o*-hydroxyphenylanisylacetic acid), which forms an *acetyl* derivative, m. p. 85·5—86·5°, and is hydrolysed by boiling alcoholic potassium hydroxide, forming 4-*hydroxy*-4′-*methoxydiphenylacetic acid* (p-*hydroxyphenylanisylacetic acid*), m. p. 148·5—149·5°. This acid does not yield a lactone (consequently the hydroxyl group is assumed to be in the para-position), and evolves two-thirds of the theoretical quantity of carbon monoxide when heated with concentrated sulphuric acid at 170° (compare Bistrzycki and Siemiradzki, Abstr., 1908, i, 635). Anisaldehydecyanohydrin and *o*-cresol yield in a similar manner 4-*hydroxy*-4′-*methoxy*-3-*methyldiphenylacetonitrile*, m. p. 142—143° (*acetyl* derivative, m. p. 74·5—76°); the corresponding *acid*, m. p. 128—129°, loses two-thirds of the theoretical quantity of carbon monoxide with sulphuric acid at 100—120°. The lactone of *p*-hydroxytolylanisylacetic [2-hydroxy-4′-methoxy-5-methyldiphenylacetic] acid (Stoermer and Hildebrandt, *loc. cit.*) is hydrolysed by 6% potassium hydroxide to the corresponding *acid*, m. p. 140° (decomp.), which exhibits considerable stability for a γ-lactone. The lactone is converted into 2-*hydroxy*-4′-*methoxy*-5-*methyldiphenylacetamide*, decomp. 137·5°, by 25% aqueous ammonia and a little alcohol, and into the *hydrazide*, $OMe\cdot C_6H_4\cdot CH(CO\cdot NH\cdot NH_2)\cdot C_6H_3Me\cdot OH$, decomp. 182·5° (*benzylidene* derivative, m. p. 184°), in boiling alcohol by 50% aqueous hydrazine hydrate.

Anisaldehydecyanohydrin and catechol condense to form 3 : 4-*dihydroxy*-4′-*methoxydiphenylacetonitrile*,

$$OMe\cdot C_6H_4\cdot CH(CN)\cdot C_6H_3(OH)_2,$$

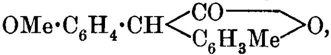
m. p. 153·5—154·5°, darkening at 130° (*diacetate*, m. p. 77—78°), which develops a blue, and by warming a bluish-violet, coloration with concentrated sulphuric acid. Anisaldehydecyanohydrin and β-naphthol yield the *lactone* of 2-*hydroxy*-α(?)-*naphthyl*-4-*methoxyphenyl*-

acetic acid,  $OMe\cdot C_6H_4\cdot CH<\begin{matrix}CO-\\C_{10}H_6\end{matrix}>O$, m. p. 145—146° (decomp.), long, prismatic needles.

Anisaldehydecyanohydrin condenses very readily with anisole to form *dianisylacetonitrile* [4 : 4′-*dimethoxyphenylacetonitrile*],

$CN\cdot CH(C_6H_4\cdot OMe)_2$,

m. p. 154·5°. Dianisylacetic acid reacts readily with phosphorus pentachloride and phosphoryl chloride to form the *chloride*, $CH(C_6H_4\cdot OMe)_2\cdot COCl$, m. p. 58—61°. In a similar manner phenetole yields *anisylphenetylacetonitrile*, m. p. 87—88°, whilst veratrole yields 3 : 4 : 4′-*trimethoxydiphenylacetonitrile*, m. p. 96°, the corresponding *acid* having m. p. 154—155°.

o-Anisaldehydecyanohydrin (rhombic crystals, $a : b : c = 0·862 : 1 : 0·462$) condenses less readily than the para-isomeride with phenols, except *p*-cresol. The *lactone* of 2-*hydroxy*-2′-*methoxy*-5-*methyldiphenylacetic acid*,  $OMe\cdot C_6H_4\cdot CH<\begin{matrix}CO-\\C_6H_3Me\end{matrix}>O$, m. p. 136°, obtained directly from the cyanohydrin and *p*-cresol with 73% sulphuric acid on the water-bath, is hydrolysed to the *acid*, $C_{16}H_{16}O_4,H_2O$, m. p. 150°, by 6% potassium hydroxide, to the *amide*, $C_{16}H_{17}O_3N$, decomp. 177—178°, by alcoholic ammonia at 100°, to the *anilide*, m. p. 192—194°, by distillation with aniline, and to the *hydrazide*, m. p. 154° (*benzylidene* derivative, m. p. 202°), by hydrazine hydrate.

The condensation of *o*-anisaldehydecyanohydrin and *o*-cresol yields a mixture of 4-*hydroxy*-2′-*methoxy*-3-*methyldiphenylacetamide* (prisms containing $C_2H_4O_2$, m. p. 130—131°, from acetic acid) and the *lactone* of 4-*hydroxy*-2′-*methoxy*-3-*methyldiphenylacetic acid*, m. p. 164°. The cyanohydrin and phenol likewise yield a mixture of the *lactone* of 2-*hydroxy*-2′-*methoxydiphenylacetic acid*, m. p. 160—162°, and 4-*hydroxy*-2′-*methoxydiphenylacetamide*, m. p. 204—205°, which is hydrolysed only slowly and incompletely by boiling concentrated potassium hydroxide. C. S.

Diphenyl Derivatives. Fritz Mayer (*Ber.*, 1911, **44**, 2298—2305).—The following substances were obtained in the course of attempts to synthesise pyrene by using Ullmann's method for the preparation of *s*-diphenyl derivatives (Abstr., 1901, i, 586).

2-Acetylamino*iso*phthalic acid, prepared by Noelting and Gachot's method (Abstr., 1906, i, 181), is best purified by heating with acetic anhydride, which gives rise to the corresponding *acetylanthranil*, m. p. 217—218°; the latter is readily re-converted into the acid by crystallisation from water. The acid softens at 195—200° and decomposes at 205—206°, and when warmed with diluted sulphuric acid yields 2-amino*iso*phthalic acid. The latter, on diazotisation and treatment with iodine in potassium iodide solution, gives 2-*iodo*iso*phthalic acid*, m. p. 205—222° (decomp.), with some of the corresponding hydroxy-acid, from which it is best separated by conversion into the *methyl* ester, m. p. 50°, long, colourless needles. The latter, when heated with copper powder at 140—150°, yields *diphenyl*-2 : 6 : 2′ : 6′-*tetracarboxylic acid*, iridescent leaflets, melting above 350°, in the form of the *tetramethyl* ester, m. p. 125—126°, which crystallises in colourless needles. The corresponding *acid chloride*, $C_{16}H_6O_4Cl_4$, m. p. 189—190°, obtained as a brittle mass by precipitation with light petroleum from benzene, does not yield pyrene on reduction with the usual agents, and when heated with copper gives an amorphous, red substance.

*2-Iodo-*m-*toluic acid*, m. p. 145—146°, prepared from the corresponding methyl aminotoluate (Müller, Abstr., 1909, i, 159) by diazotising, adding potassium iodide, and hydrolysing the *methyl* ester, b. p. 280—290°, so obtained, crystallises in needles from benzene or methyl alcohol. When heated with copper powder at 220°, it yields 2 : 2′-*dimethyldiphenyl*-6 : 6′-*dicarboxylic acid*, which crystallises from ether on addition of light petroleum, sinters strongly, and finally melts at 230°. The yield is small.

Methyl o-*iodocinnamate*, m. p. 65°, crystallises in silky, yellow needles, and does not yield pyrene when heated with copper powder.

o-Iodobenzaldehyde may be readily identified by condensing it with aniline, when it yields o-*iodobenzylideneanilene*, m. p. 75—76°, crystallising from methyl alcohol in colourless needles. When heated with copper powder at 210—220°, *o*-iodobenzaldehyde furnishes 2 : 2′-*dialdehydodiphenyl* as a viscous, brown oil with an odour similar to that of benzaldehyde; the *dioxime*, m. p. 175—176°, crystallises from methyl alcohol in yellow needles. The dialdehyde, when heated with acetic anhydride and sodium acetate, is converted into *diphenyl*-2 : 2′-*diacrylic acid*, m. p. 286° (decomp.), which crystallises from acetic acid, yields diphenic acid on oxidation with dilute alkaline permanganate, and when distilled alone or with lime, lead oxide, or zinc dust, gives an oily substance which slowly deposits a small amount of crystalline matter from which a *picrate*, m. p. 140°, can be obtained. T. A. H.

Simultaneous Reduction and Oxidation by Catalysis.

NICOLAI ZELINSKY and NIKOLAUS GLINKA (*Ber.*, 1911, **44**, 2305—2311*).—Methyl Δ^1-tetrahydroterephthalate, dissolved in dry ether, when treated with palladium black in presence of a current of hydrogen at atmospheric temperature furnishes a mixture of methyl terephthalate and methyl *cis*-hexahydroterephthalate. The same change takes place, but more slowly, with platinum black. The oxidation is not due to oxygen occluded by palladium, since it does not occur in absence of hydrogen. The mechanism of the reaction may be that the tetrahydroterephthalate is immediately reduced in part by the palladium in virtue of hydrogen occluded by the latter, the hydrogen thus lost by the palladium being recovered from the residual tetrahydroterephthalate, so that a re-distribution of the hydrogen in 3 mols. of the tetrahydroterephthalate occurs thus: $3C_{10}H_{14}O_4 = 2C_{10}H_{16}O_4 + C_{10}H_{10}O_4$; or, as suggested by Bach (Abstr., 1910, ii, 31), a labile palladium perhydride may be formed, which reacts with an oxyperhydride, OH_4, momentarily formed, in which, under the influence of palladium perhydride, the normal affinity of oxygen in the molecule of water is so distributed as to hold 4H in place of 2H. The existence of such an intermediate product would explain (1) the simultaneous occurrence of oxidation and reduction in this instance; (2) Ipatieff's observation that in catalytic reduction at high pressures the presence of oxygen favours the action, and (3) that in Sabatier's nickel reduction method, nickel prepared at 200—250°, at which temperature it may still contain oxygen, gives the best results. The palladium black used in these experiments was obtained by adding first formic acid and then alkali to an aqueous solution of palladium ammonium chloride. T. A. H.

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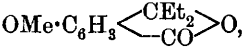
* and *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1084—1091.

[Preparation of Dichloro-*o*-carboxyphenylthiolacetic Acid.] KALLE & Co (D.R.-P. 234375).—When the di- or tri-halogenated *o*-carboxyphenylthiolacetic acid neutral esters are treated with sodium hydroxide, they yield the corresponding halogenated oxythionaphthencarboxylic acid esters, which are then hydrolysed and the resulting product oxidised to dyes.

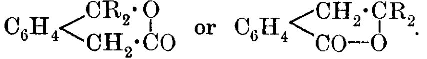
Dichloro-o-carboxyphenylthiolacetic acid, $CO_2H{\cdot}C_6H_2Cl_2{\cdot}S{\cdot}CH_2{\cdot}CO_2H$, glistening, colourless needles, was prepared as follows: Aceto-*o*-toluidide was dichlorinated, oxidised with potassium permanganate to dichloroacetylanthranilic acid, the acetyl group eliminated, and the dichloroanthranilic acid so obtained, diazotised and converted into either a dichloro-*o*-thiolbenzoic acid or a xanthate derivative, which on subsequent treatment with chloroacetic acid yielded the foregoing acid. Esterification was carried out in the usual way, and the ring subsequently closed by heating at 40—50° with concentrated sodium hydroxide, yielding *ethyl dichloro-3-oxy-(1)-thionaphthencarboxylate*, which was not isolated but hydrolysed by dilution and prolonged boiling. Subsequent oxidation with potassium ferricyanide (or air) furnished a dye which was isolated as a dark violet powder. F. M. G. M.

Action of Organo-magnesium Compounds on 4-Methoxyphthalic Anhydride. HUGO BAUER (*Arch. Pharm.*, 1911, **249**, 450—453).—It has been shown previously (Abstr., 1908, i, 274) that the nitro-group in nitrodiethylphthalide (Abstr., 1904, i, 417) probably occupies position 5, and to confirm this an attempt was made to synthesise 5-methoxydiethylphthalide, which was prepared from the nitro-compound as described already (Abstr., 1908, i, 274). By the action of magnesium ethyl bromide on 4-methoxyphthalic anhydride, either 4- or 5-methoxydiethylphthalide might be formed, and trial proved that the former only was produced.

4-*Methoxydiethylphthalide*,  $\mathrm{OMe{\cdot}C_6H_3}<\begin{smallmatrix}\mathrm{CEt_2}\\\mathrm{CO}\end{smallmatrix}>\mathrm{O}$, m. p. 86—87°, crystallises from dilute alcohol in colourless prisms. On fusion with potassium hydroxide, it furnishes anisic acid, and on nitration gives only a *mononitro*-derivative, m. p. 117°, which crystallises from alcohol in faintly yellow needles. On reduction with iron and acetic acid at 100°, this gives the corresponding *amino*-compound, m. p. 163°, which crystallises from dilute alcohol in colourless leaflets or prisms. It fluoresces blue in alcohol solution. T. A. H.

Action of Organo-magnesium Compounds on Homophthalic Anhydride. HUGO BAUER and EWALD WÖLZ (*Arch. Pharm.*, 1911, **249**, 454—458. Compare Abstr., 1904, i, 417; 1905, i, 210; 1909, i, 585, and preceding abstract).—The previous work (*loc. cit.*)

has shown that the normal action between organo-magnesium compounds and dicarboxylic anhydrides gives rise to dialkylphthalides, but in certain cases other reactions occur, such as the formation of *o*-diketones or the production of monoalkylphthalides. This condensation has therefore been further investigated with homophthalic anhydride in place of phthalic anhydride. The former may give rise to dialkyl derivatives of either type represented by the formulæ:



$$C_6H_4{<}\begin{matrix}CR_2\cdot O\\ |\\ CH_2\cdot CO\end{matrix} \quad \text{or} \quad C_6H_4{<}\begin{matrix}CH_2\cdot CR_2\\ |\\ CO—O\end{matrix}.$$

The former type should yield on fusion with potassium hydroxide, and assuming R to be Me, acetone and phenylacetic acid, whilst the second should give acetone and *o*-toluic acid. Application of this reaction to the condensation products gave unexpected results, so that at present constitutional formulæ cannot be assigned to them.

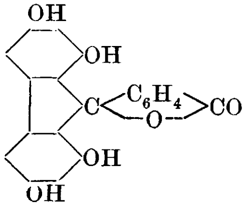
Dimethylhomophthalide, $C_{11}H_{12}O_2$, m. p. 94—95°, obtained by condensing magnesium methyl iodide with homophthalic anhydride and treating the product with dilute acid, crystallises from hot ether in slender, colourless needles, dissolves in warm alkalis, and is re-precipitated by acids, does not react with hydroxylamine or ammonia, and fluoresces green when warmed with sulphuric acid.

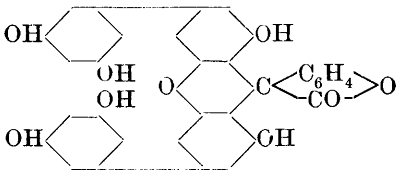
Diphenylhomophthalide, $C_{21}H_{16}O_2$, m. p. 160—161°, similarly prepared, crystallises from alcohol, and resembles the foregoing substance in properties, but gives an orange-red to brownish-red coloration with sulphuric acid.

Dibenzylhomophthalide, $C_{23}H_{20}O_2$, m. p. 163—164°, crystallises from alcohol, and gives a wine-red coloration with sulphuric acid.

T. A. H.

Phthaleins of 3 : 5 : 3′ : 5′-Diresorcinol (3 : 5 : 3′ : 5′-Tetrahydroxydiphenyl). RICHARD MEYER and KARL MEYER (*Ber.*, 1911, **44**, 2678—2684).—The soluble phthalein obtained by Benedikt and Julius (Abstr., 1884, 1139; compare also Link, *ibid.*, 1881, 95) by the condensation of phthalic anhydride and 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl in the presence of concentrated sulphuric acid has, according to the authors, the annexed constitution. When warmed with acetic anhydride and a little sulphuric acid, it yields a *tetra-acetate*, which forms long, flat, rhomb-shaped crystals, m. p. 237—238°; the *tetrabenzoate* crystallises in stout, prismatic needles, m. p. 180—181°. The *tetramethyl ether*, $C_{20}H_8O_2(OMe)_4$, obtained by the action of methyl sulphate in alkaline solution, forms colourless needles; the *tetraethyl ether*, prepared by alkylating the phthalein either with ethyl iodide and sodium ethoxide in alcoholic solution, or by means of ethyl sulphate in alkaline solution, crystallises in flat needles or leaflets, m. p. 223°. When brominated in glacial acetic acid solution the phthalein yields a *tribromo*-derivative, $C_{20}H_9O_6Br_3$, crystallising in slender needles.



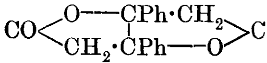


The insoluble phthalein, obtained by Benedikt and Julius (*loc. cit.*), is best prepared by the condensation of 1 mol. of phthalic anhydride with 2 mols. of 3 : 5 : 3′ : 5′ - tetrahydroxydiphenyl in the presence of concentrated sulphuric acid at 120°. It has no m. p., dissolves in alkalis with a blue coloration, and is considered to be a hexahydroxydiphenylfluoran of the annexed constitution. It yields a *hexabenzoate*, crystallising in broad leaves, m. p. 245—250° ; the *hexaethyl ether*, prepared by means of ethyl sulphate, crystallises in needles, m. p. 234—236°.

4 : 4′-(or 2 : 2′-)-*Bisbenzeneazo*-3 : 5 : 3′ : 5′-*tetrahydroxydiphenyl*,
$\mathrm{NPh{:}N\cdot C_6H_2(OH)_2\cdot C_6H_2(OH)_2\cdot N{:}NPh}$,
obtained by the combination of benzenediazonium chloride and 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl in alkaline solution, crystallises in stout, red needles having a steel-blue lustre.

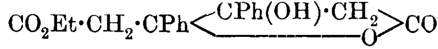
4 : 4′-(or 2 : 2′-)-*Bis*-p-*tolueneazo*-3 : 5 : 3′ : 5′-*tetrahydroxydiphenyl*,
$\mathrm{C_{12}H_8O_4(N_2\cdot C_7H_7)_2}$,
prepared in a similar manner, forms slender, red needles. F. B.

Synthesis of Chrysene. ERICH BESCHKE [with MARIAM WINOGRAD-FINKEL and GEORG KÖHRES] (*Annalen*, 1911, **384**, 143—172).—The interaction of benzil, ethyl bromoacetate, and zinc in boiling benzene leads to the formation of the racemic and meso-modifications, m. p. 137° and 168° respectively, of *ethyl βγ-dihydroxy-βγ-diphenyladipate*, $\mathrm{CO_2Et\cdot CH_2\cdot CPh(OH)\cdot CPh(OH)\cdot CH_2\cdot CO_2Et}$, which are separated by the insolubility of the latter in cold benzene. When boiled with acetic and concentrated hydrochloric acids, or heated above its m. p., the racemic modification is easily converted into the *di-lactone*,

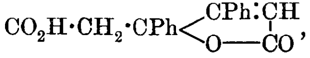


$\mathrm{CO}<\begin{array}{l}\mathrm{O{-}{-}CPh\cdot CH_2}\\ \mathrm{CH_2\cdot CPh{-}{-}O}\end{array}>\mathrm{CO}$, m. p. 194°, which is being examined.

The meso-modification forms a *diacetyl* derivative, m. p. 171°, and is hydrolysed by boiling 10% sodium hydroxide, yielding the *sodium* salt, $\mathrm{C_{18}H_{16}O_6Na_2,10H_2O}$, from which a stable, sparingly soluble *silver* salt, $\mathrm{C_{18}H_{16}O_6Ag_2,3H_2O}$, has been prepared. The anhydrous silver salt is converted into silver, carbon dioxide, and acetophenone by distillation, and regenerates the meso-ester with ethyl iodide. *βγ-Dihydroxy-βγ-diphenyladipic acid*, m. p. 205°, obtained from the sodium salt and dilute acetic acid, is converted by alcoholic hydrogen chloride, not into the original meso-ester, but into *ethyl β-hydroxy-βγ-diphenylbutyrolactone-γ-acetate* [*3-hydroxy-5-keto-2 : 3-diphenyltetrahydrofuran-2-acetate*],



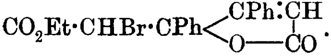
$\mathrm{CO_2Et\cdot CH_2\cdot CPh}<\begin{array}{c}\mathrm{CPh(OH)\cdot CH_2}\\ \mathrm{{-}{-}{-}{-}{-}{-}O}\end{array}>\mathrm{CO}$, m. p. 138°, which is also obtained by adding a little concentrated hydrochloric acid to a boiling concentrated solution of the meso-ester in glacial acetic acid. *β-Hydroxy-βγ-diphenylbutyrolactone-γ-acetic acid*, $\mathrm{C_{18}H_{16}O_5}$, m. p. 179°, is obtained by the action of acetic acid and a mineral acid on its ethyl ester or on βγ-dihydroxy-βγ-diphenyladipic acid, but by too prolonged action the former method yields *βγ-diphenylcrotonolactone-γ-acetic* [*5-keto-2 : 3-diphenyl-2 : 5-dihydrofuran-2-acetic*] *acid*,



$$CO_2H\cdot CH_2\cdot CPh<\begin{matrix}CPh:CH \\ | \\ O—CO\end{matrix},$$

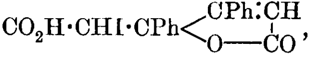
m. p. 184°. This acid, however, in the form of its *ethyl* ester, m. p. 94°, is more easily obtained by treating the above-mentioned meso-ester in acetic anhydride with concentrated sulphuric acid below 40—50°.

When ethyl βγ-diphenylcrotonolactone-γ-acetate is treated with boiling alcoholic sodium hydroxide (not in excess), the sodium salts of two acids are obtained. One of these acids is the *monoethyl* ester of βγ-diphenylmuconic acid, $CO_2H\cdot CH:CPh\cdot CPh:CH\cdot CO_2Et$, m. p. 140°, which lactonises to the original ester when boiled with acetic acid. The other acid is βγ-diphenylmuconic acid, which, however, cannot be isolated, since it at once changes to βγ-diphenylcrotonolactone-γ-acetic acid when liberated from its sodium salt. *Diethyl βγ-diphenylmuconate*, m. p. 72°, obtained from the silver salt of either of the two acids and ethyl iodide, reacts with bromine in chloroform in sunlight to form a *substance*, $C_{20}H_{17}O_4Br$, m. p. 143°, which probably has the constitution



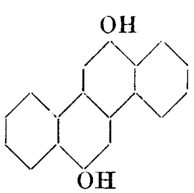
$$CO_2Et\cdot CHBr\cdot CPh<\begin{matrix}CPh:CH \\ | \\ O—CO\end{matrix}.$$

When aqueous sodium βγ-diphenylmuconate is treated with iodine in potassium iodide and the solution is acidified after prolonged keeping, *βγ-diphenylcrotonolactone-γ-iodoacetic acid*,



$$CO_2H\cdot CHI\cdot CPh<\begin{matrix}CPh:CH \\ | \\ O—CO\end{matrix},$$

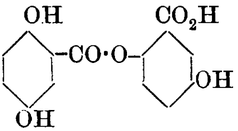
m. p. 217°, is obtained, which is reduced by zinc and acetic acid to *βγ-diphenyl-αδ-dihydromuconic acid*, $CO_2H\cdot CH_2\cdot CPh:CPh\cdot CH_2\cdot CO_2H$, m. p. 297°. This acid is best obtained by reducing sodium diphenylmuconate with sodium amalgam, whereby an *acidic* by-product, $C_{18}H_{16}O_4$, m. p. 195° (*ethyl* ester, m. p. 56°), is also formed, which is easily soluble in alcohol. Diphenyldihydromuconic acid forms an *ethyl* ester, m. p. 86°, and is converted by acetic anhydride and concentrated sulphuric acid into the *di-acetate*, m. p. 246°, of 2 : 8-*dihydroxychrysene* (annexed constitution), which is itself obtained by hydrolysing the diacetate by trituration with cold concentrated sulphuric acid. 2 : 8-Dihydroxychrysene yields yellow solutions in alkalis (becoming blue in the air), forms a *diethyl ether*, m. p. 207°, and a *dibenzoate*, m. p. 280°, and is reduced to chrysene by distillation with zinc dust. C. S.



Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. V. Emil Fischer and Karl Freudenberg (*Annalen*, 1911, 384, 225—244. Compare Abstr., 1910, i, 265).

—Didepsides of the more important di- and tri-hydroxybenzoic acids have been prepared on account of their relation to many natural products.

Dimethylcarbonatodigentisic acid, $C_{18}H_{14}O_{11}$, m. p. 166—167° (corr.), colourless, flexible needles, is obtained by shaking a mixture of 5-methyl-carbonato-2-hydroxybenzoic acid, dimethylaniline, benzene, and phosphorus trichloride for three days at the ordinary temperature; its alcoholic solution develops a deep red coloration with ferric chloride.



Digentisic acid (annexed constitution), m. p. 208—209° (corr.), is obtained by hydrolysing the preceding compound by *N*-ammonia at 18—20° in an atmosphere of hydrogen. In contrast to gentisic acid, it precipitates dilute solutions of albumin or of quinine acetate, and develops a transient, blue coloration with ferric chloride. *Dimethylcarbonatodi-β-resorcylic acid*, $C_{18}H_{14}O_{4}$, m. p. 163—164° (corr.), obtained from 4-methylcarbonato-2-hydroxybenzoic acid by a modification of the preceding process, yields by hydrolysis *di-β-resorcylic acid*, $C_6H_3(OH)_2\cdot CO\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 215° (corr., decomp.).

3-*Methylcarbonato*-4-*hydroxybenzoic acid*, $CO_2Me\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 176° (corr., decomp.), obtained by the partial hydrolysis of the dimethylcarbonatobenzoic acid (Abstr., 1908, i, 892), is converted into *iso*vanillic acid by treatment with diazomethane and subsequent hydrolysis. When treated in acetone with *N*-sodium hydroxide and 3 : 4-dimethylcarbonatobenzoyl chloride in an atmosphere of hydrogen, it yields, after hydrolysis of the product, *diprotocatechuic acid*, $C_6H_3(OH)_2\cdot CO\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 237—239° (corr., decomp.).

Digallic acid, $C_{14}H_{10}O_9$, m. p. 282° (corr., decomp.), is obtained in a similar manner to the preceding acid; it precipitates solutions of albumin and of quinine acetate, and develops the usual bluish-black coloration with ferric chloride.

The following depsides have been prepared by similar methods. [With KURT HOESCH.]—*Diferulic acid*, m. p. 241—242°; *di*-o-*coumaric acid*, m. p. 188—190°; *di-β-hydroxynaphthoic acid*, m. p. 245°; 4-*feruloyloxybenzoic acid*, m. p. 233°; 4-*α-hydroxynaphthoyloxybenzoic acid*, m. p. 246—247°. [With R. LEPSIUS.]—*Disyringic acid*, m. p. 260°; *di*-m-*hydroxybenzoic acid*, m. p. 199°; 4-*syringoyloxybenzoic acid*, m. p. 208°; p-*hydroxybenzoylsyringic acid*, m. p. 282—284°; 4-m-*hydroxybenzoyloxybenzoic acid*, m. p. 239—240°; 3-p-*hydroxybenzoyloxybenzoic acid*, m. p. 254°. C. S.

p-Cresolglycuronic Acid. CARL NEUBERG and E. KRETSCHMER (*Biochem. Zeitsch.*, 1911, **36**, 15—19).

—Phenols excreted in the urine are never found in the free state, but as derivatives of glycuronic and sulphuric acids.

p-Cresol given to dogs was found to be excreted as a *p*-cresol derivative of glycuronic acid, $C_6H_9O_7\cdot O\cdot C_6H_4Me$, and as *p*-tolyl hydrogen sulphate.

A barium salt was isolated from the urine, which proved to be a mixed salt of these two acids. W. J. Y.

Cherry-laurel Water and Solutions of Benzaldehyde and Hydrocyanic Acid in Water. P. H. WIRTH (*Arch. Pharm.*, 1911, **249**, 382—407).

—An investigation of the equilibrium point reached in aqueous solutions of benzaldehyde, benzaldehydecyanohydrin, and hydrogen cyanide under various conditions of temperature, concentration, acidity, alkalinity, etc., with special reference to the determination of the usual composition of cherry-laurel water (compare Denigès, Abstr., 1894, ii, 165; Fromm, Abstr., 1898, i, 266). The following points [are established: All three compounds co-exist in aqueous solution, and the same equilibrium is reached whether the cyanohydrin or its two components be initially added to water. With increasing concentration, the equilibrium point moves in the cyanohydrin direction, and vice versa. The cyanohydrin is progressively dissociated into its components with rise of temperature. Alkalis in small quantities accelerate the rate at which equilibrium is reached, and cause dissociation of the cyanohydrin, but even in presence of considerable quantities of alkali the cyanohydrin is never completely dissociated (compare Ultée, Abstr., 1906, i, 5, and Rosenthaler, Abstr., 1909, i, 623). Equilibrium is reached less quickly in presence of acids. Silver nitrate produces silver cyanide in these solutions in presence of alkali, and the whole of the hydrogen cyanide may be thus removed, but in presence of acids the equilibrium is more stable, except under the influence of change of temperature or concentration. The toxicity of benzaldehydecyanohydrin is proportional to the amount of hydrocyanic acid it can yield on dissociation. T. A. H.

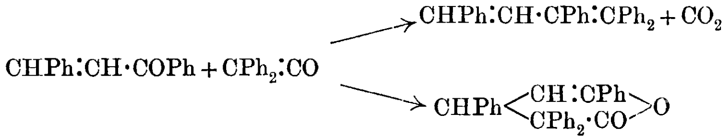
Hydrogenation of Hydroaromatic Compounds. VICTOR SKWORZOW (*J. pr. Chem.*, 1911, [ii], **84**, 422—424).—The usual methods of reduction when applied to hydroaromatic ketones either fail or give poor results. The author finds that the reduction may be effected quite easily, and with almost quantitative yield, by means of sodium and alcohol, if carried out under pressure in an autoclave. *l*-Menthone yields by this method a mixture of solid and liquid dextrorotatory menthols, whilst from *d*-pulegone a lævorotatory mixture was obtained. F. B.

Ketens. V. Reactivity of the Carbonyl Group. HERMANN STAUDINGER and N. KON (*Annalen*, 1911, **384**, 38—135. Compare this vol., i, 462).—Previous experiments have shown that diphenylketen reacts with carbonyl compounds to form β-lactones or their products of decomposition, carbon dioxide and ethylene derivatives (Abstr., 1908, i, 410, 411; this vol., i, 459), and have demonstrated, although not conclusively, on account of complications introduced by side reactions, that the reactivity of the carbonyl group is strongly influenced by the neighbouring substituents (Abstr., 1910, i, 46). The present paper describes an exhaustive examination of this influence. The efficacy of the method of examination previously employed (Abstr., 1910, i, 46) has been tested by experiments with benzophenone or fluorenone; with these ketones side reactions are not possible. It is found that with molecular quantities, 1 : 1 or 1 : 10, of the ketone and diphenylketen (in the form of the solid diphenylketen-quinoline) at 131°, the expressions $x/at(a-x)$ or $1/t.\log a/(a-x)$ respectively are approximately constant during the first hour; subsequently their value diminishes, probably owing to the gradual polymerisation of the diphenylketen-quinoline. (It has been found that extensive polymerisation of diphenylketen-quinoline occurs even at 131° in the presence of certain substances which catalytically accelerate the process. The polymeride does not react with carbonyl compounds.) Consequently, in the experiments with other carbonyl compounds, the amount of carbon dioxide evolved at the end of the first hour is taken as a measure of the reactivity of the carbonyl group, of course provided that the approximate constancy, during this interval, of one or other of the preceding expressions, according to the relative quantities of the carbonyl compound and diphenylketen employed, has afforded evidence that side-reactions have not occurred to an extent sufficient to nullify the results.

The influence of a number of like substituents on different carbonyl-containing groups has been examined in order to compare the reactivity of the carbonyl group in aldehydes, ketones, and acid derivatives. In the formula $R\cdot CO\cdot R'$, R is (I) Ph, (II) $OMe\cdot C_6H_4\cdot$, (III) $NMe_2\cdot C_6H_4\cdot$, (IV) $CHPh\colon CH\cdot$, thus giving four series of carbonyl compounds. The figures in the following list give, for different R′'s, the percentage amount of the ketone which enters into the reaction during the first hour: $R'=CHPh\colon CH$, I. 31·4, II. 32·2, III. 52·3, IV. 69·0; $R'=H$, I. 3·8, II. 17·8, III. 53·0, IV. 38·3; $R'=CN$, I. 2·2, IV. 52·6; $R'=Ph$, I. 1·4, II. 4·2, III. 37·8, IV. 31·4; $R'=Me$, I. 2·2, II. 4·9, III. 11·4, IV. 16·3; $R'=NMe_2$, I. 2·5, II. 2·5, III. 12·2, IV. 11·4; $R'=NPh_2$, I. 2·5, IV. 4·8; $R'=OMe$, I. 0·2, II. 1·1, III. 4·0, IV. 1·3; $R'=Cl$, I. 0·2, II. 0·2, III. 1·6, IV. 4·0. Unfortunately, the results do not allow any definite conclusions to be drawn as to the influence of R and R′ on the activity of the carbonyl group, because the *k* of a unimolecular or bimolecular reaction is only approximately constant when $R=Ph$ or $OMe\cdot C_6H_4$, and not at all constant in the other two series. However, several points are clearly indicated. Firstly, the reactivity of the carbonyl group is very differently influenced by different R′'s in the four series, but always in the same direction. Secondly, the reactivity of the carbonyl group is greatest in the neighbourhood of the styryl group and least in the acid chlorides and esters. Finally, compounds containing the cinnamoyl group are more reactive than those containing the benzoyl group.

The authors show that the varying reactivity of the carbonyl group cannot be explained by steric influences or by an increase or decrease in the basic character of the carbonyl group caused by the neighbouring groups, but attribute it to the varying degree of unsaturation of the carbonyl group; the greater the unsaturation of the group, the greater is its reactivity with diphenylketen. This leads them to a deduction which is emphasised throughout the paper. Since chromophores are unsaturated groups, the more unsaturated the carbonyl group the more chromophoric is its character. In their experiments the authors have observed that the carbonyl group in a coloured compound is more unsaturated (that is, more reactive) than that in a colourless compound of similar structure; moreover, influences which intensify the colour of a carbonyl compound also increase the unsaturation of the carbonyl group. A general review of these and of previous experiments shows that quinones and unsaturated ketones react most energetically with diphenylketen, then come, in order of decreasing reactivity, aldehydes, aromatic ketones, and acid derivatives; it is the first two classes of compounds which are most prone to exhibit colour.

The reactivity of the carbonyl group in a series of compounds containing the cinnamoyl group cannot be compared by the amount of carbon dioxide evolved, because the reaction proceeds in two directions; thus diphenylketen and phenyl styryl ketone react:



$$CHPh{:}CH{\cdot}COPh + CPh_2{:}CO \begin{cases} \rightarrow CHPh{:}CH{\cdot}CPh{:}CPh_2 + CO_2 \\ \rightarrow CHPh{<}\begin{matrix}CH{:}CPh\\CPh_2{\cdot}CO\end{matrix}{>}O \end{cases}$$

(this δ-lactone was previously stated to be 3-benzoyl-1 : 1 : 2-triphenyl-4-*cyclo*butanone, Abstr., 1910, i, 46).

The great reactivity of the whole conjugated system in phenyl styryl ketone is very remarkable in contrast with the slight reactivity of benzaldehyde and of styrene with diphenylketen. In the conjugated system, $\underset{4}{C}{:}\underset{3}{C}{\cdot}\underset{2}{C}{:}\underset{1}{O}$, the addition of diphenylketen occurs the more in the position 1 : 4 the more the carbon atom 4 is rendered unsaturated by neighbouring substituents; addition in the position 1 : 2 predominates when the oxygen atom is rendered more unsaturated. In the "crossed" conjugate system, $\begin{matrix}C{:}C\\\underset{4}{C}{:}\underset{3}{C}\end{matrix}{>}\underset{2}{C}{:}\underset{1}{O}$, the distribution of the residual affinity is such that the oxygen is particularly unsaturated; consequently the addition of diphenylketen occurs very largely at the carbonyl group. For example, phenyl styryl ketone and diphenylketen react to the extent of 87% in the 1 : 2 position and 63% in the 1 : 4, whilst in the case of distyryl ketone the values are 71 and 29% respectively.

It is found, in general, that compounds containing a conjugated system are more reactive than those with a simple double linking, and that substances with a "crossed" system of double linkings are particularly unsaturated. Here again a parallelism is to be observed between unsaturation and colour; substances containing a conjugated system are more coloured than similar substances which do not, the colour being especially intense when a "crossed" conjugate system is present.

A similar parallelism is observed in the case of pyrone and *p*-benzoquinone; pyrones react very slightly with diphenylketen, whilst the quinones exhibit the greatest reactivity.

One of the most important points in the paper is the examination of the influence of auxochromic groups on the reactivity of a carbonyl group. (The auxochrome must be present as OR or NR_2, since diphenylketen attacks the hydroxyl or amino-group in preference to the carbonyl group.) A study of the preceding list of compounds of the type R·CO·R′ shows that the methoxy-group, and particularly the dimethylamino-group, increases the reactivity of the carbonyl group;

their influence is greatest in the ortho-, and least in the meta-, position. Since it is well-known that auxochromes intensify colour, the parallelism between colour and unsaturation is manifested once again. The introduction of an acyl group into the hydroxyl or amino-group (which weakens the colour of the substance) causes a diminution in the reactivity of the carbonyl group.

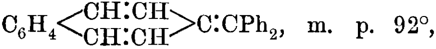
Several other points, such as Kauffmann's inversion of chromophores and an explanation of the action of auxochromic groups, are discussed in the light of the theory that the reactivity of a group is dependent on its degree of unsaturation.

The following new compounds are described. The great majority of them have been obtained by the decomposition at 130—153° of the additive compound of diphenylketen and a carbonyl compound. p-*Methoxytriphenylethylene*, $OMe\cdot C_6H_4\cdot CH{:}CPh_2$, m. p. 81—82°, white crystals; p-*dimethylaminotriphenylethylene*, $NMe_2\cdot C_6H_4\cdot CH{:}CPh_2$, m. p. 126—127°, autoxidisable, yellow or yellowish-green crystals; *triphenyl*-p-*tolylethylene*, $CPh_2{:}CPh\cdot C_6H_4Me$, m. p. 153°; *diphenyldianisylethylene*, $CPh_2{:}C(C_6H_4\cdot OMe)_2$, m. p. 159—160°, colourless needles; p-*dimethylaminotetraphenylethylene*, $NMe_2\cdot C_6H_4\cdot CPh{:}CPh_2$, m. p. 173°; *tetramethyl*-pp′-*diaminotetraphenylethylene*,

$$CPh_2{:}C(C_6H_4\cdot NMe_2)_2,$$

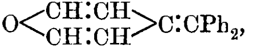
m. p. 211—212°, yellowish green crystals; *αε-tetramethyl*-pp′-*diaminodiphenyl-γ-diphenylmethylene-Δ^{αδ}-pentadiene*,

$$CPh_2{:}C(CH{:}CH\cdot C_6H_4\cdot NMe_2)_2,$$

m. p. 169—170°, yellowish-brown crystals; *benzhydrylidenebenzo*cyclo*heptadiene*,  $C_6H_4{<}\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}{>}C{:}CPh_2$, m. p. 92°, yellow crystals; *benzhydrylidenedimethylbenzo*cyclo*heptadiene*,

$$C_6H_4{<}\begin{matrix}CH{:}CMe\\CH{:}CMe\end{matrix}{>}C{:}CPh_2,$$

m. p. 128·5—129°, colourless crystals; *benzhydrylidenediphenylbenzo*cyclo*heptadiene*, m. p. 181—182°.

p-*Dimethylaminoacetophenone*, m. p. 105·5°, is obtained in small yield by boiling dimethylaniline, acetic anhydride, and zinc chloride for four hours (the substance, m. p. 58°, described as *p*-dimethylaminoacetophenone in the literature is the monomethylated compound). *γ-Benzhydrylidenepentamethylene oxide*,  $O{<}\begin{matrix}CH{:}CH\\CH{:}CH\end{matrix}{>}C{:}CPh_2$, m. p. 86°, unlike pyrone itself, possesses very weak basic properties. *Dimethylaminomethylenecamphor*, $C_8H_{14}{<}\begin{matrix}C{:}CH\cdot NMe_2\\|\\CO\end{matrix}$, m. p. 63—64°, is prepared by treating a well-cooled, methyl-alcoholic solution of oxymethylenecamphor with the calculated amount of alcoholic dimethylamine.

C. S.

Stereoisomeric Chloroimino-ketones. PETER P. PETERSON (*Amer. Chem. J.*, 1911, **46**, 325—344).—In a preliminary paper, Stieglitz and Peterson (Abstr., 1910, i, 323) have described the *α*- and *β*-chloroimides of *p*-chlorobenzophenone. A full account of the work is now given, together with a description of the *α*- and *β*-chloroimides of *p*-methoxybenzophenone and *pp*-chloromethoxybenzophenone.

Chloroiminobenzophenone, $CPh_2{:}NCl$, m. p. 37°, prepared by the action of hypochlorous acid on iminobenzophenone, forms yellow crystals.

α-*Chloroimino*-p-*methoxybenzophenone*, $OMe{\cdot}C_6H_4{\cdot}CPh{:}NCl$, m. p. 90°, crystallises in thin plates; the *β-compound*, m. p. 54°, forms large, asymmetric crystals. The two forms were proved to be structurally identical by treating them with dry hydrogen chloride, thus converting them both into chloroimino-*p*-methoxybenzophenone *hydrochloride*, which is decomposed by water into ammonium chloride and *p*-methoxybenzophenone.

p-*Chloro*-p-*methoxybenzophenone*, $C_6H_4Cl{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$, m. p. 125°, was prepared by the action of anisole on *p*-chlorobenzoyl chloride in presence of aluminium chloride. α-*Chloroimino*-p-*chloro*-p-*methoxybenzophenone*, $ClC_6H_4.C({:}NCl){\cdot}C_6H_4{\cdot}OMe$, m. p. 94°, forms thin plates, and the *β*-compound, m. p. 65°, large crystals; their structural identity was proved in the same way as in the previous case.

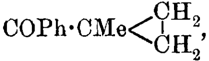
o-*Chloro*-p-*methoxybenzophenone*, $C_6H_4Cl{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$, obtained from *o*-chlorobenzoyl chloride and anisole, has b. p. 250°/50 mm.

E. G.

δ-Phenylbutyl Ketones and δ-Phenylvaleric Acid. WALTHER BORSCHE (*Ber.*, 1911, **44**, 2594—2596).—The unsaturated condensation products of cinnamaldehyde and ketones obtained by the author (Abstr., 1910, i, 680) have been reduced by Paal's method with hydrogen and colloidal palladium to the corresponding saturated substances, thus yielding a series of ketones containing the group $CH_2Ph{\cdot}[CH_2]_3{\cdot}CO{\cdot}$, and therefore designated δ-phenylbutyl ketones. The simplest member, *δ-phenylbutyl methyl ketone*, $CH_2Ph{\cdot}[CH_2]_3{\cdot}COMe$, prepared from cinnamylideneacetone in cold methyl alcohol, is a highly refractive liquid, b. p. 268—269°, with a characteristic sweet odour; its *oxime* has b. p. 179—180°/12 mm. When shaken with a solution of bromine in 5% sodium hydroxide at 0°, the ketone yields bromoform, *δ-phenylvaleric acid*, m. p. 61°, in 35% yield, and the *methyl* ester, b. p. 173°/35 mm., of the acid.

C. S.

β-Keto-αα-dialkyl Alcohols. III. EDMOND E. BLAISE and I. HERMAN (*Ann. Chim. Phys.*, 1911, [viii], **23**, 522—544. Compare Abstr., 1910, i, 534).—A continuation of the work described already (*loc. cit.*), the investigation being now extended to keto-alcohols containing a phenyl group.

*Phenyl acetoxy*tert.-*butyl ketone*, $OAc{\cdot}CH_2{\cdot}CMe_2{\cdot}COPh$, b. p. 155·5—156·5°/11 mm., prepared by the general method (Abstr., 1908, i, 248), furnishes a p-*nitrophenylhydrazone*, m. p. 125°, crystallising in long, orange-yellow needles from alcohol, and on hydrolysis by a cold 10% solution of potassium hydroxide in water yields *phenyl hydroxy*tert.-*butyl ketone*, b. p. 152—153°/12 mm. The latter furnishes an *oxime*, m. p. 122·5°, crystallising in slender needles, a p-*nitrophenylhydrazone*, m. p. 157°, forming yellow needles, and a *phenylurethane*, m. p. 89°, crystallising in long needles from benzene on addition of light petroleum. Both phenyl hydroxy*tert.*-butyl ketone and its acetyl derivative give on hydrolysis by warm alkalis phenyl *iso*propyl ketone and formaldehyde. On dehydration by phosphoric oxide, phenyl hydroxy*tert.*-butyl ketone might be expected to yield tiglylbenzene or dimethylacrylbenzene, but the substance actually produced in this reaction appears to be *benzoylmethyl*cyclo*propane*,  $COPh{\cdot}CMe{<}\genfrac{}{}{0pt}{}{CH_2}{CH_2}$, b. p. 117—119°. This gives a p-*nitrophenylhydrazone*, m. p. 175°, as a crystalline, yellow powder. *Tiglylbenzene* [*phenyl* α-*methylpropenyl ketone*], $COPh{\cdot}CMe{:}CHMe$, b. p. 117·5°/10 mm., obtained by condensing tiglyl chloride with zinc phenyl bromide, yields a p-*nitrophenylhydrazone*, m. p. 136°, crystallising in long, yellowish-red needles. *Dimethylacrylbenzene* [*phenyl* iso*butenyl ketone*],

$$COPh{\cdot}CH{:}CHMe_2,$$

b. p. 117°/10 mm., similarly prepared, gives a p-*nitrophenylhydrazone*, m. p. 132°, which crystallises from warm alcohol.

β-Acetoxy-β-phenylpivalyl chloride, $OAc{\cdot}CHPh{\cdot}CMe_2{\cdot}COCl$, b. p. 151°/9 mm., m. p. 41°, is readily converted into the corresponding p-*toluidide*, m. p. 191—192°. With zinc ethyl iodide, it condenses to form *ethyl β-acetoxy-β-phenyl*tert.-*butyl ketone*, $OAc{\cdot}CHPh{\cdot}CMe_2{\cdot}COEt$, b. p. 160—165°/11 mm., m. p. 42°, with some acetoxyphenylpivalyl anhydride and *iso*butenylbenzene (nitrosite, m. p. 154°). From the first of these products the corresponding keto-alcohol could not be prepared, since in contact with alkalis the acetoxy-compound readily decomposed into benzaldehyde and ethyl *iso*propyl ketone. As the keto-alcohol could not be isolated, its dehydration could not be studied. It should furnish *dimethylatropylethane*, $CMe_2{:}CPh{\cdot}COEt$, b. p. 124°/12 mm., which was prepared by condensing *dimethylatropyl chloride*, b. p. 120·5°/11 mm. (p-*toluidide*, m. p. 135—136°, slender needles), with zinc ethyl iodide. It furnishes a p-*nitrophenylhydrazone*, m. p. 129°, crystallising in yellowish-red needles from alcohol. T. A. H.

The Nature of the Carbon Double Linking. III. The Bromides of Anisylidenecinnamylideneacetone. HUGO BAUER and HEDWIG DIETERLE (*Ber.*, 1911, **44**, 2691—2697).—Anisylidenecinnamylideneacetone (*p*-methoxystyryl β-styrylvinyl ketone),

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}OMe,$$

may be prepared by condensing *p*-methoxystyryl methyl ketone with cinnamaldehyde by means of potassium hydroxide in alcoholic solution (compare Scholtz and Einhorn, Abstr., 1896, i, 368). When treated with bromine in glacial acetic acid solution, it yields a *dibromide*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_4{\cdot}OMe,$$

and a *tetrabromide*,

$$CHPh{:}CH{\cdot}CHBr{\cdot}CHBr{\cdot}CO{\cdot}CHBr{\cdot}CHBr{\cdot}C_6H_4{\cdot}OMe,$$

crystallising in small, colourless needles, m. p. 139—140° and 155—156° respectively. The bromine atom adjacent to the anisyl group in these compounds is very mobile, and is readily replaced by alkyloxy-groups.

*ζ-Bromo-η-methoxy-α-phenyl-η-*p-*anisyl-*$\Delta^{\alpha\gamma}$*-heptadien-ε-one*,

$$CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CHBr{\cdot}CH(OMe){\cdot}C_6H_4{\cdot}OMe,$$

prepared by boiling the dibromide with methyl alcohol, crystallises in light yellow plates, and gives a deep bluish-violet coloration with strong sulphuric acid; the corresponding *ethoxy*-compound is an oil.

*ζ-Bromo-η-acetoxy-α-phenyl-η-*p*-anisyl-$\Delta^{\alpha\gamma}$-heptadien-ε-one,*
$CHPh\colon CH\cdot CH\colon CH\cdot CO\cdot CHBr\cdot CH(OAc)\cdot C_6H_4\cdot OMe$,
obtained by the action of magnesium acetate on the dibromide in the alcoholic solution, crystallises in stout, pale yellow prisms, m. p. 78—79°.

*γδζ-Tribromo-η-methoxy-α-phenyl-η-*p*-anisyl-Δ^{α}-hepten-ε-one,*
$CHPh\colon CH\cdot [CHBr]_2\cdot CO\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe$,
prepared either by boiling *p*-methoxystyryl β-styrylvinyl ketone tetrabromide with methyl alcohol or by the addition of bromine to the preceding bromomethoxy-compound in glacial acetic acid solution, crystallises in slender, white needles, m. p. 176—177·5°. When heated with pyridine, it loses hydrogen bromide, yielding *γζ-dibromo-η-methoxy-α-phenyl-η-*p*-anisyl-$\Delta^{\alpha\gamma}$-heptadien-ε-one,*
$CHPh\colon CH\cdot CBr\colon CH\cdot CO\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe$,
which forms yellowish-brown leaflets, m. p. 174—175°.

That the addition of bromine to *p*-methoxystyryl β-styrylvinyl ketone takes place at the double linking adjacent to the anisyl group was proved by the oxidation of the above-mentioned ζ-bromo-η-methoxy-phenylanisylheptadienone by means of potassium permanganate in acetone solution to anisaldehyde and αβ-dihydroxy-γ-phenyl-γ-butyrolactone (Fischer and Stewart, Abstr., 1892, 1447). F. B.

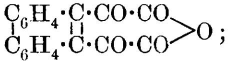
Acylated Phenanthrenes and Some of their Derivatives.

CONRAD WILLGERODT and BRUNO ALBERT (*J. pr. Chem.*, 1911, [ii], **84**, 383—394).—*9-Acetylphenanthrene*, $C_{16}H_{12}O$, prepared by the interaction of acetyl chloride and phenanthrene in carbon disulphide solution in the presence of aluminium chloride, crystallises in leaflets, m. p. 123°, having a bluish fluorescence; it yields an *oxime*, crystallising in leaflets, m. p. 80°, and a *phenylhydrazone*, light yellow leaflets, m. p. 181°. When oxidised with five to six times its weight of chromium trioxide in glacial acetic acid solution, the ketone yields the ordinary form of phenanthraquinone, crystallising in needles, m. p. 205°. Oxidation with twice its weight of chromium trioxide results in the formation of a second modification, which crystallises in lustrous, golden leaflets, m. p. 204—205°, and is converted by dissolving in cold concentrated sulphuric acid or by prolonged heating with alcoholic potassium hydroxide into the ordinary form; the same transformation takes place when the leaflets are heated at 180—200°. Both forms yield with *o*-phenylenediamine the same phenanthraphenazine, m. p. 219—220°. When heated with yellow ammonium sulphide at 170—180°, acetylphenanthrene yields *9-phenanthrylacetamide*, $C_{16}H_{13}ON$, crystallising in white leaflets, m. p. 250—252°, together with *9-phenanthrylacetic acid*, $C_{14}H_9\cdot CH_2\cdot CO_2H$, which crystallises in small needles, m. p. 213—215°, and forms a yellow, gelatinous *silver* salt.

9-αα-Dichloroethylphenanthrene, $C_{14}H_9\cdot CMeCl_2$, prepared from 9-acetylphenanthrene and phosphorus pentachloride, crystallises in small, yellow needles, which decompose at 80—100° without melting.

Acetylphenanthrene is reduced by zinc and glacial acetic acid to 9-phenanthrylmethylcarbinol (Pschorr, Abstr., 1906, i, 820), and by hydriodic acid and phosphorus to *9-ethylphenanthrene*, $C_{16}H_{14}$, which forms lustrous needles, m. p. 61°.

The interaction of phenanthrene and excess of acetyl chloride in the presence of aluminium chloride yields 9 : 10-*diacetylphenanthrene*, $C_{14}H_8(COMe)_2$, which crystallises in white needles, m. p. 178°, having a green fluorescence, and forms a *phenylhydrazone*, m. p. 189°, a *bisphenylhydrazone*, $C_{14}H_8(CMe{:}N\cdot NHPh)$, small, yellow needles, m. p. 238°, and a *dioxime*, leaflets, m. p. 258—260°. When oxidised with chromium trioxide in glacial acetic acid solution, the diacetyl derivative is converted into *phenanthrene*-9 : 10-*diketodicarboxylic anhydride*.



$$\begin{array}{l} C_6H_4\cdot C\cdot CO\cdot CO \\ \,| \qquad \| \\ C_6H_4\cdot C\cdot CO\cdot CO \end{array}\!\!>O\ ;$$

this forms a light yellow powder, m. p. above 360°, and yields a yellow *silver* salt, $C_{14}H_8(CO\cdot CO_2Ag)_2$.

By methods similar to those described in the case of the monoacetyl derivative, 9 : 10-diacetylphenanthrene has been converted into 9 : 10-*di-α-hydroxyethylphenanthrene*, $C_{14}H_8(CHMe\cdot OH)_2$, crystallising in leaflets, m. p. 165—166°, 9 : 10-*di-αα-dichloroethylphenanthrene*,

$$C_{14}H_8(CMeCl_2)_2,$$

which forms yellow leaflets, decomposing at 130—140° without melting, and 9 : 10-*diethylphenanthrene*, which crystallises in large, lustrous leaflets, m. p. 90—91°.

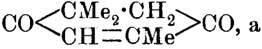
9-*Benzoylphenanthrene*, $C_{14}H_9\cdot COPh$, forms lustrous, white needles, m. p. 127°, and yields 9-*benzylphenanthrene*, crystallising in large, white leaflets, m. p. 91—92°, when distilled with zinc dust in a stream of hydrogen.

9 : 10-*Dibenzoylphenanthrene* forms leaflets, m. p. 317°; it is reduced by phosphorus and hydriodic acid at 180—190° to 9 : 10-*dibenzylphenanthrene*, which crystallises in needles, m. p. 180—182°. F. B.

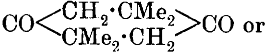
The Two Forms of *o*-Benzoquinone. FRIEDRICH KEHRMANN (*Ber.*, 1911, 44, 2632—2633).

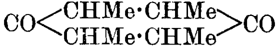
—The author is of opinion that the question, whether the two modifications of *o*-benzoquinone are isomeric and desmotropic, has not been answered; especially, a certain proof has not been given that the colourless form has the peroxide formula and the coloured form the diketo-formula. The colourless form has not been analysed, and might well be a hydrated *o*-benzoquinone, $O{:}C_6H_4{:}(OH)_2$, or even an additive compound containing ether (compare Willstätter and Müller, this vol., i, 728). C. S.

Action of Magnesium Methyl Iodide on *p*-Xyloquinone and Toluquinone. EUGEN BAMBERGER and LOUIS BLANGEY (*Annalen*, 1911, 384, 272—322).

—The action of magnesium methyl iodide on *p*-xyloquinone has been examined very thoroughly, and on toluquinone more superficially. In the former reaction the product obtained after the usual operations consists of unchanged material, amorphous substances, about 25% of *p*-xyloquinol, ψ-cumoquinol (1 : 2 : 5-trimethylquinol), ψ-cumenol, 2 : 2 : 5-*trimethyl*-2 : 3-*dihydro*-p-*benzoquinone*,  $CO<\begin{smallmatrix} CMe_2\cdot CH_2 \\ CH{=}CMe \end{smallmatrix}>CO$, and smaller amounts of prehnitol, *tetramethyl*cyclo*hexandione*, and *di*-p-*xyloquinol monomethyl ether*, together with resinous and oily substances.

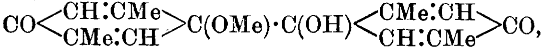
2 : 2 : 5-*Trimethyl*-2 : 3-*dihydro*-p-*benzoquinone*, [1 : 1 : 4-*trimethyl*-

Δ^3-cyclo*hexene*-2 : 5-*dione*] m. p. 86°, crystallises in large, highly refractive, yellow prisms, has an odour of camphor, is extremely volatile with steam, and forms a p-*nitrophenylhydrazone*, $C_{15}H_{17}O_3N_3$ (two forms, one having m. p. 244·5—245·5°, and the other decomposing at 306—308°), and a *bis-semicarbazone*, $C_{11}H_{18}O_2N_6$, blackening at 400°. *Tetramethyl*cyclo*hexandione*, which may have the constitution  $CO<^{CH_2\cdot CMe_2}_{CMe_2\cdot CH_2}>CO$ or



$$CO<^{CHMe\cdot CHMe}_{CHMe\cdot CHMe}>CO$$

(the former being the more probable), forms colourless prisms, m. p. 110—111°, has an odour of borneol and peppermint, is extremely volatile with steam, and forms a *bis-semicarbazone*, $C_{12}H_{22}O_2N_6$, m. p. 330° (decomp.). *Di*-p-*xyloquinol monomethyl ether*,



$$CO<^{CH:CMe}_{CMe:CH}>C(OMe)\cdot C(OH)<^{CMe:CH}_{CH:CMe}>CO,$$

m. p. 220—220·5°, colourless needles, forms an *acetyl* derivative, $C_{19}H_{22}O_5$, m. p. 191—192°, p-*nitrophenylhydrazone*, $C_{23}H_{25}O_5N_3$, m. p. 272—272·5°, and a *semicarbazone*, $C_{18}H_{23}O_4N_3$, m. p. 272—273°.

3 : 4-Xyloquinol, toluhydroquinone, *p*-xylohydroquinone, and *p*-xyloquinol have been isolated from the product obtained from toluquinone and magnesium methyl iodide.

An examination of the constitutions of the preceding substances shows that in *p*-xyloquinone and toluquinone, which contain the system $\overset{1}{O}:\overset{2}{C}\cdot\overset{3}{C}:\overset{4}{C}\cdot\overset{5}{C}:\overset{6}{O}$, the addition of the magnesium methyl iodide occurs in the 1 : 2- or the 1 : 4-, but not in the 1 : 6-, position (compare Kohler, Abstr., 1905, i, 358). Consequently, the authors believe that during the reduction of quinones to hydroquinones the addition of the hydrogen does not take place directly at the oxygen atoms of the quinone, but in the 1 : 2- and 1 : 4-positions (above scheme), the hydroquinone being produced subsequently by intramolecular change.

C. S.

[Preparation of Anthraquinone Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 234518).—When halogenated aromatic sulphones are boiled with α-aminoanthraquinones in a suitable solvent (such as nitrobenzene or naphthalene) in the presence of a condensing agent (copper acetate), compounds having valuable tinctorial properties are formed.

The *product* from α-aminoanthraquinone (1 mol.) and *pp*-dibromosulphobenzide forms brownish-red crystals, whilst the employment of 4-amino-1-benzylaminoanthraquinone and the foregoing sulphone furnishes a *compound*, violet crystals, which in the vat dyes wool a very fast violet colour.

The tinctorial properties of these and other compounds of a similar nature are tabulated in the original.

F. M. G. M.

Preparation of Aminoanthraquinones and of Aminonaphthanthraquinones or their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234917).—Aminoanthraquinones and aminonaphthanthraquinones may be prepared by heating halogenated benzoylbenzoic acids with ammonium hydroxide under pressure in the presence of a catalyst (such as copper), and submitting the amino-acids so obtained to the action of a dehydrating agent.

4(5)-*Chloro*-2-p-*toluoylbenzoic acid*, m. p. 168—170° (prepared from toluene and 4-chlorophthalic anhydride), was heated at 190—195° during twelve hours with 20% ammonium hydroxide in the presence of copper powder, the solution just acidified, and then neutralised with sodium acetate, when the *amino-acid* separated as a greyish-yellow powder.

2-*Amino*-6(7)-*methylanthraquinone*, orange-yellow needles, m. p. 256—257°, was obtained by heating the foregoing amino-acid at 200° with 10 parts of 90% sulphuric acid and subsequent crystallisation from xylene.

3(6)-*Chloro*-2-p-*toluoylbenzoic acid* (prepared from toluene and 3-chlorophthalic anhydride) yielded an *amino-acid* (pale grey powder), which was subsequently converted into 1-*amino*-6(7)-*methylanthraquinone*, red needles, m. p. 175°.

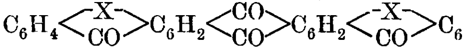
5′-*Chloro*-2-m-*xyloylbenzoic acid*, m. p. 162°, obtained from phthalic anhydride and *o*-chloro-*m*-xylene, gave an *amino-acid* crystallising in pale yellow needles, m. p. 140° (decomp.), and subsequently furnished 1-*amino*-2 : 4-*dimethylanthraquinone*, dark red crystals, m. p. 293°.

4(5)-*Chloro*-2-*naphthoylbenzoic acid*, m. p. 175° (prepared from naphthalene and 4-chlorophthalic anhydride), yielded a grey *amino-acid*, which was converted into an *aminonaphthanthraquinone*, glistening, red needles, m. p. 238°.

2′-*Chloro*-2-*naphthoylbenzoic acid*, m. p. 217—220°, obtained from phthalic anhydride and 2-chloronaphthalene, gave an *amino-acid* (a dark yellow powder), and finally an *aminonaphthanthraquinone*, brownish-violet, glistening needles, m. p. 182°. F. M. G. M.

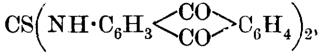
Preparation of Condensation Products in the Anthracene Series.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234977).—*Anthraquinone*-1 : 5-*bisanthranilic acid*, a dark violet powder, is prepared by heating potassium anthranilate in nitrobenzene solution with 1 : 5-dichloroanthraquinone in the presence of a condensing agent; when this is heated at 100° with concentrated sulphuric acid, it furnishes a condensation product in the form of a blue powder.

Anthraquinone-1 : 5-*bis*-o-*thiolbenzoic acid*, an orange-red powder, obtained in a similar manner from 1 : 5-dichloroanthraquinone and potassium *o*-thiolbenzoate in alcoholic solution, yields when heated at a higher temperature with sulphuric acid (23% anhydride) a product which forms a red powder. These compounds have probably the constitution :  $C_6H_4\left<\begin{matrix}X\\CO\end{matrix}\right>C_6H_2\left<\begin{matrix}CO\\CO\end{matrix}\right>C_6H_2\left<\begin{matrix}X\\CO\end{matrix}\right>C_6H_4$, where X is either sulphur or an imino-group. F. M. G. M.

Preparation of Anthraquinone Condensation Products.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234922).—When 2-amino-anthraquinone is boiled (in nitrobenzene solution) with trichloromethyl mercaptan in the presence of a condensing reagent (such as copper), s-*dianthraquinonylthiocarbamide*,



$$CS\left(NH\cdot C_6H_3<\begin{matrix}CO\\CO\end{matrix}>C_6H_4\right)_2,$$

is obtained in the form of a red powder.

The tinctorial properties of this and similar compounds obtained from 1 : 4-diaminoanthraquinone, αβ-diaminoanthraquinone, *p*-diaminoanthrarufin, 1-aminoanthraquinone, 1 : 4-aminohydroxyanthraquinone, and 1 : 5-diaminoanthraquinone respectively are tabulated in the original. F. M. G. M.

Chrysophanic Acid, Frangula-Emodin, and Some Oxonium Compounds of Anthracene Derivatives. Otto Fischer and Hans Gross (*J. pr. Chem.*, 1911, [ii], **84**, 369—382).—Chrysophanic acid may be obtained from chrysarobin by oxidation with chromic acid and demethylation of the resulting product by heating with hydrochloric acid in acetic acid solution. The mixture of chrysophanic acid and emodin thus obtained is separated by means of aqueous sodium carbonate. Successive treatment of the mixture with potassium hydroxide and methyl sulphate yields emodin trimethyl ether and chrysophanic acid dimethyl ether.

The transformation of diacetylchrysophanic acid into diacetylrhein is best accomplished by oxidation with chromic acid at 50—60° in a solution of equal parts of acetic anhydride and glacial acetic acid.

Dibenzoylchrysophanic acid, prepared by heating chrysophanic acid with benzoyl chloride in the presence of pyridine, crystallises in slender needles, m. p. 212° (compare de la Rue and Müller, this Journ., 1857, **10**, 298). It is converted by oxidation with chromic acid into *dibenzoylrhein*, which crystallises in stellar aggregates of yellow prisms, m. p. 253—255°, and gives a red coloration with concentrated sulphuric acid.

When heated with concentrated ammonia, chrysophanic acid yields a *compound*, $C_{15}H_{11}O_3N$, crystallising in slender needles of a bronze lustre. The compound has the character of an amide, dissolves in alkalis and ammonia, forming reddish-violet solutions, and gives an orange coloration with sulphuric acid; the *ammonium* salt is unstable.

Triacetylemodin, prepared from frangula-emodin by heating with acetic anhydride and sodium acetate, has m. p. 196—197° (Liebermann gives 190°). It is oxidised by chromic acid to *triacetylemodic acid*, $C_{21}H_{14}O_{10}$, which crystallises in slender, yellow needles, and is hydrolysed by aqueous potassium hydroxide to *emodic acid*, $C_{15}H_8O_7$. The latter compound crystallises in orange-yellow needles, which decompose at 340—360°, and dissolve in alkalis with a reddish-violet coloration; it has the constitution of a trihydroxy-β-anthraquinonecarboxylic acid.

[With P. Neber.]—A large number of anthracene derivatives have been studied with respect to their ability to form oxonium salts. Whilst anthracene and its methyl and chloro-derivatives together with anthraquinone, the methylanthraquinones, dimethyldihydroanthraquinone, and diethyldihydroanthraquinone do not yield oxonium salts with perchloric and hydrobromic acids, and the hydroxyanthraquinones give at most yellowish-red or red solutions, the alkyloxy-derivatives of anthraquinone often yield stable salts. From this the conclusion is drawn that the presence both of carbonyl and alkyloxy-groups is essential for the formation of stable oxonium salts in the anthracene series.

The following salts, all of which are red in colour, were isolated: the *hydrobromide*, $C_{18}H_{17}O_5Br$, the *zincibromide*, $C_{18}H_{17}O_5Br_3Zn$, and the *perchlorate*, $C_{18}H_{17}O_9Cl$, of emodin trimethyl ether; the *hydrobromide* and *zincibromide*, $C_{17}H_{15}O_4Br_3Zn$, of chrysophanic acid dimethyl ether, and the *hydrobromide* and *zincibromide* of dimethylchrysazin (1 : 8-dimethoxyanthraquinone). The hydrochlorides and zincichlorides may also be isolated, but these are more unstable than the corresponding bromides. The salts of 1 : 2-, 1 : 4-, 1 : 5-, and 1 : 6-dimethoxyanthraquinone and of rufigallol hexamethyl ether with perchloric or hydrobromic acid are too unstable to be isolated.

Rufigallol hexamethyl ether, $C_{20}H_{20}O_8$, prepared by the action of methyl sulphate on its potassium salt in the presence of anhydrous potassium carbonate, crystallises in light yellow needles, m. p. 240°.

F. B.

Relationship between Chrysophanic Acid, Aloe-Emodin, and Rhein. OTTO A. OESTERLE (*Arch. Pharm.*, 1911, **249**, 445—449).—It is now shown that on reduction aloe-emodin furnishes chrysophanhydranthrone, and this on oxidation by air in presence of sodium hydroxide solution furnishes chrysophanic acid. This observation in conjunction with those recorded already (Abstr., 1903, i, 356; 1908, i, 905; 1909, i, 946, and following abstract; Léger, Abstr., 1902, i, 549; Frobenius and Hepp, Abstr., 1907, i, 428; Robinson and Simonsen, Trans., 1909, **95**, 1085; Fischer, Falco, and Gross, Abstr., 1911, i, 309, and Tutin and Clewer, Trans., 1911, **99**, 946) indicates that rhein, aloe-emodin, and chrysophanic acid are 1 : 8-dihydroxyanthraquinones containing respectively a $-COOH$, $-CH_2OH$, and $-CH_3$ group in position 2.

T. A. H.

Constitution of Frangula-Emodin. OTTO A. OESTERLE and W. SYPKENS-TOXOPÉUS (*Arch. Pharm.*, 1911, **249**, 311—321).—The previous formulation of emodin as 3 : 6 : 7-trihydroxy-2-methylanthraquinone (Oesterle and Tisza, Abstr., 1908, i, 350) is of doubtful validity in view of Oesterle and Johann's observation (Abstr., 1910, i, 860) that methyl sulphate methylates both hydroxyl groups of chrysophanic acid, although one is probably in the α- and the other probably in the β-position. The results of investigations of the action of ethyl chloroacetate on emodin, and of aniline on tetranitro-emodin, indicate that two hydroxyls are in the α-position and one in the β-position, whence emodin is either 1 : 6 : 8-trihydroxy-2-methylanthraquinone or 1 : 5 : 7-trihydroxy-2-methylanthraquinone.

Emodin reacts with ethyl chloroacetate to form chiefly *ethyl* *emodinglycollate diacetate*, $C_{14}H_4O_2Me(OAc)_2\cdot O\cdot CH_2\cdot CO_2Et$, m. p. 192—193°, which crystallises from alcohol on addition of chloroform, and when heated with potassium hydroxide in alcohol furnishes *potassium emodinglycollate*, crystallising in red needles. A small amount of *ethyl emodindiglycollate acetate*,

$$C_{14}H_4O_2Me(O\cdot CH_2\cdot CO_2Et)_2\cdot OAc,$$

m. p. 152°, crystallising from 95% alcohol in bright yellow, slender needles, or from dry alcohol in thick needles, is formed. On hydrolysis this furnishes a *product*, m. p. 252—253° (decomp.), crystallising from pyridine on addition of alcohol.

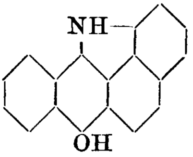
Tetranitro-emodin, obtained by nitration of emodin with nitric acid (D 1·486—1·500), crystallises from acetic acid in orange-yellow needles and explodes when heated. When boiled with aniline during two hours, it furnished bluish-violet flocks of a *substance*, which agreed in ultimate composition with that required by the formula

$$C_{15}H_3O_2(NHPh)_3(NO_2)_2(NHPh)_2,$$

that is, tetranitro-emodin in which two nitro-groups have reacted with aniline and the three hydroxyl groups have been replaced by aniline residues (D.R.-P. 89080). This substitution of hydroxyl groups by aniline residues takes place most readily when the hydroxyl groups occupy para-positions with respect to nitro-groups in hydroxy-anthraquinones (*loc. cit.*) T. A. H.

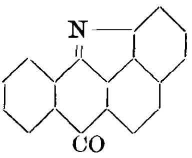
Existence of Quinonoid Properties in Anthraquinone Derivatives.

ROLAND SCHOLL [with G. VON WOLODKOWITSCH] (*Ber.*, 1911, **44**, 2370—2377. Compare Bally and Scholl, this vol., i, 676).—1 : 2-Benzanthraquinone when nitrated with a mixture of nitric and acetic acids and acetic anhydride yields a mixture of two yellow mono-nitro-derivatives, $C_{18}H_9O_4N$, m. p. 277—278^c, and 250—251°. On reduction of the less fusible isomeride with phenylhydrazine, the corresponding amine, $C_{18}H_{11}O_2N$, is not obtained, water being eliminated between the amino- and carbonyl group, and the anhydro-compound further reduced to *O*,*N*-dihydro-2 : 9-indoloanthrone (formula I), $C_{18}H_{11}ON$, a green substance. When dissolved in sodium hydroxide this compound is oxidised by the air to a brown substance, 2 : 9-indoloanthrone (formula II).



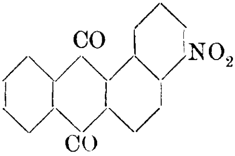
(I.)

This compound, in contrast to anthraquinone itself and its derivatives, exhibits marked quinonoid properties. It reacts energetically with phenylhydrazine, being reduced to the dihydro-compound (formula I above). It acts at the ordinary temperature in benzene or ethereal solution as an oxidising agent towards hydrogen iodide and sulphurous acid, colours hæmatoxylin red, but does not blue guaiacum resin. These pronounced quinonoid properties are considered to be due to the influence of the pyrrole nucleus attached to another nucleus of entirely different character, and so causing the existence of a carbon-nitrogen double bond of a highly unsaturated nature. This

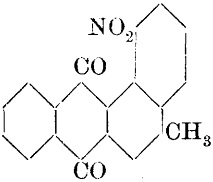


(II.)

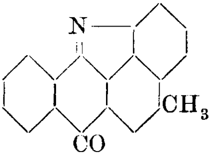
influences the conversion of a neighbouring benzenoid linking into an ethenoid, and brings out the quinonoid properties of the anthraquinone.


(III.)

The more fusible isomeric nitro-1 : 2-benzanthraquinone is converted on reduction into a red amino-1 : 2-benzanthraquinone, m. p. 215°, which, since it does not give a vat dye when fused with potassium hydroxide or heated with antimony pentachloride in nitrobenzene solution, is considered to have the amino-group in the benzene nucleus. The nitro-derivative accordingly has formula III.


(IV.)

3 - Methyl - 1 : 2 - benzanthraquinone when nitrated yields only one mononitro-derivative; this must have the formula IV, since it is converted on reduction into a 3-methyl-2 : 9-indoloanthrone (V), which possesses typical quinonoid properties. An isomeric 4-nitro-derivative could not be obtained, owing to the steric hindrance of the methyl group occupying the α-position in the naphthalene nucleus.


(V.)

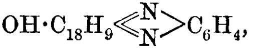
1-*Nitro*-1 : 2-*benzanthraquinone* forms yellow plates or prisms, m. p. 277—278°. The isomeric 4-*nitro*-1 : 2-*benzanthraquinone* crystallises in slender needles, m. p. 250—251°. Both isomerides dissolve in concentrated sulphuric acid with an orange-red coloration.

4-*Amino*-1 : 2-*benzanthraquinone* forms red crystals, m. p. 215°, and dissolves in concentrated sulphuric acid with a reddish-brown coloration.

O,N-*Dihydro*-2 : 9-*indoloanthrone* is a green powder, but forms brown or brownish-red solutions with a green fluorescence.

2 : 9-*Indoloanthrone* is obtained in violet-brown flakes, which sinter at 160°, but do not melt. E. F. A.

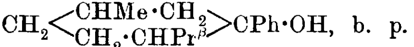
2 : 8- or *amphi*-Chrysoquinone. ERICH BESCHKE [with FRANZ DIEHM] (*Annalen*, 1911, **384**, 173—192. Compare this vol., i, 873).—2 : 8- or amphi-*Chrysoquinone*, $C_{18}H_{10}O_2$, m. p. 288—290° (decomp.), obtained by the action of lead dioxide on a suspension of 2 : 8-dihydroxychrysene in boiling acetic acid, crystallises in reddish-yellow needles, is odourless and non-volatile with steam, reacts instantly with phenylhydrazine or acidified potassium iodide, and forms a yellow, crystalline *compound*, $C_{18}H_{10}O_2,NaHSO_3,2H_2O$, with sodium hydrogen sulphite. Its suspension in hot alcohol reacts in the presence of atmospheric oxygen with dilute sodium hydroxide to form, after acidification, 8-*hydroxy*-1 : 2-*chrysoquinone*, $OH\cdot C_{18}H_9O_2$, dark red needles, decomp. above 300°, and with aniline or ethylaniline to form 8-*hydroxy*-1 : 2-*chrysoquinone*-1-*anil*, $OH\cdot C_{18}H_9O{:}NPh$, bluish-violet crystals, m. p. 230° (decomp. at 220°). The constitutions given to the two preceding substances are based on Willstätter and Parnas' experiences of the oxidising power of quinones of different types (Abstr., 1907, i, 1056), and are supported by the following evidence.

The chief proof is the fact that aniline or ethylaniline, reacting with 2 : 8-chrysoquinone, produce the same anil. 8-Hydroxy-1 : 2-chrysoquinone, which is also easily obtained by the action of sodium hydroxide and air on a boiling alcoholic suspension of 2 : 8-diacetoxychrysene, forms a *sodium* salt, $C_{18}H_9O_3Na$, bluish-violet, almost black needles, is reduced by sodium hyposulphite to the colourless 1 : 2 : 8-*trihydroxychrysene*, and forms an *acetyl* derivative, m. p. 252°, red needles, *ethyl ether*, m. p. 246°, and *benzoyl* derivative, m. p. 232°. It does not appreciably react at the ordinary temperature with phenylhydrazine, acidified potassium iodide, or sulphurous acid. A hot saturated solution of the quinone in glacial acetic acid reacts with concentrated alcoholic *o*-phenylenediamine to form 8-*hydroxy*-1 : 2-*chrysophenazine*,  $OH\cdot C_{18}H_9{<}\substack{N\\N}{>}C_6H_4$, m. p. 292°, yellow needles, the *benzoyl* derivative, m. p. 270°, *acetyl* derivative, m. p. 252°, and *ethyl ether*, m. p. 215°, of which are respectively identical with the substituted chrysophenazines obtained by condensing *o*-phenylenediamine with the corresponding derivatives of 8-hydroxy-1 : 2-chrysoquinone.

8-Hydroxy-1 : 2-chrysoquinone-1-anil yields 8-hydroxy-1 : 2-chrysoquinone by hydrolysis with mineral acids, and yields with acetic anhydride an *acetyl* derivative, $C_{26}H_{17}O_3N$, m. p. 215°, which is converted by dilute hydrochloric and a little acetic acid into 8-acetoxy-1 : 2-chrysoquinone.

1 : 2 : 8-*Triacetoxychrysene*, $C_{18}H_9(OAc)_3$, colourless crystals, m. p. 195°, is obtained by treating a solution of 8-acetoxy-1 : 2-chrysoquinone in boiling acetic anhydride with zinc dust. 1 : 2 : 8-*Triethoxychrysene*, $C_{18}H_9(OEt)_3$, colourless crystals, m. p. 142°, is prepared by treating an aqueous alcoholic suspension of the sodium salt of 8-hydroxychrysoquinone, with dilute sodium hydroxide and sodium hyposulphite, and subsequently with ethyl sulphate. It has been found that 2-hydroxy-α-naphthaquinoneanil is produced when β-naphthaquinone is boiled with ethylaniline in alcoholic solution. C. S.

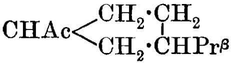
Condensation of Menthones with Organomagnesium Compounds. Synthesis of Homologues of Menthol. MARCEL MURAT (*J. Pharm. Chim.*, 1911, [viii], 4, 294—299).

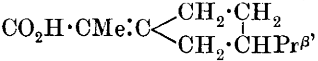
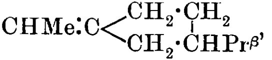
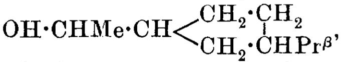
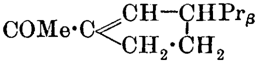
—Magnesium phenyl bromide reacts with menthone to give 1-3-*phenyl*-1-*methyl*-4-iso*propyl*-3-cyclo*hexanol*,  $CH_2{<}\substack{CHMe\cdot CH_2\\CH_2\cdot CHPr^{\beta}}{>}CPh\cdot OH$, b. p. 175°/20 mm., D^0 0·9962, n_D 1·527, $[\alpha]_D^{20}$ − 16·32°. The *racemic* form prepared in the same way from thymomenthone had b. p. 170°/18 mm., D^0 0·9950. When treated with phenylcarbimide, or passed over alumina at 300°, dehydration occurs with production of the corresponding menthenes; 3-*phenyl*-1-*methyl*-4-iso*propyl*cyclo*hexene* has b. p. 268—272°/760 mm., D^0 0·9700, n_D 1·537. $[\alpha]_D$ + 13·9°.

Magnesium *cyclo*hexyl bromide slowly acts on menthone, giving 3-cyclo*hexyl*-1-*methyl*-4-iso*propyl*-3-cyclo*hexanol*, monoclinic needles, m. p. 92°, together with 3-cyclo*hexyl*-1-*methyl*-4-iso*propyl*cyclo*hexene*, b. p. 265°/760 mm., D^0 0·9897, n_D 1·498, $[\alpha]_D$ + 6·2°.

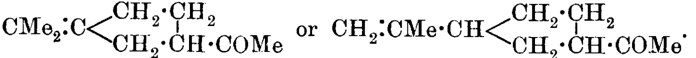
Thymomenthone (inactive menthone) was prepared by passing the vapour of Brunel's thymomenthol (Abstr., 1906, i, 81) over copper at

300°; it occurs as a viscid liquid, b. p. 212°, having a less pronounced odour than natural methone. When treated with magnesium *cyclo*hexyl bromide, it yields r-cyclo*hexylthymomenthol*, b. p. 164°/15 mm. (decomp.), D^0 0·9931, n_D^{17} 1·529; the corresponding cyclo*hexylthymomenthene* has b. p. 260°/756 mm. W. O. W.

Terpenes and Ethereal Oils. CVII. Constitution and Synthesis of Pinolone and of Dihydropinolone (3-Acetyl*iso*propyl*cyclo*pentane). OTTO WALLACH (*Annalen*, 1911, **384**, 193—208).—Dihydropinolone, when prepared by the reduction of pinolone by Paal's method and purified through the *semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 164—165°, is a colourless liquid with an odour of amyl acetate; it has b. p. 211°, D^{21} 0·8885, and n_D^{21} 1·4466. Its recognition as 3-acetyl*iso*propyl*cyclo*pentane,  $CHAc<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{array}$, has been accomplished by its degradation to *iso*propyl*cyclo*pentan-3-one, and by its synthesis from this substance. Its degradation is represented essentially by the scheme: dihydropinolone $\xrightarrow{NaOBr}$ $>CH\cdot CO_2H$ (b. p. 153—156°/16 mm.) $\longrightarrow$ $>CH\cdot CO\cdot NH_2$ (m. p. 164—165°; identical with Semmler's dihydrocamphoceenamide *b* [Abstr., 1906, i, 681]) $\xrightarrow[KOH]{Br\ and}$ $>CH\cdot NH_2$ $\longrightarrow$ $>CH\cdot OH$ $\xrightarrow{CrO_3}$ *iso*propyl*cyclo*pentan-3-one.

The synthesis has been accomplished as follows: The interaction of *iso*propyl*cyclo*pentan-3-one (prepared from tanacetophorone), zinc, and ethyl α-bromopropionate in benzene leads to the formation of an hydroxy-ester, which by successive boiling with acetic anhydride, hydrolysis by alcoholic potassium hydroxide, and acidification yields an acid,  $CO_2H\cdot CMe{:}C<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{array}$, the distillation of which in hydrogen produces a *hydrocarbon*, $C_{10}H_{18}$, b. p. 172—174°, D^{20} 0·809, n_D^{20} 1·4506. This hydrocarbon has assigned to it the constitution  $CHMe{:}C<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{array}$, on account of its exalted molecular refraction and its behaviour. It is practically identical with the *hydrocarbon*, $C_{10}H_{18}$, b. p. 171—174°, D^{22} 0·812, n_D 1·4515, obtained by heating *dihydropinolol*,  $OH\cdot CHMe\cdot CH<\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{array}$, b. p. 215—216°, D^{19} 0·8920, n_D 1·4569 (prepared by the reduction of dihydropinolone), with zinc chloride. The synthetic hydrocarbon (from the *iso*propyl*cyclo*pentanone) forms a blue *nitrosochloride*, which by successive treatment with boiling acetic acid and sodium acetate and with sulphuric acid is converted into a *ketone*,  $COMe\cdot C<\begin{array}{l}CH-CHPr_{\beta}\\ CH_2\cdot CH_2\end{array}$ (*semicarbazone*, m. p. 182—184°), isomeric with pinolone. This ketone yields dihydropinolone when reduced by Paal's method.

The series of transformations whereby pulegone dibromide is converted into pulegenic acid (Abstr., 1903, i, 567) has suggested an explanation of the course followed by pinyl tribromide during its conversion into pinolone. This explanation leads to the conclusion that pinolone may be either



$$CMe_2:C<\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH\cdot COMe\end{matrix} \text{ or } CH_2:CMe\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ | \\ CH_2\cdot CH\cdot COMe\end{matrix}.$$

In harmony with this, the author finds that pinolonesemicarbazone, m. p. 158°, can be separated by repeated crystallisation into two portions, the less fusible of which has m. p. 173°. C. S.

Degradation of Nerol and its Constitution.

A. Blumann and Otto Zeitschel (*Ber.*, 1911, **44**, 2590—2593).—When nerol or geraniol is oxidised by 1% potassium permanganate at 0° and the product is subsequently treated with dilute chromic and sulphuric acids, acetone, lævulic acid, and oxalic acid are obtained, the amount of lævulic acid being practically the same in each case. These results confirm the view that nerol and geraniol are stereoisomerides (Zeitschel, Abstr., 1906, i, 521). C. S.

Influence of Water on the Rotatory Power of Camphor Solutions.

Endre von Kazay (*Pharm. Post*, 1911, **44**, 495—496).—The value of $[\alpha]_D$ for camphor in a number of organic solvents is about $+43{\cdot}6°$, independent of the nature of the solvent. The addition of water to the alcoholic or acetic acid solution causes a very marked alteration in the rotation. When the proportion of water in the alcoholic solution containing about 12% of camphor is increased from 4% to 37%, the rotation diminishes from 8·3° to 7·1°. When in acetic acid solution containing about 10% of camphor, the proportion of water is gradually increased from zero to 32·3%, the rotation gradually diminishes from 8·3° to 6·0°. If the proportion of water in a solution is known, the percentage of camphor, p, can be calculated from the formula : $p=(100d)/(l[\alpha]_D B)$, where B is 0·1308 for acetic acid solutions, and 0·12822 for alcoholic solutions. G. S.

Effect of Molecular Symmetry on the Optical Activity and Relative Rotatory Power of Aromatic Position Isomerides.

Thomas P. Hilditch (*Zeitsch. physikal. Chem.*, 1911, **77**, 482—497. Compare Trans., 1908, **93**, 1618; 1909, **95**, 1578).—A more detailed account of work already published (compare Proc., 1910, **26**, 141). The relative effects of ortho-, meta- and para-isomerides on the rotatory power is illustrated by the behaviour of compounds containing methyl, halogen, hydroxy-, methoxy-, nitro-, and amino-groups.

Sodium camphor-β-thiosulphonate, $C_{10}H_{15}O\cdot SO_2\cdot SNa$, is prepared by interaction of camphor-β-sulphonyl chloride and sodium sulphide in boiling alcohol. It occurs in soft, colourless, crystalline masses. The corresponding *acid* is an oily substance, and unstable. The *silver* salt forms a cream-coloured powder. The *anhydride*, $[(C_{10}H_{15}O)\cdot SO_2]_2S$, is obtained in almost theoretical yield by boiling equivalent amounts of the sulphonyl chloride and the sodium salt dissolved in carbon tetrachloride. It occurs in pale yellow needles, m. p. 144°.

Dicamphor-β-sulphonyl disulphide, $[(C_{10}H_{15}O)\cdot SO_2]S_2$, was obtained by the action of iodine, dissolved in potassium iodide solution, on sodium camphor-β-thiosulphonate, and also by acting on the latter with sulphur monochloride in cold carbon tetrachloride. It occurs in colourless needles, m. p. 130°.

The phenyl camphor-β-sulphonates were all prepared by a modification of the Schotten-Baumann method. *Catechol dicamphor-β-sulphonate*, $C_6H_4(SO_3{\cdot}C_{10}H_{15}O)_2$, forms colourless or slightly red crystals, m. p. 124°; the corresponding *resorcinol* compound melts at 129—130°, and the *quinol* compound at 187° (slight decomp.).

Pyrogallol tricamphor-β-sulphonate, $C_6H_3(SO_3{\cdot}C_{10}H_{15}O_3)_3$, occurs in long, soft, colourless needles, m. p. 148° (decomp.). The corresponding *phloroglucinol* compound forms prismatic crystals, m. p. 104—106°.

G. S.

[Essential Oils.] SCHIMMEL & Co. (*Bericht*, October 1911, pp. 17—152).—*Artemisia biennis*, according to Rabak, yields 0·03% of a dark brownish-red, sweet-smelling oil, D^{25} 0·893, $[\alpha]_D$ +4·39°, n_D^{30} 1·5181, acid number 0, ester number 16, acetyl ester number 17·28, which dissolves in 4 vols. or more of 95% alcohol, and probably contains methylchavicole. According to the same author, *Artemisia serrata* yields 0·3% of a reddish-brown, bitter oil, D^{25} 0·913, α_D +6·8°, n_D^{30} 1·4602, acid number 1·6, ester number 10·0, acetyl ester number 43, which dissolves in 0·5 or more vols. 80% alcohol, and probably contains thujone.

Barosma crenulata (round buchu) leaves yield 1·7% oil, D_{15}^{20} 0·9364, α_D −15°22′, n_D^{20} 1·48005, which dissolves in 2·5 or more vols. of 70% alcohol with separation of paraffin, is brownish-yellow in colour after removal of traces of copper by acid, has mint-like odour, possibly due to menthone, and contains very little diosphenol.

Mandarin oil pressed from unripe fruits in Valencia had D^{15} 0·8665, n_D^{30} 1·47900, acid number 0·2, ester number 17·3, was incompletely soluble in 90% alcohol, and was of dark olive-green colour.

Helichrysum angustifolium oil from Dalmatia had D^{15} 0·9005, n_D^{20} 1·48209, acid number 0·9, ester number 61·1, and dissolved in 9 or more vols. of 90% alcohol. It was of olive-green colour, and resembled camomile oil in odour.

The Jalpaiguri (Indian) lemon-grass oils referred to previously (Abstr., 1910, i, 328) have now been found to be derived from *Cymbopogon pendulus*, Stapf.

Cayenne linaloe oil, like the Mexican product, contains methylheptenol.

Dalmatian laurel-leaf oil has D^{15} 0·9268, α_D −14°36′, n_D^{20} 1·46813, acid number 0·5, ester number 29·9, acetyl ester number 68·6, and is soluble in 2·5 or more vols. of 70% alcohol.

Dalmatian myrtle oil has D^{15} 0·9254, α_D +13°20′, n_D^{20} 1·46694, acid number 1·0, ester number 134·8, acetyl ester number 186·7, and is soluble in 3·2 or more vols. of 70% alcohol.

French peppermint, cultivated in Dalmatia, gave oils which after rectification had the following range of constants, D^{15} 0·9094—0·9141, α_D −11°45′ to −18°12′, n_D^{20} 1·46041—1·46783, acid number 0—1·0, total menthol 39·6—54·1%, ester menthol 2·6—3·8% and were soluble in 2·8 to 3 vols. of 70% alcohol with slight opalescence. According to

Henderson (*Chem. & Drug.*, 1911, **79**, 216), English peppermint grown on the banks of a river yielded only 0·1% oil, D 0·9046, a_D $-27°$, total menthol 59·2%, ester menthol 3·9%, whilst that grown in open fields on clay soil gave 0·409% oil, D 0·9065, a_D $-27·4°$, total menthol 61·35%, ester menthol 5·57%, and a third sample grown on sandy soil gave 0·19% oil, D 0·9046, a_D $-28·2°$, total menthol 59·46%, ester menthol 4·74%. Italian peppermint oil from Pancalieri had D^{15} 0·915, a_D $-22°56'$ to $-26°51'$, was soluble in 2·9 vols. of 70% alcohol, and deposited solid matter on cooling (Bourdet, *Bull. Sci. pharm.*, 1911, **18**, 372).

Sage oil distilled in Dalmatia in August from dry herb had the following normal constants, D^{15} 0·9165, $a_D+25°$, n_D^{20} 1·45871, acid number 1·0, ester number 9·3, whilst oil distilled from fresh herb in May had D^{15} 0·9111, a_D $+20°22'$, ester number 10·3, and was less soluble in alcohol than the August oil.

Origanum hirtum a-albiflorum herb grown in Dalmatia furnished origanum oil having the following range of constants, D^{15} 0·9231—0·94000, a_D $+0°6'$ to $0°20'$, n_D^{20} 1·49394—1·50436, soluble in from 2·8 vols. of 70% alcohol to 1·5 vols. of 80% alcohol, and containing from 51 to 60% thymol.

Dalmatian spike oil had D^{15} 0·9022—0·9033, a_D $-0°10'$ to $0°53'$, acid number 0·9, ester number 5·4—5·6, and was soluble in from 4 to 5 vols. of 60% alcohol. *Lavandula spica* herb from Spain yielded 1·9% of brownish-yellow oil, D^{15} 0·9100, a_D $-2°20'$, n_D^{20} 1·46823, acid number 3·7, ester number 7·0, and was soluble in 2 vols. of 70% alcohol, but became opalescent with more alcohol.

According to Jeancard and Satie (*Perf. and Essent. Oil Rec.*, 1911, **2**, 79) a so-called sandalwood from Guiana yielded oil having the following range of constants, D^{15} 0·963 to 1·0122, a_D $+0°30'$ to $-6°$, saponification value 13 to 65, after acetylation 65 to 117. On distillation it gave the following fractions: below 155°/20 mm., 18 to 27·4%, 155—160°/20 mm., 59 to 80%, and above 160°/20 mm., 2 to 13·6%. The second fraction contained a new constituent, *maroniol*, b. p. 158—159°/20 mm., D^{23} 1·0378, a_D $-6°$, which dissolved in 1·7 vols. 70% alcohol, and was colourless, viscous, and of agreeable odour; this substance is probably a tertiary alcohol.

Star anise oil contains *d*-*a*-pinene, *d*-*β*-phellandrene, dipentene, and *l*-limonene in the lower boiling fractions; as well as a fraction, 163—168°, having a turpentine-like odour, but which is free from *β*-pinene and sabinene.

Strobilanthes lupulinus flower buds yield an oil, D 0·9648, $a-16°30'$, *n* 1·4688, acid number 1·7, ester number 257 (*Perf. and Essent. Oil Rec.*, 1911, **2**, 96), having a strong, pleasant odour recalling those of tarragon and lavender.

A "wormwood" oil from Dalmatia had D^{15} 0·9188, acid number 1·3, ester number 64·4, and dissolved in 1 vol. 80% alcohol; it differed in odour from true wormwood oil, and was probably derived from another species of Artemisia. Wisconsin "wormwood" oil had D^{22} 0·9168, saponification number 150 (forty minutes), after acetylation 234·8 to 236·2, and was dark, with a mint-like odour. It contained much thujone, and on hydrolysis gave formic and salicylic acids.

Oil from *Gaultheria fragrantissima* of the Nilgiris, India, had D^{15} 1·1877, α_D ± 0, n_D^{20} 1·53485, ester number 364·8, was reddish-brown in colour and resembled winter green oil in odour.

Cananga oil from German East Africa distilled from fresh flowers had D^{15} 0·9366, $\alpha_D - 17°1'$, n_D^{20} 1·48451, acid number 1·1, ester number 136·3 and was soluble, with opalescence in 8 or more vols. of 80% alcohol.

Artemisia coerulescens herb from Turin gave 0·24% oil, D^{40} 0·9179, α_D $- 5°50'$, acid number 11·3, ester number 42·0, which was brown and of buttery consistence, and had an odour recalling that of hyssop oil. The crystalline matter deposited by the oil melted at 108°.

Cardamom roots from Indo-China yielded 0·64% citron-yellow oil, D^{15} 0·9066, α_D $- 32°57'$, n_D^{20} 1·48151, acid number 3·7, ester number 87·9, acetyl ester number 96·7, which was different from the seed oil in odour. It contained bisabolene, cineole, and paraffin.

Juniperus procera wood sawdust from German East Africa yielded 3·2% of oil, D^{15} 0·9876, n_D^{20} 1·50893, acid number 14·9, ester number 8·4, acetyl ester number 70. Fragments of the wood gave 3·2% of oil, which was semi-solid, and, after removal of solid matter, had D^{15} 1·0289, n_D^{20} 1·51011, acid number 27·06, ester number 7·93, acetyl ester number 89·6. The deposited crystals were cedar-camphor.

Cinnamomum Burmanni bark from Timor and the Celebes gave 0·5% oil, D^{15} 1·0198, α_D $- 1°50'$, n_D^{20} 1·58282, which was not so pleasant n aroma as Ceylon cinnamon bark oil, but contained 77% of aldehydes and 11% phenols.

Meriandra benghalensis leaves from Erythraea gave 1·5% bright brown oil, D^{15} 0·9513, α_D $- 2°5'$, n_D^{20} 1·47490, acid number 3·7, ester number 14·8, which had an odour resembling those of rosemary and sage. It deposited *d*-camphor when cooled.

Santolina chamaecyparissus herb from Turin gave 0·47% dark brown oil, D^{15} 0·9065, n_D^{20} 1·50040, acid number 6·6, ester number 16·4, acetyl ester number 74·2, with an odour resembling that of wormwood oil.

Satureja cuneifolia oils from Dalmatia had the following range of constants, D^{15} 0·9182 to 0·9440, α_D $- 1°50'$ to 5°15', n_D^{20} 1·49816 to 1·50556, and contained from 28 to 59% of phenols, chiefly carvacrol, whilst the non-phenolic portion had a strong odour of cymene.

A résumé of literature published since April, 1911, on the analysis, physical properties, chemistry, etc., of essential oils and their constituents is also given. T. A. H.

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1911, [iii], 2, 1—25).—[JUSTIN DUPONT and LOUIS LABAUNE.]—"Linalyl" bromide, obtained by esterifying either geraniol or linalool (Abstr., 1910, i, 184), condenses with ethyl sodiomalonate to form the *ester*, $C_{10}H_{17}\cdot CH(CO_2Et)_2$, b. p. 158—159°/5 mm., and this on hydrolysis gives the corresponding acid, $C_{10}H_{17}\cdot CH(CO_2H)_2$, which on distillation under reduced pressure furnishes the monobasic *acid*,

$$C_{10}H_{17}\cdot CH_2\cdot CO_2H,$$

b. p. 145—146°/5 mm., the *ethyl* ester of which has b. p. 127—128°/5 mm. The $\cdot C_{10}H_{17}$ group in the ester does not appear to have the geranyl configuration, since it is unaffected by sulphuric acid of 66° Bé. On reduction with sodium in alcohol, the ester yields a new *alcohol*,

$C_{10}H_{17}\cdot CH_2\cdot CH_2\cdot OH$, D^{18} 0·8956, n_D^{18} 1·4755, b. p. 119°/5 mm., which gives a crystalline *pyruvate*, b. p. 135°/6 mm., the *semicarbazone* of which crystallises from alcohol and melts at 103°. The alcohol is not converted into the corresponding alcohol by Sabatier and Senderens' method. All these substances possess weak and not very characteristic odours.

Linalyl bromide condenses similarly with ethyl sodioacetoacetate to form the *ester*, $C_{10}H_{17}\cdot CHAc\cdot CO_2Et$, b. p. 145°/6 mm., which on hydrolysis by potassium hydroxide in alcohol gives the *ketone*, $C_{10}H_{17}\cdot CH_2Ac$. The latter was not obtained pure, but it gives a *semicarbazone*, m. p. 86°, and on oxidation yields lævulic acid as chief product.

Ruta montana from Algeria furnishes an oil, D^{15} 0·8307, $\alpha_D + 0°42'$, soluble in 2·25 vols. 70% alcohol, which contains about 90% of methyl nonyl ketone. *Ruta bracteosa* from Algeria gives an oil, D^{15} 0·8410, $\alpha_D - 4°12'$, soluble in two vols. 70% alcohol, and containing 90% of ketones. This oil differs also from the foregoing in congealing partly at − 5°, whilst the first oil is solid at + 10°.

Inula viscosa oil from Algeria had D^{15} 0·9436 $\alpha_D - 24°0'$, and consisted chiefly of cineol.

Syrian origanum oil had D^{15} 0·9309 and $\alpha_D + 1°6'$, and was soluble in 1·2 or more vols. 80% alcohol; on standing it deposited a translucent "camphor." Syrian thyme oil, D^{15} 0·9120, $\alpha_D - 0°56'$, contained 43% phenols, composed of thymol and carvacrol. Syrian sage oil, D^{15} 0·9843, $\alpha_D - 6°8'$, was soluble in 1·5 or more vols. of 70% alcohol. Syrian laurel-leaf oil had D^{15} 0·9161 and $\alpha_D - 14°20'$, and was soluble in one or more vols. of 80% alcohol. Syrian neroli oil, D^{15} 0·8758, $\alpha_D + 1°6'$, saponification number 51·5, is similar to French neroli oil in constants. Syrian petit-grain oil had D^{15} 0·8857, α_D 3°24', saponification number 77·4, and was soluble in 1·25 or more vols. of 70% alcohol. T. A. H.

Essential Oil of Bupleurum fructicosum. II. LUIGI FRANCESCONI and G. SANNA (*Gazzetta*, 1911, **41**, i, 796—813. Compare this vol., i, 658).—By fractional distillation of the essential oil of *Bupleurum fructicosum*, a large amount of a *terpene* is obtained as a mobile, colourless liquid, b. p. 167—169°, D^{14} 0·8416, $\alpha^{17} + 35·7°$, n_D 1·4862, which polymerises at 200°. The *polymeride* is a white, amorphous substance, m. p. 90—100° (becoming yellow), α^{14} − 66·14° (in chloroform solution). The action of bromine on the terpene yields a colourless, viscous, non-crystalline substance, the amount of bromine absorbed indicating that the substance contains two double linkings. Hydrogen chloride also gives a non-crystalline product. With nitrosyl chloride, a small quantity of a *substance* was obtained, crystallising in small prisms, which begin to melt at 97°, and are entirely decomposed at 102°. When the residue from this reaction is distilled in steam, an *oil* is obtained, b. p. about 200° (partial resinification), which is dextrorotatory in alcoholic solution. The action of hydrazine and of phenylhydrazine does not yield crystalline compounds, but semicarbazide gives a *semicarbazone*, which forms silvery scales, m. p. 197—198°, and is dextrorotatory.

The essential oil also contains an *alcohol* and an *ether*. R. V. S

Extraction of an Aldehydic Perfume from Pine-wood Tar. FRIEDRICH MÜLLER (D.R.-P. 234794).—The fractional distillation of pine-wood tar furnishes at 150—200° substances of aldehydic nature and powerful odours, an *aldehyde* thus obtained formed a light brown oily liquid of high refractive index and characteristic odour; the crude distillate (b. p. 168—185°) after refractionation had b. p. 170—175° under atmospheric pressure, 75—85°/23 mm. and 51—56°/7 mm. with D^{17} 1·117. The *semicarbazone*, m. p. 184—186°, rhombic crystals; and an *oxime*, b. p. 170° (about) and D 0·8388 were also prepared. F. M. G. M.

Analysis of a Resin from an Egyptian Sarcophagus. REUTTER (*Compt. rend.*, 1911, **153**, 597—599).—The resin from a sarcophagus of the thirtieth dynasty has been shown to contain gum styrax from *Liquidambar orientalis*, Aleppo resin from *Pinus halepensis*, mastic from *Pistacia lenticus*, cedar wood oil, and asphalt. The ash contained sodium, calcium, aluminium, magnesium, traces of arsenic, chromium, iron, and manganese, carbonates, silicates, phosphates, chlorides, sulphates, and nitrates. The resin also contained sand, vegetable particles, and mineral fragments, of which an account is given.

W. O. W.

Constituents of Guayule, Parthenium argentatum. P. ALEXANDER (*Ber.*, 1911, **4**, 2320—2328).—This investigation was undertaken to ascertain, if possible, whether this plant, which is the source of guayule caoutchouc, contains any substance which can be regarded as the raw material from which caoutchouc is formed in plants. The results were negative from this point of view.

Guayule contains about 8—10% of caoutchouc, expressed on the dry material. The commercial caoutchouc from this source contains 75% of caoutchouc hydrocarbons, and does not differ from "hard Para rubber" to any greater extent than other second class rubbers. The dry plant yields about 6·5% of dark green, extractive matter to acetone, and of this 54%, 31%, and 15% are successively dissolved by light petroleum, ether, and hot alcohol, and of the three component parts thus separated, 12·1%, 7·0%, and 2·0% respectively consist of "unsaponifiable matter." The acids produced on hydrolysis of the extract include one melting at 119° and belonging to the cinnamic acid group, and phenylacetic acid. Weil states (Priv. com.) that he has found cinnamic acid in the products of hydrolysis of resin from guayule. The crude acetone extract on distillation with steam gives a *sesquiterpene alcohol*, m. p. 127—128°, with a camphoraceous odour.

On distillation with steam, guayule yields from 0·5 to 4% of volatile oil, D_{15}^{15} 0·8861, which is lævorotatory, possesses a peculiar pepper-like aroma, and consists almost wholly of hydrocarbons. On fractional distillation it gives 30%, b. p. 50—60°/17 mm.; 20·3%, b. p. 60—80°/17 mm.; 24·8%, b. p. 120—160°/17 mm., with 5% of resinous residue. The first fraction is mainly *l*-pinene, and the third fraction a *sesquiterpene*, D_{15}^{15} 0·9349, $[\alpha]_D^{16}$ − 21°24′, n_D^{16} 1·496. No styrene is present. The above relates to oil distilled from guayule in a fairly fresh state. Oil distilled from plants which had been stored several years contained much oxygenated material, and although pinene was obtained from this oil no sesquiterpene fraction could be isolated. The presence of volatile oil in guayule is the cause of the difficulty at first experienced in the industrial use of caoutchouc from this source, since the oil hinders vulcanisation. T. A. H.

Cerebrosides of the Brain. HERMANN LOENING and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1911, **74**, 282—289).—Methods are described for obtaining pure the galactoside known as cerebron (Thudichum's phrenosin) The presence of other galactosides of the nature of Thudichum's kerasin was also found. The work is to be carried further. W. D. H.

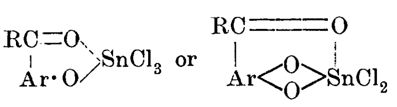
Saponins. RUDOLF KOBERT (*Chem. Zentr.*, 1911, **1**, 1589; from *Unna Festschrift*, 1911, **1**, 161—183).—Tables are given in the original of the chief members of the saponin series, $C_nH_{2n-8}O_{10}$, as well as of those of the digitonin series, $C_nH_{2n-16}O_{28}$, of the primary sapogenins (secondary glucosides), $C_nH_{2n-6}O_7$, and endsapogenins, $C_nH_{2n-6}O_2$, and also of sapogenins, $C_nH_{2n-6}O_3$. E. F. A.

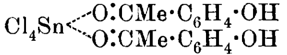
Artemisinphenylhydrazone. PASQUALE BERTOLO (*Gazzetta*, 1911, **41**, i, 705—708. Compare Abstr., 1901, i, 718; 1908, i, 560).—*Artemisinphenylhydrazone*, $C_{15}H_{18}O_3\colon N\cdot NHPh$, crystallises in yellowish-white, feathery needles, m. p. 144—145° (rapid heating), 221—222° (slow heating); $[\alpha]_D^{24}$ $+180°$ (in alcohol). After the substance has been kept at 160° for a few minutes, the rotatory power is unchanged. The compound dissolves in concentrated sulphuric acid, giving a green coloration, which becomes cherry-red on addition of a trace of nitric acid. The phenylhydrazone differs from artemisin in that it is not acted on by alkalis. Prolonged reduction with sodium amalgam yields an acid *substance*. R. V. S.

The Chlorophyll Group. The Duality of the Chlorophyllans and *allo*Chlorophyllan. LEON MARCHLEWSKI and J. MARSZAŁEK [with Z. LEYKO] (*Biochem. Zeitsch.*, 1911, **35**, 413—433).—Crude chlorophyll solutions from different sources, and even from the same plants, react in different ways when treated with zinc hydroxide and carbon dioxide. The chlorophyll from stinging nettles gives after treatment with these reagents for one day a fairly rapid change, but only a slight precipitate which has not the character of a zinc salt. In the chlorophyll, on the other hand, from maple leaves (*Acer pseudoplantanus*), only a small amount of the material enters into reaction with the zinc salt, and by such treatment the part which does not enter into combination can be separated from the other part. The "zinc chlorophyll" prepared from nettles contains more methoxyl and phytol when zinc acetate is employed for its preparation than when zinc hydroxide is used, and the latter exerts a slight hydrolytic action. The spectral measurements and extinction coefficients of this zinc derivative are given in some detail. Chlorophyllans were prepared from leaves of *Acer platanoides* from Poland and *A. pseudoplantanus* from Galicia, and analyses are given of the products obtained and also spectroscopic measurements. The analyses do not differ markedly from one another.

The spectroscopic measurements of the preparation from *A. platinoides* are intermediate between those obtained from nettles and maple. It is concluded that there is here a mixture of two chlorophyllans (chlorophyllan and *allo*chlorophyllan), and that certain varieties of plants are rich in the latter substance. By the separation of chlorophyllan by means of zinc hydroxide and carbon dioxide from *allo*chlorophyllan (the method for which is given in detail) in a preparation rich in the latter and obtained from *A. platinoides*, a specimen of *allo*chlorophyllan was obtained of which the properties and spectroscopic measurements are given in some detail; this on saponification yields *allo*chlorophyllanic acids. These are reddish (and not olive-green) substances, from which fractions can be obtained by treating the ethereal solution with hydrochloric acid in various strengths. Only when 5% acid is used is any appreciable quantity of the pigment dissolved, and the basic character is therefore weak. By 7% acid a preparation of crystalline form was obtained. S. B. S.

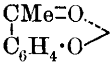
Lakes. I. Paul Pfeiffer [with Z. Goldberg and J. Kuntner] (*Ber.*, 1911, 44, 2653—2662).—The author hopes to bring Tschugaeff's (Abstr., 1907, i, 17, 392, 830) and Werner's (Abstr., 1908, i, 441) theories of the constitution of lakes into line with the theory by which he explains the phenomena of halochromy (Abstr., 1910, i, 852; this vol., i, 788). With this object in view, he has prepared, by heating the following *o*-hydroxy-ketones with tin tetrachloride (1·5 to 2 mols.) in dry benzene on the water-bath, coloured substances, which are represented by the annexed constitution. These substances are closely allied to the lakes of the tin series, which are obtained by replacing the chlorine atoms by hydroxyl groups. The important question whether the tin is united co-ordinatively with the carbonyl oxygen atom is answered in the affirmative, not only because the author has already shown (*loc. cit.*) that carbonyl compounds of the most diverse character exhibit quite universally a tendency to unite co-ordinatively with tin tetrahalides, but also for the following reason. *m*- and *p*-Hydroxyacetophenone and tin tetrachloride in benzene, cold or hot, form normal additive compounds,





$$Cl_4Sn<\begin{matrix}O{:}CMe{\cdot}C_6H_4{\cdot}OH\\O{:}CMe{\cdot}C_6H_4{\cdot}OH\end{matrix}$$

; *o*-hydroxyacetophenone and tin tetrachloride form in cold benzene a mixture of the normal additive compound and of the substituted compound, which evolves hydrogen chloride by warming, and changes entirely to the substituted *compound*,



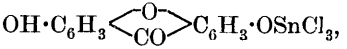
$$\begin{matrix}CMe{=}O\\C_6H_4{\cdot}O\end{matrix}>SnCl_3$$

yellow crystals, m. p. about 238°.

In a similar manner, *o*-hydroxybenzophenone yields the similarly constituted *substance*, $C_6H_4Bz{\cdot}OSnCl_3$, pale yellow leaflets containing $\frac{1}{2}C_6H_6$, m. p. about 250° to a brown liquid; resacetophenone yields the *substance*, $OH{\cdot}C_6H_3Ac{\cdot}OSnCl_3$, pale yellow crystals, m. p. 235—248° to a red liquid (the additive *compound*,

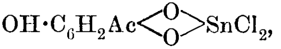
$$2C_6H_3Ac(OH)_2,SnCl_4,$$

is precipitated first, and then changes to the substituted compound); quinacetophenone yields the *substance*, $OH{\cdot}C_6H_3Ac{\cdot}OSnCl_3$, deep yellow prisms; euxanthone yields the *substance*,

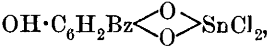


$$OH{\cdot}C_6H_3{<}\substack{O\\CO}{>}C_6H_3{\cdot}OSnCl_3,$$

orange-yellow crystals; gallacetophenone yields the *substance*,

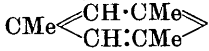
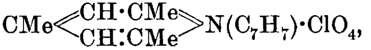


$$OH{\cdot}C_6H_2Ac{<}\substack{O\\O}{>}SnCl_2,$$

deep yellow powder; and gallobenzophenone yields the *substance*,  $OH{\cdot}C_6H_2Bz{<}\substack{O\\O}{>}SnCl_2$, orange powder containing $\frac{1}{4}$—$\frac{1}{2}C_6H_6$. Of course, in all of these substances the tin is attached co-ordinatively to the carbonyl oxygen atom. C. S.

Aniline Black and its Intermediate Products. ARTHUR G. GREEN and SALOMON WOLFF (*Ber.*, 1911, **44**, 2570—2582).—In connexion with the series of quinonoid derivatives constituting the primary oxidation products of aniline, the various points of controversy between Green and Willstätter appear to turn on the claim of Willstätter and Dorogi (Abstr., 1909, i, 535, 975) that their triquinonoid black is identical with emeraldine [which is diquinonoid, according to Green and Woodhead (Trans., 1910, **97**, 2388)], but has the formula of Green and Woodhead's nigraniline; or, generally, the number of quinonoid nuclei in Willstätter's series of primary oxidation products of aniline is one greater than the number in Green's series. Willstätter and Cramer (this vol., i, 90) confirm Willstätter and Dorogi's views by estimating the number of quinonoid nuclei by means of phenylhydrazine at temperatures up to 150°. The authors now show that the phenylhydrazine process, although giving good results below 90°, is quite inaccurate at temperatures above 100°, owing to the spontaneous decomposition of the phenylhydrazine; emeraldine or nigraniline is completely reduced to the leuco-compound by phenylhydrazine at 80—90°, but when this temperature is exceeded a further evolution of nitrogen occurs without any further change in the reduced product.

In the preparation of their quinonoid blacks, Willstätter and Dorogi submit the product to a prolonged treatment with sulphuric acid. The authors condemn this process, since its effect is to convert triquinonoid and tetraquinonoid blacks into a mixture of emeraldine and polymerisation or decomposition products insoluble in 80% acetic acid. Dichromate black, prepared by Willstätter and Dorogi's method, omitting the acid treatment, is identical with Green and Woodhead's emeraldine; it dissolves completely in 80% acetic acid, forming a pale green solution, and yields by treatment with phenylhydrazine at 80—90° a volume of nitrogen corresponding with the diquinonoid formula. The preceding remarks serve to answer most of the recent criticisms of Willstätter and Cramer (this vol., i, 736). Their contention that Green and Woodhead's leucoemeraldine is not the real leuco-base, but is a monoquinonoid black, $C_{48}H_{40}N_8$, is regarded as extremely improbable. C. S.

Dimethylpyrone. ADOLF VON BAEYER and JEAN PICCARD (*Annalen*, 1911, **384**, 208—224).—2 : 4 : 6-*Trimethylpyroxonium perchlorate*,  $CMe\!<\!\begin{matrix}CH\cdot CMe\\ CH{:}CMe\end{matrix}\!>\!O\cdot ClO_4$, colourless, indistinct prisms, m. p. 141—151° (decomp.), is obtained under the following definite conditions. A solution of dimethylpyrone in dry anisole at the ordinary temperature is cooled in a freezing mixture and treated with ethereal magnesium methyl iodide within the course of a minute. After one minute the mixture is added to 20% perchloric acid at −10°, and the perchlorate begins to crystallise almost immediately. 4-*Phenyl*-2 : 6-*dimethylpyroxonium perchlorate*, $C_{13}H_{13}O_5Cl$, sulphur-yellow leaflets, m. p. 210—212° (decomp.), is prepared in a similar manner; the *picrate*, $C_{19}H_{15}O_8N_3$, has m. p. 193°. All pyroxonium salts are converted into the corresponding pyridine compounds by aqueous ammonia in the cold; thus trimethylpyroxonium perchlorate yields 2 : 4 : 6-trimethylpyridine (*perchlorate*, m. p. 243—244°), the methiodide of which is converted by aqueous perchloric acid into 1 : 2 : 4 : 6-*tetramethylpyridinium perchlorate*, $C_9H_{14}O_4NCl$, m. p. 206—207°, which is also produced from trimethylpyroxonium perchlorate and methylamine. Trimethylpyroxonium perchlorate is converted by boiling alcoholic *p*-toluidine into 1-p-*tolyl*-2 : 4 : 6-*trimethylpyridinium perchlorate*,  $CMe\!<\!\begin{matrix}CH\cdot CMe\\ CH{:}CMe\end{matrix}\!>\!N(C_7H_7)\cdot ClO_4$, m. p. 141—142°, whilst phenyldimethylpyroxonium perchlorate is converted similarly into 4-*phenyl*-1-p-*tolyl*-2 : 6-*dimethylpyridinium perchlorate*, m. p. 205°.

When an aqueous solution of trimethylpyroxonium perchlorate is boiled with barium carbonate in a current of hydrogen, δ-*methyl*-Δγ-*hepten*-βζ-*dione*, COMe·CH·CMe:CH·COMe, is obtained as an unstable oil, which has an odour of peppermint, regenerates the original perchlorate by warming with dilute perchloric acid, and forms a *disemicarbazone*, $C_{10}H_{18}O_2N_6$, m. p. 210—210·5°. δ-*Phenyl*-Δγ-*hepten*-βζ-*dione*, m. p. 51°, obtained in a similar manner from phenyldimethylpyroxonium perchlorate, is an unstable, colourless, crystalline powder. By reduction with palladium chloride and gum arabic in an atmosphere of hydrogen, it yields δ-*phenylheptane*-βζ-*dione*,

$$COMe\cdot CH\cdot CHPh\cdot CH_2\cdot COMe,$$

m. p. 61—62°. δ-*Methylheptane*-βζ-*dione*, b. p. 95—96°/12 mm., obtained in a similar manner, reacts very readily with semicarbazide, forming the *disemicarbazone*, $C_{10}H_{20}O_2N_6$, m. p. 199°. None of these δ-diketones give a reaction with ferric chloride. C. S.

β-Phenylcoumarins. I. GUIDO BARGELLINI and G. LEONARDI (*Gazzetta*, 1911, **41**, i, 737—746).—In the hope of obtaining compounds related to certain substances found in plants, the preparation of some hydroxyl derivatives of β-phenylcoumarin has been undertaken, using an old method for the preparation of coumarin derivatives (compare Komarovski and von Kostanecki, Abstr., 1894, i, 506).

2 : 3 : 4-Trihydroxybenzophenone, when heated for twenty hours with sodium acetate and acetic anhydride, yields the diacetyl-β-phenyldaphnetin of von Kostanecki and Weber (Abstr., 1894, i, 88).

2 : 4-Dihydroxy-4′-methoxybenzophenone (Komarovski and von

Kostanecki, *loc. cit.*) when heated for twenty hours with sodium acetate and acetic anhydride yields (1) a substance, probably the *diacetyl* derivative of 2 : 4-dihydroxy-4′-methoxybenzophenone; and (2) an *acetyl* derivative of *4-hydroxy-4′-methoxy-β-phenylcoumarin*, $C_{18}H_{14}O_5$, which forms colourless, woolly needles, m. p. 185—186°. By dissolving this substance in concentrated sulphuric acid and pouring the solution into water, *4-hydroxy-4′-methoxy-β-phenylcoumarin*, $C_{16}H_{12}O_4$, is obtained; it forms yellowish-white needles, m. p. 261—263°. The compound dissolves in alkalis, giving yellow solutions with a green fluorescence; the solution in alcohol is also fluorescent, but the fluorescence disappears on the addition of acid. The substance dissolves in concentrated sulphuric acid, giving a green coloration. When it is treated with methyl iodide, *4 : 4′-dimethoxy-β-phenylcoumarin*, $C_{17}H_{14}O_4$, m. p. 156°, is obtained.

2 : 4 : 4′-Trihydroxybenzophenone yields, when heated with sodium acetate and acetic anhydride, (1) *triacetoxybenzophenone*, which forms colourless needles, m. p. 96—98°; (2) *4 : 4′-diacetoxy-β-phenylcoumarin*, $C_{19}H_{14}O_6$, which crystallises in colourless needles, m. p. 189—190°. *4 : 4′-Dihydroxy-β-phenylcoumarin*, $C_{15}H_{10}O_6$, prepared from it, forms yellowish-white needles, m. p. 238—240°. When treated with methyl iodide, it yields 4 : 4′-dimethoxy-β-phenylcoumarin, previously described. R. V. S.

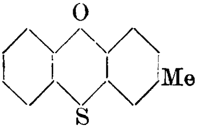
β-Phenylcoumarins. II. GUIDO BARGELLINI and G. FORLÌ-FORTI (*Gazzetta*, 1911, **41**, i, 747—756. Compare preceding abstract) —The synthesis of β-phenylcoumarins has been continued by another method (compare von Kostanecki and Weber, Abstr., 1894, i, 88), namely, the condensation of *p*-cyanoacetylanisole or cyanoacetylveratrole (1 : 2-dimethoxy-4-cyanoacetophenone) with resorcinol or phloroglucinol.

p-*Cyanoacetylanisole*, $C_{10}H_9O_2N$ (from *p*-chloroacetylanisole and potassium cyanide), crystallises in tufts of long, colourless needles, m. p. 128—130°. When it is heated with resorcinol and 73% sulphuric acid on the water-bath, two products are obtained: (1) a *substance*, soluble in water, which forms colourless needles, m. p. 234—236°, and is probably the nitrile or amide of the coumarin derivative, m. p. 260—262°, which it yields on addition of hydrochloric acid; (2) 4-hydroxy-4′-methoxy-β-phenylcoumarin, m. p. 260—262°, identical with that described in the preceding abstract.

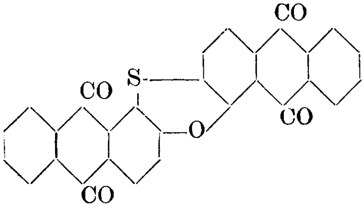
Condensation of *p*-cyanoacetylanisole with phloroglucinol yields a *substance*, m. p. about 200°, from which an *acetyl* derivative can be prepared, which crystallises in colourless needles, m. p. 179—180°.

Chloroacetylveratrole can be obtained: (1) by the action of methyl sulphate on chloroacetylcatechol; and (2) by condensation of chloroacetyl chloride with veratrole in presence of aluminium chloride. In the second case another substance (? *chloroacetylguaiacol*) is the principal product; in both cases the yield is exceedingly small. *Chloroacetylveratrole*, $C_{10}H_{11}O_3Cl$, crystallises in white scales, m. p. 102—104°. *Cyanoacetylveratrole*, $C_{11}H_{11}O_3N$, forms colourless needles, m. p. 134—135°. With resorcinol in presence of 73% sulphuric acid, it yields a *substance*, which crystallises in yellowish-white needles, m. p. 228—229°, whilst with phloroglucinol a reddish-yellow condensation product is obtained. R. V. S.

Preparation of Phenothioxin and its Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234743).—It is found that the phenothioxin, m. p. 60—61°, b. p. 183—184°/12 mm., prepared by Mauthner (Abstr., 1906, i, 448) can be readily obtained by heating (with continual stirring) phenyl ether at 60—70° with sulphur in the presence of aluminium chloride; the temperature is subsequently slowly raised to 100° and maintained until evolution of hydrogen sulphide ceases. Under these conditions, *p*-tolylphenyl ether yields *3-methylphenothioxin* (annexed formula), m. p. 36°, b. p. 185—187°/12 mm., whilst *p*-chlorophenyl ether furnishes *3-chlorophenothioxin*, m. p. 37°, b. p. 176°/12 mm. F. M. G. M.



[Preparation of Anthracene Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 235094).—When anthraquinone-1-thiol is heated with 1-hydroxyanthraquinone at 160—170° in 98% sulphuric acid, it yields a *compound* (annexed formula), which crystallises from hot quinoline in brownish-red needles. The tinctorial properties of this and the following analogous condensation products are tabulated in the original.



1 : 5-Dithiolanthraquinone with 1- and 2-hydroxyanthraquinones (2 mols.) respectively; 1-thiolanthraquinone (2 mols.) and anthrarufin; 1-thiol-5-aminoanthraquinone and 5-amino-1-hydroxyanthraquinone; 1-thiolanthraquinone with 2-hydroxyanthraquinone; and 1-thiolanthraquinone (2 mols.) with anthraflavic acid; 2-thiolanthraquinone (1 mol.) with 2-hydroxyanthraquinone and (2 mols.) with anthraflavic acid. F. M. G. M.

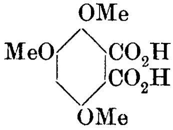
Solubility of Alkaloids in an Aqueous Boric Acid-Glycerol Solution. E. BARONI and O. BORLINETTO (*Chem. Zentr.*, 1911, ii, 93—94; from *Giorn. Farm. Chim.*, 1911, **60**, 193—195).—A solution containing 3·0 grams of boric acid, 50·0 grams of glycerol, and water to 100 c.c., dissolves the following quantities of various alkaloids, the figures in parentheses giving the solubility of the respective alkaloids in water: Codeine, 4% (1·66%); atropine, 10% (0·5%); cocaine, 8% (0·14%); morphine, 5·5% (0·1%); strychnine, 3·5% (0·01%); eserine, 7·5% (trace); veratrine, 6% (trace). The solubility of the alkaloids increases with the proportion of boric acid present in the solution. W. P. S.

Crystalline Alkaloid of Calycanthus glaucus. IV. Some Salts of a New Quaternary Base obtained by Methylating *iso*-Calycanthine. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1911, **33**, 1626—1632).—When *iso*calycanthine (Abstr., 1910, i, 62) is treated with methyl iodide, about 35% of the alkaloid is converted into the hydriodide, about 35% remains unchanged, and the remainder is converted into a quaternary iodide, $C_{24}H_{28}ON_3I,H_2O$. It is suggested that the oxygen of the air takes part in the reaction, as shown by the equations: $2C_{11}H_{14}N_2 + 2MeI + O_2 = C_{24}H_{28}ON_3I,H_2O + NH_4I$ and $C_{11}H_{14}N_2 + NH_4I = C_{11}H_{14}N_2,HI + NH_3$.

The quaternary *iodide* forms white, flat, lustrous needles, becomes brown at 213—214°, does not melt below 325°, and is soluble in about 30 parts of hot methyl alcohol; its *hydriodide* is described. The corresponding *chloride*, $C_{24}H_{28}ON_3Cl,3H_2O$, m. p. 220°, crystallises in flat, lustrous needles, and is soluble in about 50 parts of cold water; its *hydrochloride* is described. The *nitrate*, $C_{24}H_{28}ON_3{\cdot}NO_3$, m. p. 192—194°, forms white, rectangular prisms. The quaternary *picrate*, m. p. 155°, and *picrolonate*, m. p. 164—166°, are also described.

E. G.

Colchicine. I. and II. ADOLF WINDAUS (*Chem. Zentr.*, 1911, i, 1637—1638, 1638—1641; from *Sitzungsber. Heidelberger Akad. Wiss.*, 1910, 1—7; 1911, 1—27).—On oxidation of colchicine in 5% potassium hydroxide with potassium permanganate, in addition to oxalic acid, *trimethoxy*-o-*phthalic acid*, $C_{11}H_{12}O_7$, is obtained, which must have the annexed structure, since it differs from the trimethoxygallocarboxylic acid described by Feist.



By cautious sublimation of the reaction product in a vacuum at 220°, the *anhydride*, $C_{11}H_{10}O_6$, is obtained in needles, m. p. 143—144°. This is converted into the acid when boiled with water, which crystallises in transparent plates, m. p. 175—176°; the *silver* and *lead* salts are insoluble; the *barium* salt forms needles. The *anil* crystallises in colourless needles, m. p. 146°.

Derivatives of Trimethylcolchicinic Acid.—Colchicine was regarded by Zeisel as the methyl ester of an acid, colchiceine, but it is now considered to be an enolic methyl ether, colchiceine being an enol, since it gives a characteristic green coloration with ferric chloride. Zeisel has shown further, that colchiceine contains an acetyl group attached to nitrogen, so that the structure of colchicine may be expressed: $C_6H(OMe)_3{:}C_{10}H_8O(OMe){\cdot}NH{\cdot}COMe$.

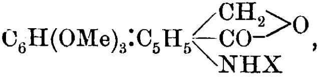
The almost colourless aqueous or alcoholic solutions of colchicine and its derivatives become deep yellow on the addition of hydrochloric acid, owing to the formation of acid additive products. *Trimethylcolchicinic acid dihydrochloride*, $C_{19}H_{21}O_5N,2HCl,H_2O$, forms dark yellow crystals; it still contains the free enolic group, and when heated at 100°, regenerates the monohydrochloride. *Trimethylcolchicinic acid dibenzoate*, $C_6H(OMe)_3{:}C_{10}H_8O(O{\cdot}COPh){\cdot}NH{\cdot}COPh$, crystallises in faint yellow, three-sided prisms, m. p. 298° (decomp.); it gives no coloration with ferric chloride. N-*Benzoyltrimethylcolchicinic acid*, $C_6H(OMe)_3{:}C_{10}H_8O(OH){\cdot}NH{\cdot}COPh$, prepared by heating the dibenzoate with 25% potassium hydroxide, separates in pale yellow needles, m. p. 253—254°, and gives a dark green ferric chloride coloration.

N-p-*Nitrobenzoyltrimethylcolchicinic acid* forms prisms, m. p. 256°. N-p-*Bromobenzoyltrimethylcolchicinic acid* separates in platelets, m. p. 253°. N-*Benzenesulphonyltrimethylcolchicinic acid,*

$$C_6H(OMe)_3{:}C_{10}H_8O(OH){\cdot}NH{\cdot}SO_2Ph,$$

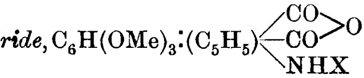
forms greenish-yellow, rhombic plates, m. p. 255°, and gives an intense green ferric chloride reaction. *Trimethylcolchicinic acid dibenzenesulphonate,* prepared by the action of benzenesulphonyl chloride on the hydrochloride in pyridine solution, crystallises in yellow, four-sided, rhombic plates, m. p. 196°. The mother liquors contain an isomeric *dibenzenesulphonate,* crystallising in greenish-yellow prisms and plates, m. p. 141—142°. Neither isomeride gives any coloration with ferric chloride, and they are regarded as cis-, trans-isomerides.

Oxidation of Colchicine Derivatives with Potassium Permanganate.—By cautious oxidation with potassium permanganate, a lactone, *colchide,*



$$C_6H(OMe)_3{:}C_5H_5\left<\begin{array}{l}CH_2\\ CO\\ NHX\end{array}\right.\!\!>O$$

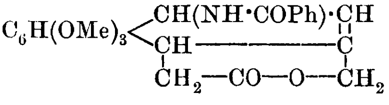
, and an acid anhydride, *colchinic anhydride,*

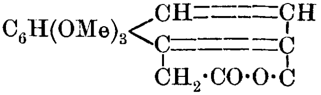


$$C_6H(OMe)_3{:}(C_5H_5)\left<\begin{array}{l}CO\\ CO\\ NHX\end{array}\right.\!\!>O$$

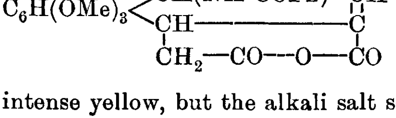
, have been obtained.

N-*Benzoylcolchide,* $C_{23}H_{23}O_6N$ (annexed formula), formed on oxidation of *N*-benzoyltrimethylcolchicinic acid, forms needles, m. p. 239°, $[\alpha]_D^{17}$ −275°; it gives no coloration with ferric chloride, and is neutral towards litmus paper. On further oxidation trimethoxyphthalic acid is formed. It dissolves in alcoholic potassium hydroxide, the equilibrium between hydroxy-acid and lactone depending on the amount of alkali present. When heated for two hours at 250° under diminished pressure, benzamide and *trimethoxyhomonaphthide,* $C_{16}H_{16}O_5$, are obtained. The latter (annexed formula) crystallises in needles, m. p. 138°, is optically inactive, and behaves as a lactone; it is also formed on boiling *N*-benzoylcolchide with alcoholic hydrogen chloride, whereby, in part, benzoic acid and the corresponding amine, colchide, are formed; *colchide picrate,* $C_{16}H_{19}O_5N,C_6H_3O_7N_3$, crystallises in yellow prisms, m. p. 165°.

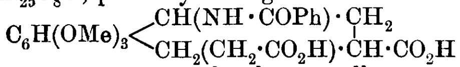




N-*Benzoylcolchinic anhydride* (annexed formula), prepared by oxidation of *N*-benzoyltrimethylcolchicinic acid, forms straggling, four-sided platelets, m. p. 207°, $[\alpha]_D^{18}$ −288°. The solutions in water and organic solvents are intense yellow, but the alkali salt solutions are colourless and remain so at first on the addition of acid; later they become yellow, and the anhydride crystallises. The *anil,* $C_{29}H_{26}O_6N_2$, forms almost colourless needles, m. p. 226°.



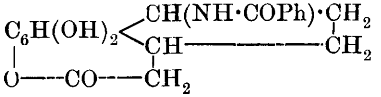
On heating with zinc dust and acetic acid, a tetrahydronaphthalene derivative, $C_{23}H_{25}O_8N$, probably having the formula



$$C_6H(OMe)_3<\begin{matrix}CH(NH\cdot COPh)\cdot CH_2\\ CH_2(CH_2\cdot CO_2H)\cdot CH\cdot CO_2H\end{matrix}$$

is obtained; it separates in colourless needles, m. p. 158° after previously sintering.

When the anhydride is warmed with hydriodic acid, the methyl groups and carbon dioxide are eliminated, and a compound, $C_{19}H_{17}O_5N$, having possibly the annexed formula is obtained; it crystallises in colourless needles, which darken at 200°, decomp. 230°.



The reasons for assigning the formula given to benzoylcolchinic anhydride are discussed at length.

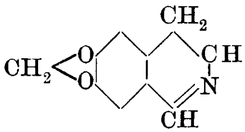
N-*Acetylcolchide* forms needles, m. p. 221°; the lactone ring is only opened with difficulty.

N-*Acetylcolchinic anhydride* forms deep yellow needles, m. p. 201°, and dissolves without colour in alkali hydroxides.

N-*Benzenesulphonylcolchinic anhydride*, $C_{28}H_{21}O_8NS$, crystallises in long, four-sided plates, m. p. 242—243° (decomp.). When hydrolysed and again acylated, it is converted into *N*-benzoylcolchinic anhydride.

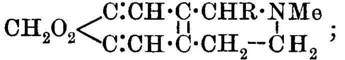
E. F. A.

Preparation of Hydrastinine Salts. HERMAN DECKER (D.R.-P. 234850. Compare Abstr., 1908, i, 901).—When *formylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot COH$, needles, m. p. 51—52° (prepared by heating homopiperonylamine formate at 160—170°), is heated with phosphoric oxide, it yields 6 : 7-*methylenedioxy*-3 : 4-*dihydro*iso*quinoline* (annexed formula), nodular crystals, m. p. 90—91°; its salts exhibit blue fluorescence, and the *picrate* has m. p. 238°; on treatment with methyl iodide, it furnishes hydrastinine hydriodide, and with methyl sulphate yields *hydrastinine methosulphate*, a yellow powder, m. p. 117—119°; the *picrate* has m. p. 175°.



F. M. G. M.

Action of Organic Magnesium Compounds on Hydrastinine. MARTIN FREUND and KARL LEDERER (*Ber.*, 1911, 44, 2356—2362).—Hydrastinine interacts with organo-magnesium compounds in a similar manner to cotarnine (Freund and Reitz, Abstr., 1906, i, 600), forming α-alkylhydrohydrastinine compounds of the type



$$CH_2O_2<\begin{matrix}C{:}CH\cdot C\cdot CHR\cdot NMe\\ C{:}CH\cdot C\cdot CH_2-CH_2\end{matrix} ;$$

these are 1-alkyltetrahydro*iso*quinoline derivatives. Free hydrastinine gives a 50% yield; the hydrochloride reacts quantitatively with the Grignard reagent.

α-*Methylhydrohydrastinine* is an oil; the *hydriodide* crystallises in plates, m. p. 227°; the *methiodide* also forms plates, m. p. 229—230°.

α-*Ethylhydrohydrastinine* crystallises in hard, colourless plates, m. p. 70—71°.

α-*Phenylhydrohydrastinine* + H_2O forms long, pointed crystals, m. p. 88°; the anhydrous substance forms a yellow, resinous mass.

α-*Propylhydrohydrastinine* is oily; the *hydriodide* crystallises in plates, m. p. 185—186°; the *platinichloride* forms rhombic crystals, decomp. 230°; the *methiodide* separates in plates, which sinter at 163°, m. p. 168—169°.

iso*Propylhydrohydrastinine* is likewise oily. The *hydrobromide* crystallises in pointed needles, m. p. 190°; the *hydriodide* forms colourless, rhombic plates, m. p. 217—218°; the *picrate* forms plates, m. p. 143—145°; the *platinichloride* separates in needles, m. p. 223°; the *methiodide* forms bunches of needles, m. p. 219—220°.

α-*Butylhydrohydrastinine* is oily; it is characterised by the *picrate*, plates, m. p. 147—148°; the *platinichloride*, rhombic plates, m. p. 222—223°, and the *methiodide*, leaflets, m. p. 205—206°.

α-iso*Butylhydrohydrastinine* gives a *picrate*, crystallising in prisms, which sinter at 125°, m. p. 130°; a *platinichloride*, separating in four-sided plates, decomp. 220°, and a *methiodide*, which forms bunches of leaflets, m. p. 197—198°.

α-*Benzylhydrohydrastinine* is an oil, but forms crystalline salts. The *hydrochloride* forms six-sided crystals, m. p. 182°; the *hydrobromide* has m. p. 187—188°; the *hydriodide* crystallises in hexagonal plates, m. p. 195—196°; the *acid sulphate* sinters at 185°, m. p. 189°; the *picrate* forms octahedra, m. p. 178—180°; the *platinichloride* forms plates, decomp. 224°, whilst the *methiodide* forms aggregates of columnar crystals, m. p. 245°.

α-p-*Anisylhydrohydrastinine* crystallises in columns united in bundles, m. p. 98—99°; the *hydrochloride* forms needles; the *hydrobromide* is similar, m. p. 243—244°; also the *hydriodide*, m. p. 223—224°.

α-*Naphthylhydrohydrastinine* forms rhombic plates, which sinter at 125°, m. p. 127—128°. The *hydrochloride*, m. p. 254—255°; the *hydrobromide*, needles, m. p. 265°; the *hydriodide*, needles, m. p. 262°; the *acid sulphate*, matted crystals, which sinter at 225°, m. p. 228—229° (decomp.), and the *picrate*, plates, decomp. 201°, are described.

E. F. A.

Formation of Alkaloidal Periodides. W. C. Holmes (*Philippine J. Sci.*, 1911, *A*, 6, 253—275).—A résumé of the literature relating to the formation of alkaloidal periodides and the use of these compounds in the estimation of alkaloids is given. It is shown that morphine, codeine, and heroine, free or in the form of salts, have a remarkable affinity for iodine, and readily combine with it even in the absence of a solvent. There is no tendency to form definite compounds. The reactions are apparently dependent on the concentration of the iodine, and the phenomena observed are those of equilibrium involving vapour and osmotic pressures as factors. The amount of "free" iodine combined with the alkaloids cannot be determined by thiosulphate solution, and consequently it is considered that the formation and constitution of the periodides are much more complex than has been supposed.

When $N/10$-iodine solution is added to a 1% solution of codeine, morphine, or heroine sulphate in *N*/10-sulphuric acid, and the uncombined iodine titrated wth *N*/10-sodium thiosulphate after standing overnight, the amounts of iodine absorbed by the alkaloids increase with the total concentration of iodine in the mixed solutions, but a maximum is soon reached in the case of heroine. When other factors are varied and the concentration of iodine and alkaloid kept constant, the amount of iodine absorbed varies inversely with rise in temperature, or increase in concentration of (*a*) sulphuric acid, (*b*) potassium iodide. Equilibrium appears to be reached in about thirty minutes. All the codeine precipitates were crystalline, as were also two of the morphine precipitates, whilst with heroine only amorphous deposits were obtained. The belief that in using Wagner's reagent for the estimation of alkaloids a definite amount of iodine combines with the alkaloid and may be determined by titration of the residual iodine is fallacious (compare Prescott and Gordin, Abstr., 1899, i, 89).

Aqueous solutions of free morphine, codeine, and heroine are precipitated by Wagner's reagent, and here, also, the amount of iodine absorbed is proportional to the concentration of iodine, and is inversely proportional to the amount of acid, which may be added subsequently. The free alkaloids and their sulphates also absorb iodine vapour when exposed to it, the salts being distinctly less active than the free bases.

T. A. H.

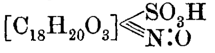
Methylation of the Alcoholic Hydroxyl Group in Morphine, Codeine, and the Methylmorphimethines. ROLAND PSCHORR and F. DICKHÄUSER [and, in part, C. D'AVIS] (*Ber.*, 1911, **44**, 2633—2640).—The alkylation of the alcoholic hydroxyl group in morphine, which has not hitherto been effected, proceeds quite easily in the cold when the alkaloid is shaken with methyl sulphate or methyl iodide and *N*-sodium hydroxide ($2\frac{1}{2}$ mols.). The product of the reaction, which is also obtained by starting with codeine, is precipitated by concentrated potassium iodide, whereby *methylcodeine methiodide*, decomp. 257° (corr.), $[\alpha]_D^{22}$ $-107{\cdot}2°$ in water, is obtained. A boiling aqueous solution of the methiodide is converted by 25% sodium hydroxide into *α-dimethylmorphimethine*, $C_{20}H_{25}O_3N$, leaflets or needles, m. p. 94°, $[\alpha]_D^{24}$ $-251{\cdot}9°$ in methyl alcohol (*methiodide*, $C_{21}H_{28}O_3NI$, decomp. 256° (corr.), $[\alpha]_D^{23}$ $-134{\cdot}4°$ in water), which is changed by heating with aqueous-alcoholic potassium hydroxide or with acetic anhydride at 210° to *β-dimethylmorphimethine*, isolated in the form of the *methiodide*, $C_{21}H_{28}O_3NI$, prismatic needles, decomp. 318—320° (corr.), $[\alpha]_D^{22}$ 268·5—278·5° in water.

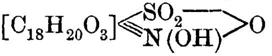
The methylation of α- and β-methylmorphimethine is effected as in the case of morphine or codeine, the methiodides obtained being identical with those of α- and β-dimethylmorphimethine mentioned above. *γ-Dimethylmorphimethine methiodide*, $C_{21}H_{28}O_3NI$, leaflets, has decomp. 259° (corr.) and $[\alpha]_D^{20}$ $+14°$ in water. *δ-Dimethylmorphimethine methiodide*, needles, has decomp. 286° (corr.), and $[\alpha]_D^{28}$ 170·9° in water. *ε-Dimethylmorphimethine methiodide*, long needles, has decomp. 277° (corr.), and $[\alpha]_D^{20}$ $-79{\cdot}4°$ in methyl alcohol.

β-Dimethylmorphimethine methiodide is decomposed by aqueous-alcoholic potassium hydroxide at 165°, forming morphenol, ethylene, and trimethylamine.

The methylation of various alcohols by sodium hydroxide and methyl sulphate has been examined. The method yields good results with benzyl alcohol and cinnamyl alcohol, but is unsatisfactory with *ter.*-amyl alcohol, octyl alcohol, borneol, and *iso*borneol. C. S.

Codeine Oxide. MARTIN FREUND and EDMUND SPEYER (*Ber.*, 1911, **44**, 2339—2353. Compare this vol., i, 76).—When codeine oxide, dissolved in acetic anhydride, reacts with sulphuric acid, two isomeric substances, $C_{18}H_{20}O_7NS$, are formed, both of which are acid in character, codeineoxidesulphonic acid (I.) and α-codeineoxidesulphonic acid (II.), these probably have the annexed constitutions; the α compound is

(I.) 
$[C_{18}H_{20}O_3]\lessgtr\begin{matrix}SO_3H\\N{:}O\end{matrix}$

(II.) 
$[C_{18}H_{20}O_3]\lessgtr\begin{matrix}SO_2\text{—}\\N(OH)\end{matrix}\!>O$

easily converted into the isomeride.

On reduction, both are converted into the same codeinesulphonic acid, $N{:}[C_{18}H_{20}O_3]\cdot SO_3H$. This, on treatment with nitric acid, yields the nitrocodeine described by Anderson. Proof that no change in the structure of the alkaloid complex has taken place is afforded by the fact that all the sulphonic acids described yield codeine when superheated with water. When dissolved in cold concentrated sulphuric acid, the sulphonic acids, however, are more profoundly altered, and new products are obtained which await further investigation.

Codeinesulphonic acid when treated with methyl iodide in alkaline solution forms codeinesulphonic acid methyl hydroxide,

$$NMe{:}[C_{18}H_{20}O_3](OH)\cdot SO_3H.$$

On boiling with alkali, βγ-dimethylbutylene-βγ-diamine is eliminated and a nitrogen-free product obtained, which could not be isolated. After remaining in alkaline solution with methyl iodide and alcohol for some time and then boiling, the methyl hydroxide is converted into a crystalline salt, $C_{16}H_{11}O_6SK$, which is regarded as a morphenol derivative, $O{:}C_{14}H_5(OMe)_2\cdot SO_3K$.

α-Codeineoxidesulphonic acid behaves in many respects otherwise than the isomeride. With nitric acid a nitro-compound,

$$O{:}N{:}[C_{18}H_{19}O_3](NO_2)\cdot SO_3H,$$

is obtained. Sulphurous acid converts this into a nitrocodeine isomeric with Anderson's, but both isomerides give the same aminocodeine when reduced.

When α-codeineoxidesulphonic acid is treated with bromine water, and the perbromide formed is boiled with alcohol, a compound, $C_{15}H_{17}O_4Br_3$ or $C_{15}H_{15}O_4Br_3$, is obtained of unknown constitution.

Morphine oxide, when similarly treated with acetic anhydride and sulphuric acid, forms a bimolecular hydroxysulphonic acid, $C_{34}H_{40}O_{15}N_2S_2$, which is converted by sulphurous acid into a compound, $C_{17}H_{21}O_7NS$.

Codeineoxidesulphonic acid forms small crystals of the hexagonal system, decomp. 272°, $[\alpha]_D$ $-115\cdot4°$, and forms a crystalline *potassium* salt.

Codeinesulphonic acid is dimorphous, crystallising in well-formed prisms and silky needles, which can be converted into one another. It decomposes above 300° and has $[\alpha]_D$ $-136\cdot3°$.

Codeinesulphonic acid methylhydroxide separates in needles, decomp. 284°, $[\alpha]_D$ −63·2°. Treatment with methyl iodide and alcohol and subsequent boiling with alkali gives a *compound*, $C_{16}H_{11}O_6SK$, crystallising in well-formed plates, decomp. 295°. On treatment of codeineoxidesulphonic acid with cold concentrated sulphuric acid, a substance, $C_{18}H_{21}O_6NS$, provisionally termed *β-codeinesulphonic acid*, is obtained. It forms bundles of microscopic plates, decomp. 243°, $[\alpha]_D$ −190·1°. Sulphurous acid converts this into an isomeric substance, provisionally termed *γ-codeinesulphonic acid*, which crystallises in matted needles, decomp. 280°.

Potassium chromate oxidises codeineoxidesulphonic acid into *codeineoxidesulphonic acid hydrate*, $C_{18}H_{23}O_8NS$, crystallising in needles; on heating at 180° with water under pressure, a *base* separating in stunted, prismatic plates or long needles, m. p. 180°, is obtained; the *hydrochloride* forms long needles, m. p. 310°.

Concentrated sulphuric acid converts codeinesulphonic acid into a *compound*, $C_{19}H_{18}O_3N{\cdot}SO_3H$, which crystallises in very slender needles, decomp. 285—290°.

α-Codeineoxidesulphonic acid crystallises in stunted prisms; it is converted into the isomeride on heating with 10% sodium hydroxide or 20% hydrochloric acid.

Nitro-α-codeineoxidesulphonic acid crystallises in yellow plates, decomp. 167—170°.

α-Nitrocodeine, prepared by the action of sulphurous acid on the sulphonic acid, crystallises in microscopic, four-sided plates, m. p. 197°.

By the interaction of bromine and α-codeineoxidesulphonic acid, a *compound*, $C_{15}H_{17}O_4Br_3$, is obtained in long needles, m. p. 258—260° (decomp.).

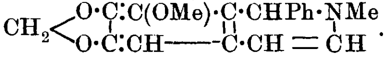
Codeinesulphonic acid is without physiological action.

Both the isomeric nitrocodeines when reduced electrolytically yield the same *aminocodeine*, $C_{18}H_{20}O_3N{\cdot}NH_2$, crystallising in plates, m. p. 228°. The *hydrochloride* forms needles, m. p. 290°.

Hydroxycodeine, prepared by diazotisation of aminocodeine and boiling, crystallises in colourless plates, which when heated lose water at 176—185°, m. p. 234°. The *hydrochloride* crystallises in needles.

E. F. A.

Cotarnine. VI. MARTIN FREUND and KARL LEDERER (*Ber.*, 1911, **44**, 2353—2356).—Tarconine methiodide reacts with magnesium phenyl iodide, forming 8-*methoxy*-6 : 7-*methylenedioxy*-1-*phenyl*-2-*methyl*-1 : 2-*dihydro*iso*quinoline*,

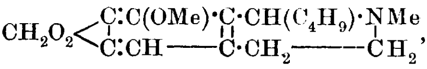


$$CH_2{<}\begin{array}{l}O{\cdot}C{:}C(OMe){\cdot}C{\cdot}CHPh{\cdot}NMe\\ O{\cdot}C{:}CH{-\!-\!-}C{\cdot}CH{=}CH\end{array}$$

. On reduction this is converted into α-phenylhydrocotarnine (8-methoxy-6 : 7-methylenedioxy-1-phenyl-2-methyltetrahydro*iso*quinoline), previously prepared by Freund and Reitz (Abstr., 1906, i, 600) from cotarnine salts and magnesium phenyl iodide.

α-Phenyltarconine forms colourless bunches of pointed crystals, which sinter at 97°, m. p. 102°. The salts and methiodide are oily, and decompose with a red coloration.

α-Butylhydrocotarnine,



$$CH_2O_2{<}\begin{array}{l}C{:}C(OMe){\cdot}C{\cdot}CH(C_4H_9){\cdot}NMe\\ C{:}CH{-\!-\!-}C{\cdot}CH_2{-\!-\!-\!-}CH_2\end{array}$$

, prepared from cotarnine hydrochloride and magnesium butyl bromide is an oil. The following crystalline salts have been analysed: *hydrochloride*, plates, m. p. 215—216°; *hydrobromide*, plates, m. p. 207—208°; *hydriodide*, columns, m. p. 190—191°; *picrate*, plates, m. p. 165—166°; *platinichloride*, plates, m. p. 205—206°; *methiodide*, long, rhombic plates, m. p. 190—193°. E. F. A.

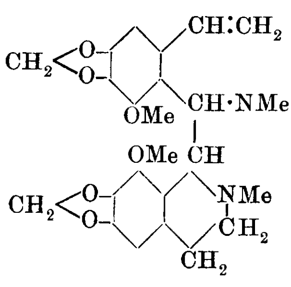
Stereochemistry of Nitrogen Compounds. Isomeric Bishydrocotarnines. Martin Freund and Otto Kupfer (*Annalen*, 1911, **384**, 1—38).—Bis-hydrocotarnine (di-hydrocotarnine) has been prepared by Freund and Reitz (Abstr., 1906, i, 600), and the constitution ascribed to it by these authors has been confirmed by Freund and Lederer (see Lederer, *Diss.*, Giessen, 1909) and yet again by the present authors, who have oxidised the substance to cotarnine nearly quantitatively by dilute sulphuric acid and 10% potassium dichromate. From its constitution (the molecule consists of two structurally identical halves, each containing an asymmetric carbon atom) it is obvious that a stereoisomeride should exist, and, indeed, a repetition of Freund and Reitz's experiment has shown that, in addition to the bis-hydrocotarnine already isolated, a small quantity of the isomeride, iso-*bishydrocotarnine*, $C_{24}H_{28}O_6N_2$, is formed. The two compounds have the same m. p., 163—164° (when mixed m. p. about 20° lower), but show marked dissimilarities in the solubilities of their salts; they are easily separated almost quantitatively by means of their *hydrogen sulphates*, that of bishydrocotarnine being very sparingly soluble in dilute sulphuric acid. Bishydrocotarnine forms a dihydrochloride, m. p. 231—232°, dihydrobromide, decomp. 228—229°, dihydriodide, m. p. 228—230°, *dihydrofluoride*, m. p. 227—229°, and *dinitrate*, m. p. 169—171°, whilst *iso*-bishydrocotarnine forms corresponding salts having the same m. p. (the mixed m. p. is always lower). It is changed to bishydrocotarnine at 160°, and gives a quantitative yield of cotarnine by oxidation with potassium dichromate and sulphuric acid.

Possibly bishydrocotarnine and *iso*bishydrocotarnine represent racemic and meso-modifications. However, all attempts to resolve either of them having been unsuccessful, this problem has been put aside for the present, although the suggestion is advanced that the two substances may be cis- and trans-modifications of the meso-form, as in the case of coniine and *iso*-coniine. *iso*-Bishydrocotarnine forms a *methiodide*, $C_{24}H_{28}O_6N_2,MeI$, m. p. 233°. The fact that bishydrocotarnine forms only a monomethiodide (*loc. cit.*) is due to steric hindrance, because when the methiodide is converted into the corresponding *hydroxide*, $C_{24}H_{28}O_6N_2,MeOH,10H_2O$, m. p. 75—80°, and this is treated with methyl iodide, the *methiodide*,

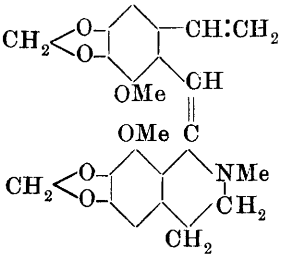
$$C_{24}H_{28}O_6N_2,MeOH,MeI,$$

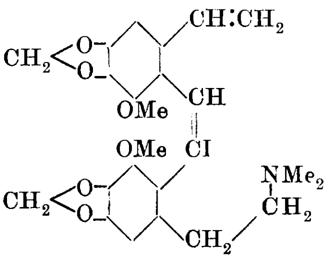
m. p. 215—216°, is obtained, which is converted by acetic acid and potassium iodide into *bishydrocotarnine dimethiodide* $C_{24}H_{28}O_6N_2,2MeI$, m. p. 201—202°.

When treated with silver oxide and water and subsequently boiled with concentrated potassium hydroxide, bishydrocotarnine methiodide and *iso*-bishydrocotarnine methiodide yield respectively *de*-N-*methylbishydrocotarnine*, $C_{25}H_{30}O_6N_2$, m. p. 120—122° (*dihydriodide*, m. p.

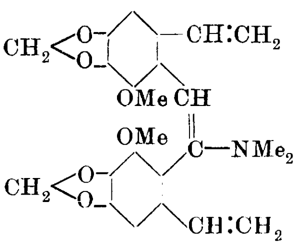


173—175°) and *de*-N-*methyl*iso-*bishydrocotarnine*, m. p. 136° (*dihydriodide*, m. p. 146—149°), which are regarded as structural isomerides on account of their different chemical behaviour. Although their constitutions have not been definitely settled, that annexed is ascribed to de-*N*-methylbishydrocotarnine, because the substance reacts with bromine to form an additive *compound*, $C_{25}H_{30}O_6N_2Br_2$, m. p. 164—166°, which contains only one ionisable bromine atom. Both substances yield cotarnine by oxidation, and form only monomethiodides. *De*-N-*methylbishydrocotarnine methiodide*, $C_{25}H_{30}O_6N_2,MeI$, m. p. 151°, is decomposed by alcoholic sodium ethoxide yielding trimethylamine and *cotarnylidenehydrocotarnine* (annexed formula), m. p. 100—102° (decomp.). *De*-N-*methyl*iso*bishydrocotarnine methiodide*, $C_{25}H_{30}O_6N_2,MeI$, m. p. 159—162°, reacts with silver oxide and water and subsequently with potassium hydroxide to form a substance called *bis-de*-N-*methyl*iso*bishydrocotarnine*, $C_{26}H_{32}O_6N_2$, m. p. 218—220° (*hydriodide*, decomp. 248°), the *methiodide*, $C_{26}H_{32}O_6N_2,MeI$, m. p. 156—158°, of which is decomposed by sodium ethoxide, yielding trimethylamine and *cotarnylidene-de*-N-*methylhydrocotarnine* (see below).





Cotarnylidenehydrocotarnine yields cotarnine by oxidation, and forms with methyl iodide a substance, $C_{24}H_{26}O_6NI$, m. p. 115—117°, called *cotarnylidene-de-N-methyliodohydrocotarnine* (probable constitution annexed), which has pronounced basic properties (*hydriodide*, m. p. 209—211°), and yields by the evaporation of its solution in 50% alcohol the corresponding hydroxy-compound, *cotarnyl-de*-N-*methylhydroxycotarnine*, $C_{24}H_{27}O_7N$, m. p. 73—75° (*methiodide*, m. p. 160—162°).



Bishydrocotarnine dimethiodide, by treatment with silver oxide and water, and subsequently with boiling potassium hydroxide, yields *bis-de*-N-*methylbishydrocotarnine*, $C_{26}H_{32}O_6N_2$, m. p. 118—120° (*hydrobromide*, m. p. 166—168°; *hydriodide*, m. p. 160—162°), the *methiodide*, m. p. 113—115°, of which yields trimethylamine and *cotarnylidene-de*-N-*methylhydrocotarnine* (annexed formula), m. p. 68—71°, by treatment with alcoholic sodium ethoxide. The last-mentioned derivative does not react with methyl iodide.

A table is given showing the genetic relations of the preceding substances. C. S.

Alkaloids of Pareira Root. Max Scholtz (*Arch. Pharm.* 1911, **249**, 408—418. Compare Abstr., 1896, i, 710; 1899, i, 92; 1907, i, 79).—It has been shown already (*loc. cit.*) that pareira root contains either *l*- or *d*- bebeerine. A second alkaloid, chondrodine, has now been isolated from the total alkaloids of the root, and this paper deals with the isolation and characterisation of this substance, which may be regarded provisionally as a hydroxybebeerine.

Chondrodine, $C_{18}H_{21}O_4N$, m. p. 218—220°, $[\alpha]_D$ $-75°$ in alcohol, was obtained as an amorphous substance by a complicated process of separation from that portion of the total alkaloids which was insoluble both in ether and chloroform. The *hydrochloride*, B,HCl, m. p. 274—275°, crystallises in yellow leaflets; the *mercurichloride*, m. p. 288—290° (decomp.), is a crystalline powder; the *ferrichloride*, $B,HCl,FeCl_3$, m. p. 183—184°, occurs in microscopic crystals (?); the *perchlorate*, m. p. 232—233°, crystallises from hot water; the *picrate*, m. p. 193—194°, is a greenish-yellow, crystalline powder, and the *picrolonate*, m. p. 185—186°, forms greenish-yellow, stellate clusters of needles. The *methiodide*, m. p. 273° (decomp.), crystallises from water. The alkaloid contains a methoxyl and an $\vdots NMe$ group. With acetic anhydride at 50—60° it furnishes an amorphous *diacetyl* derivative, which blackens above 270°. The *dibenzoyl* compound, m. p. 295°, separates from hot alcohol in crystalline granules. When heated with ethyl iodide in presence of alcohol and potassium hydroxide, chondrodine furnishes a *diethyl ether*, m. p. 205—207°, as a yellowish-white, sandy powder; the *hydrochloride* of this forms yellow needles and melts at 258°.

Bebeerine methiodide on further treatment with methyl iodide yields a *methyl ether*, $C_{16}H_{14}O(OMe)_2 \cdot NMe_2I$, m. p. 263—264°, which separates from water as a yellow, crystalline powder. *Ethyl bebeerine*, m. p. 150°, obtained by the action of ethyl iodide on bebeerine in presence of potassium hydroxide and alcohol, is a colourless powder, soluble in alcohol, but not in ether; it is lævorotatory, $[\alpha]_D = -250°$ in alcohol, gives a crystalline *hydrochloride*, yellow leaflets, m. p. 109—110°, and furnishes a *methiodide*, m. p. 255—256°, which crystallises from hot water in needles. T. A. H.

Brucine Polyhydrosulphides. Ernst Schmidt and D. Bruns (Reprint from *Apoth. Zeit.*, 1911, No. 67).—Schmidt has shown already (this Journ., 1876, ii, 94) that when hydrogen sulphide is passed through a solution of brucine in alcohol, a yellow and a red polyhydrosulphide are formed, to which the formulæ $B_3,H_2S_6,2H_2O$ and $B_3,2H_2S_6$ were assigned respectively. Doebner subsequently prepared (Abstr., 1895, i, 403) by the addition of ammonium polysulphide to brucine in alcohol, an orange-red polyhydrosulphide, to which he assigned the formula $B_2,H_2S_8,2H_2O$. It is now shown that Doebner's compound is identical with Schmidt's red polyhydrosulphide.

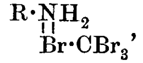
T. A. H.

Dihydroterpenylamine. GEORGE FRANCIS MORRELL (*Ber.*, 1911, **44**, 2560—2565).—When dihydrocarvylamine in dry ether is saturated with hydrogen chloride, at first at 0° and finally without cooling, an unstable *dihydrochloride*, $C_{10}H_{20}NCl,HCl$, white needles, m. p. 205°, is obtained. When this salt is heated with pyridine at 140—145°, it is converted into a *substance*, $C_{10}H_{19}N$, b. p. 96—100°/16 mm., $D_{16\cdot5}^{16\cdot5}$ 0·8909, $n_D^{16\cdot5}$ 1·49284 (*picrate*, m. p. about 176°), which is found to be a mixture of two stereoisomerides, α- and β-dihydroterpenylamine. Methods for their separation are indicated. *α-Dihydroterpenylamine*, b. p. 96—97°/15 mm., forms a *benzoyl* derivative, m. p. 219°, a suspension of which in glacial acetic acid is converted, by treatment with 10—12% ozone and subsequent heating on the water-bath, into acetone and a ketonic *substance*, $C_{14}H_{17}O_2N$, m. p. 183—185°, which is stated to be 2-benzoylamino-1-methyl*cyclo*hexan-4-one.

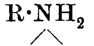
β-Dihydroterpenylamine, b. p. 100—101°/16 mm., forms more sparingly soluble salts than the α-base; the *nitrate*, m. p. 179° (decomp.), *picrate*, m. p. 195°, *hydrochloride*, m. p. 235° (decomp.), and *benzoyl* derivative, m. p. 178—179°, are described.

When a suspension of benzoyldihydrocarvylamine in acetic acid is ozonised and the product heated on the water-bath, a ketonic *substance*, $C_{16}H_{21}O_2N$, m. p. 218—219°, is obtained, which is regarded as 2-benzoylamino-4-acetyl-1-methyl*cyclo*hexane. C. S.

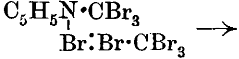
Action of Carbon Tetrabromide on Organic Bases. WILLIAM M. DEHN and ALBERT H. DEWEY (*J. Amer. Chem. Soc.*, 1911, **33**, 1588—1598).—Carbon tetrabromide unites with organic bases to form molecular compounds, the best results being obtained by mixing solutions of the substances in dry ether. In order to explain the mechanism of formation of these compounds, it is suggested that a "coalescence" first takes place, due to the residual valencies of the nitrogen and bromine, thus



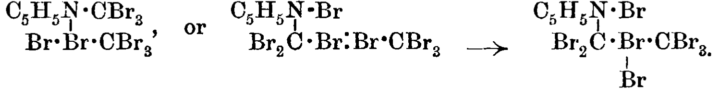
$\begin{array}{c}R\cdot NH_2\\ \vdots\\ Br\cdot CBr_3\end{array}$, and that this is followed by a shifting of the bonds, as shown by the formula



$\begin{array}{c}R\cdot NH_2\\ \diagup\diagdown\\ Br\ \ CBr_3\end{array}$. In the case of pyridine and piperidine, one molecule of the base unites with two molecules of carbon tetrabromide. It is evident that these two molecules are held with different degrees of tenacity, since vapour-pressure curves indicate a dissociation of one molecule at 100°, and of the second molecule between 100° and 210°. Moreover, the complex compound is decomposed by water in accordance with the equation: $C_5H_7N,2CBr_4 + 2H_2O \longrightarrow CBr_4 + CO_2 + 3HBr + C_5H_7N,HBr$. The pyridine compound therefore has the structure:



$\begin{array}{l}C_5H_5N\cdot CBr_3\\ \quad\ \ |\\ \quad\ Br\vdots Br\cdot CBr_3\end{array} \longrightarrow$

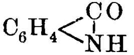
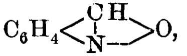
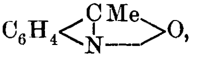


$\begin{array}{l}C_5H_5N\cdot CBr_3\\ \quad\ \ |\\ \ Br\cdot Br\cdot CBr_3\end{array}$, or $\begin{array}{l}C_5H_5N\cdot Br\\ \quad\ \ |\\ Br_2C\cdot Br\vdots Br\cdot CBr_3\end{array} \longrightarrow \begin{array}{l}C_5H_5N\cdot Br\\ \quad\ \ |\\ Br_2C\cdot Br\cdot CBr_3.\\ \qquad\ \ |\\ \qquad\ Br\end{array}$

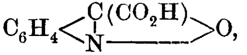
The *piperidine* compound, $C_5H_{11}N,2CBr_4$, m. p. 148°, crystallises in prismatic needles. The *pyridine* compound, $C_5H_5N,2CBr_4$, m. p. 218—220°, D^{21} 2·70, forms iridescent crystals, and is not decomposed by boiling alcohol. The *quinoline* compound, C_9H_7N,CBr_4, m. p. 142°, crystallises in white, prismatic needles. The 2-*picoline* compound, $C_6H_7N,2CBr_4$, m. p. 214°, forms large needles. With 2 : 6-lutidine, a product, m. p. 106°, was obtained in clusters of short needles; this may have been either the compound, $C_5H_3Me_2N,CBr_4$, or a mixture of the compound $C_5H_3Me_2N,2CBr_4$ with lutidine hydrobromide. Carbon tetrabromide reacts with phenylhydrazine with evolution of nitrogen and formation of bromoform and phenylhydrazine hydrobromide. On the addition of carbon tetrabromide to benzylamine, benzylamine hydrobromide separates. Di*iso*amylamine and dipropylamine yield products which are probably mixtures of the carbon tetrabromide compound with the hydrobromide of the base. With ethylamine, ethylamine *hydrobromide*, m. p. 157°, and the *compound*, $4NH_2Et,CBr_4$, m. p. 150°, are produced.

The following salts were obtained during the course of this work. Piperidine *auribromide*, m. p. 242°; pyridine *auribromide*, m. p. 319°; quinoline *hydrobromide*, m. p. 62—65°, and *auribromide*, m. p. 209°; picoline *auribromide*, m. p. 209°; 2:6-lutidine *hydrobromide*, m. p. 114°, and *auribromide*, m. p. 180°; benzylamine *auribromide*, m. p. 178°; and ethylamine *auribromide*, m. p. 190°. E. G.

Homologous Nature of Anthranil and Methylanthranil.

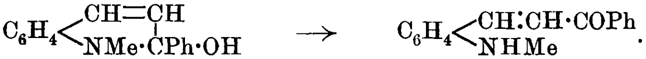
JOHANNES SCHEIBER (*Ber.*, 1911, **44**, 2409—2418).—The question whether anthranil,  $C_6H_4<\begin{matrix}CO\\NH\end{matrix}$ or  $C_6H_4<\begin{matrix}CH\\N\end{matrix}>O$, and methylanthranil,  $C_6H_4<\begin{matrix}CMe\\N\end{matrix}>O$, are homologous has very frequently been the subject of discussion. It is shown by measurement of the ultra-violet absorption that the two compounds behave absolutely identically, and are therefore homologous.

Heller (Abstr., 1908, i, 267; 1909, i, 832) has shown that anthranil and methylanthranil behave differently towards 23% hydrochloric acid and sodium nitrite, but that they behave similarly when 39% acid is used. Measurements of the ultra-violet absorption of the two compounds in acids of these strengths show them to be identical in 4·9% acid, to differ in 24·5% acid, and to be identical again in 39% acid. Anthranil is shown to be very stable towards hydrogen chloride, and the change in absorption is not due to an opening of the ring. When kept for twelve days in 4·9% acid solution, anthranil gives slightly different curves; those for methylanthranil correspond with the readings taken immediately on dissolution.

Anthroxanic acid,  $C_6H_4<\begin{matrix}C(CO_2H)\\N\end{matrix}>O$, likewise shows the same ultra-violet absorption as the two anthranils. The absorption in this case is not altered by solution in hydrochloric acid; possibly the alteration in the case of the homologous anthranils is due to salt formation. E. F. A.

Constitution of the ψ-Bases of Quinoline. II.

ADOLF KAUFMANN and J. M. PLÁ Y JANINI (*Ber.*, 1911, **44**, 2670—2677).—Kaufmann and Strübin (this vol., i, 321) have recently obtained experimental evidence in support of the view that the pseudo-bases (quinolanols) of the quinoline series slowly undergo transformation into the isomeric *o*-alkylaminocinnamaldehydes, owing to the rupture of the pyridine ring. According to this view, 2-substituted quinoline bases should give rise to derivatives of cinnamic acid. The present paper contains an account of the reactions of 2-hydroxy-2-phenyl-1-methylquinoline (I) and its transformation into phenyl *o*-methylaminostyryl ketone (II):



$$C_6H_4{<}\begin{matrix}CH{=}CH\\ NMe\cdot CPh\cdot OH\end{matrix} \longrightarrow C_6H_4{<}\begin{matrix}CH{:}CH\cdot COPh\\ NHMe\end{matrix}.$$

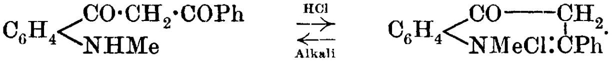
(I.) (II.)

2-Phenylquinoline methiodide (Doebner and Miller, Abstr., 1886, 721) is best prepared by the action of magnesium phenyl bromide on quinoline methiodide and subsequent oxidation of the resulting 2-phenyl-1-methyl-1 : 2-dihydroquinoline (compare Freund, Abstr., 1905, i, 156) with alcoholic iodine; its solution in water is colourless, in alcohol yellow, and in chloroform orange-red. When treated with aqueous sodium hydroxide, it yields the corresponding ψ-base (Decker and Fellenberg, Abstr., 1907, i, 1064), which is converted by the action of aqueous hydrochloric acid on its benzene solution into 2-*phenylquinoline methochloride.* This crystallises in long, almost colourless needles, which begin to decompose at 170°, and melt at 195—200° to a clear liquid; it is identical with the compound obtained by the interaction of silver chloride and 2-phenylquinoline methiodide. When treated with aniline and potassium hydroxide, the methiodide yields *phenyl* o-*methylaminostyryl ketoneanil*,

$$NHMe\cdot C_6H_4\cdot CH{:}CH\cdot CPh{:}NPh,$$

which crystallises in greenish-yellow needles, melting at 140° to a green liquid. The anil is unstable, and readily decomposes when heated alone or in benzene solution, yielding a green dye. It is hydrolysed by cold mineral acids into its components; thus, with hydrochloric acid, it yields aniline and 2-phenylquinoline methochloride.

An alkaline suspension of the above-mentioned ψ-base is oxidised by exposure to air, or more rapidly by potassium ferricyanide, to ω-*benzoyl*-o-*methylaminoacetophenone* (III), which crystallises from benzene in stout needles, m. p. 123°. The latter compound dissolves in acids, yielding salts of 4-keto-2-phenyl-1-methyl-3 : 4-dihydroquinolium hydroxide (IV); the *chloride*, $C_{16}H_4ONCl$, crystallises in stellar aggregates of almost colourless needles, m. p. 237° (decomp.); the *iodide* is light yellow, m. p. 220°; the *picrate*, $C_{22}H_{16}O_8N_4$, forms yellow crystals, m. p. 180°. The salts are reconverted by the action of sodium carbonate or ammonia, or even by boiling with water, into ω-benzoyl-*o*-methylaminoacetophenone, as represented in the following scheme:



$$C_6H_4{<}\begin{matrix}CO\cdot CH_2\cdot COPh\\ NHMe\end{matrix} \underset{\text{Alkali}}{\overset{\text{HCl}}{\rightleftarrows}} C_6H_4{<}\begin{matrix}CO{-\!-\!-}CH_2\\ NMeCl{:}CPh\end{matrix}.$$

(III.) (IV.)

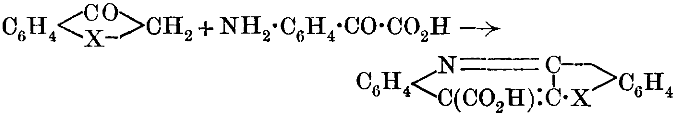
When heated at 250—260°, the chloride loses methyl chloride, yielding 4-hydroxy-2-phenylquinoline, m. p. 256° (Conrad and Limpach, Abstr., 1888, 505), which is transformed by distillation with zinc dust into 2-phenylquinoline, and by the action of phosphorus pentachloride into 4-chloro-2-phenylquinoline (Knorr and Fertig, Abstr., 1897, i, 371). An explanation is also given of the oxidation of 4-cyano-1-alkyldihydroquinolines to 4-cyano-1-alkyl-2-quinolones, observed by Kaufmann and Albertini (Abstr., 1909, i, 958). It is assumed that the hydrogen in the 4-position is first oxidised to hydroxyl with the formation of the compound (V), which then undergoes transformation into (VI) by the addition of water and simultaneous rupture of the pyridine ring:

$$C_6H_4\left\langle\begin{matrix}C(CN)(OH)\cdot CH\\ \| \\ NR\text{———}CH\end{matrix}\right. \longrightarrow C_6H_4\left\langle\begin{matrix}C(CN)(OH)\cdot CH_2\cdot CHO\\ NHR\end{matrix}\right. ;$$

(V.) (VI.)

4-cyano-1-alkyl-2-quinolones are formed from this intermediate product by oxidation and loss of two molecules of water. The above-mentioned formation of ω-benzoyl-*o*-methylaminoacetophenone may be explained in a similar manner. F. B.

Condensation Products of Isatic Acid and Hydroxythionaphthen, Indandione, and Indanone. EMILIO NOELTING and ALEX. HERZBAUM (*Ber.*, 1911, **44**, 2585—2590).—Isatin in alkaline solution reacts with hydroxythionaphthen, indandione, or indanone just as with indoxyl (Noelting and Steuer, this vol., i, 165), yielding the following substances in accordance with the scheme:



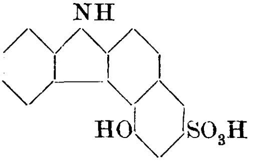
$$C_6H_4\left\langle\begin{matrix}CO\\ X\end{matrix}\right\rangle CH_2 + NH_2\cdot C_6H_4\cdot CO\cdot CO_2H \longrightarrow C_6H_4\left\langle\begin{matrix}N\text{===}C\text{—}\\ C(CO_2H){:}C\cdot X\end{matrix}\right\rangle C_6H_4,$$

where X = S, CO, or CH_2. Thus hydroxythionaphthen yields "*thioquindolinecarboxylic acid*," $C_{16}H_9O_2NS$, yellow needles, which decomposes above its m. p., about 335°, forming "thioquindoline," m. p. 172° (not 169°, *loc. cit.*). Indandione yields *quinolylenephenyleneketonecarboxylic acid*, $C_{17}H_9O_3N$, colourless needles, which is converted into the corresponding ketone (Noelting and Blum, Abstr., 1901, i, 728) above its m. p., about 340°. Indanone yields *quinolylenephenylenemethanecarboxylic acid*, $C_{17}H_{11}O_2N$, m. p. 330° (decomp), which is converted by fusion into quinolylenephenylenemethane (Noelting and Blum, *loc. cit.*); the latter has also been obtained by condensing indanone and *o*-aminobenzaldehyde in boiling dilute hydrochloric acid.

The sodium salts of the three preceding acids yield with metallic salts precipitates, the colours of which are tabulated. C. S.

[Preparation of Carbazole Derivatives.] KALLE & Co. (D.R.-P. 234338).—Carbazole derivatives obtained from 6-amino-1-naphthol-3-sulphonic acid and hydrazines have previously been described, and the reaction has now been extended to the case of 7-amino-1-naphthol-3-sulphonic acid.

The carbazole, 1-*hydroxybenzo-β-naphthindole*-3-*sulphonic acid*



(annexed formula), is prepared by heating this acid in aqueous solution with phenylhydrazine in the presence of sodium hydrogen sulphite and sodium hydroxide; on cooling, the carbazole separates in microcrystalline form.

The action is stated to be widely applicable, both with regard to the acid and hydrazine or other aromatic base employed.

The dyes obtained from tetrazotised benzidine, coupled with the foregoing carbazole (1 mol.) and salicylic acid and resorcinol respectively, are described in the original. F. M. G. M.

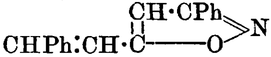
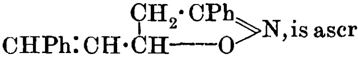
Action of Hydroxylamine on Ketones of the Type $R{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COPh$.

Roberto Ciusa and A. Terni (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 25—30. Compare Abstr., 1908, i, 762; Ciusa and Bernardi, Abstr., 1910, i, 684).—The present paper is concerned with the further examination of α-cinnamylideneacetophenonehydroxylamineoxime, previously described.

Benzylidene-α-cinnamylideneacetophenonehydroxylamineoxime,

$$C_{24}H_{22}O_2N_2,$$

is obtained by boiling for one hour alcoholic solutions of benzaldehyde and the hydroxylamineoxime; it has m. p. 175°.

α-Cinnamylideneacetophenonehydroxylamineoxime, when oxidised with permanganate, yields benzoic acid and a 3-*phenyl*-5-*styryl*iso-*oxazole*,  $\begin{array}{l}CH{\cdot}CPh \\ \| \\ CHPh{:}CH{\cdot}C\text{——}O\end{array}\!\!>\!N$, which forms lustrous scales, m. p. 138°. The hydroxylamineoxime yields with nitrous acid (sodium nitrite and glacial acetic acid in the cold) an isomeride of α-cinnamylideneacetophenoneoxime, m. p. 124°, identical with the substance previously obtained among the secondary products of the reaction between cinnamylideneacetophenone and hydroxylamine (compare Ciusa and Terni, *loc. cit.*). To this substance the constitution of a 3-*phenyl*-5-*styryldihydro*iso*oxazole*,  $\begin{array}{l}CH_2{\cdot}CPh \\ | \\ CHPh{:}CH{\cdot}CH\text{——}O\end{array}\!\!>\!N$, is ascribed. It yields a *dibromo*-derivative, $C_{17}H_{15}ONBr_2$, which crystallises in small, colourless needles, m. p. 145°. When α-cinnamylideneacetophenonehydroxylamineoxime is boiled with 90% acetic acid or normal hydrochloric acid, it gives the α-oxime of m. p. 135°. This explains the fact that when hydroxylamine hydrochloride reacts with unsaturated ketones in the absence of sodium acetate only oximes, and not hydroxylamineoximes, are obtained (compare Ciusa and Bernardi, *loc. cit.*). R. V. S.

Aromatic ψ-Thiocarbamides and their Conversion into Aryl *ortho*-Thiocarbonates.

Fritz Arndt (*Annalen*, 1911, **384**, 322—351).—The interaction of *p*-tolyl mercaptan and cyanamide, with the addition of ether to moderate the violence of the reaction, gives an almost quantitative yield of p-*tolyl*-ψ-*thiocarbamide*,

$$NH{:}C(NH_2){\cdot}S{\cdot}C_7H_7,$$

m. p. 110° (decomp.) The substance decomposes when heated alone or in boiling alcohol, yielding *p*-tolyl mercaptan and dicyanodiamide It forms a *dibenzoate*, $NBz\colon C(NHBz)\cdot S\cdot C_7H_7$, m. p. 122—123°, with benzoyl chloride in cold pyridine, and also yields well crystallised salts, of which the *acetate, sulphate, chromate, chloride*, and *nitrate*, m. p. 173°, are described. Very characteristic is its behaviour in the presence of nitric and sulphuric acids, whereby a *nitrate-sulphate*,

$$3C_8H_{10}N_2S,H_2SO_4,HNO_3,$$

is obtained, even when the dilution of the nitric acid is one in 100,000; provided an excess of the reagent is present, this salt is so insoluble that it can be employed for the estimation of nitrates. Similar, sparingly soluble double salts are obtained in the presence of sulphuric acid and the majority of the monobasic acids or hydroferrocyanic acid, but not hydroferricyanic acid, hydrogen cyanide, phosphoric acid, or organic acids; however, the place of the sulphuric acid cannot be taken by any other acid. (The isomeric benzyl-ψ-thiocarbamide does not form double salts corresponding with the preceding.)

p-Tolyl-ψ-thiocarbamide chloride or acetate reacts with concentrated sodium nitrate (not potassium nitrite) in neutral solution to form the *nitrite*, m. p. 112°, but in the presence of hydrochloric acid, *nitroso*-p-*tolyl-ψ-thiocarbamide*, $C_8H_9ON_3S$, decomp. 112°, is obtained, which receives the constitution $C_7H_7S\cdot C(\colon NH)\cdot NH\cdot NO$ or

$$C_7H_7S\cdot C(\colon NH)\cdot N\colon N\cdot OH$$

on account of its absence of colour, insolubility in dilute acids, response to the Liebermann test, and conversion by glacial acetic acid into nitrogen and *p*-tolyl thiocyanate. When the nitroso-compound is recrystallised from methyl alcohol without the addition of a little ammonia, it is partly converted into a yellow *substance*, decomp. about 130°, which is probably $C_7H_7S\cdot CO\cdot NH\cdot NO$.

When its methyl-alcoholic solution is warmed with aqueous ammonia, nitroso-*p*-tolyl-ψ-thiocarbamide is converted into p-*tolyl orthothiocarbonate*, $C(S\cdot C_7H_7)_4$, needles, m. p. 147°, which forms with bromine in chloroform an unstable *perbromide*, $C(S\cdot C_7H_7)_4,Br_8$, dark red leaflets, m. p. below 100° (of freshly prepared specimen), which readily changes to a yellow, crystalline *tetrabromide*, $C(S\cdot C_7H_7)_4,Br_4$, m. p. 169°. By boiling the tetrabromide with alcohol or warming the thiocarbonate itself with acetic and a little concentrated sulphuric acid, the *disulphoxide*, $C(S\cdot C_7H_7)_2(SO\cdot C_7H_7)_2$, m. p. 92°, is obtained. An attempt to synthesise *p*-tolyl orthothiocarbonate from sodium *p*-tolylmercaptide and carbon tetrachloride in boiling alcohol resulted in the formation of p-*tolyl orthothioformate*, $CH(S\cdot C_7H_7)_3$, m. p. 111°, which is also produced by the reduction of the orthothiocarbonate by zinc and acetic acid.

Benzyl-ψ-thiocarbamide and sodium nitrite react in acid solution to form a stable *nitrite*, m. p. 126° (decomp.), which yields benzyl disulphide by heating; a substance corresponding with nitroso-*p*-tolyl-ψ-thiocarbamide is not formed.

p-Tolyl mercaptan and phenylcyanamide react in ether to form *phenyl*-p-*tolyl-ψ-thiocarbamide*, $NHPh\cdot C(NH)\cdot S\cdot C_7H_7$, m. p. 148°, which forms a *hydrochloride*, *nitrate*, m. p. 132°, and *benzoyl* derivative, m. p. 151·5°, and is easily methylated, yielding *phenyl*-p-*tolylmethyl-ψ-thiocarbamide*, $NPhMe\cdot C(NH)\cdot S\cdot C_7H_7$, m. p. 121°.

Diphenyl-p-*tolyl*-*ψ*-*thiocarbamide*, $NHPh\cdot C(NPh)\cdot S\cdot C_7H_7$, m. p. 119—120°, is obtained by desulphurising diphenylthiocarbamide in benzene by mercuric oxide and treating the resulting solution of carbodiphenylimide with *p*-tolyl mercaptan.

Hofmann's triphenyl*iso*melamine, m. p. 185° (Abstr., 1886, 233), is shown to be an additive compound of triphenylmelamine and phenylcyanamide; the former constituent can be removed by dilute acid or boiling water. C. S.

Conversion of Nitroaldehydes into Cyanoaldehydes. GIACOMO PONZIO (*Gazzetta*, 1911, 41, i, 787—793. Compare Ponzio and Giovetti, Abstr., 1910, i, 194).—The author has shown previously that an aliphatic nitro-group may be substituted by $-NH_2$ or $-NHPh$ (compare Abstr., 1910, i, 339, 442, 699), and he now finds that it may also be replaced by $-CN$. A new method of preparation is thus provided for the hydrazones of ω-cyanobenzaldehyde, which, although longer than that formerly given, has the advantage that the *o*- and *m*-substituted phenylhydrazones can also be obtained.

ω-Cyanobenzaldehyde-*o*-nitrophenylhydrazone (*loc. cit.*) is the only substance produced when ω-nitrobenzaldehyde-*o*-nitrophenylhydrazone is boiled for two hours in aqueous alcoholic solution with potassium cyanide.

ω-Cyanobenzaldehyde-m-*nitrophenylhydrazone*,

$$CN\cdot CPh{:}N\cdot NH\cdot C_6H_4\cdot NO_2,$$

which cannot be obtained by the method formerly given, crystallises in small, yellow prisms, m. p. 197—198°. It is soluble in alkali to which a drop of alcohol has been added, and it gives a yellow coloration. The *ω-nitrobenzaldehyde*-m-*nitrophenylhydrazone* employed for its preparation is obtained by heating the sodium salt of ω-nitrotoluene with *m*-nitrobenzenediazonium sulphate; it crystallises in small, brick-red prisms, m. p. 132° (decomp.).

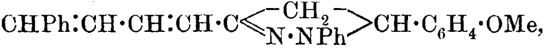
ω-Cyanobenzaldehyde-*p*-nitrophenylhydrazone, ω-cyanobenzaldehyde-*o*-chloro-*p*-nitrophenylhydrazone, and ω-cyanobenzaldehyde-*o*-*p*-dinitrophenylhydrazone can also be prepared by the new method. The *ω-nitrobenzaldehyde*-o-p-*dinitrophenylhydrazone* necessary for the preparation of the last-named substance is obtained by diazotising 2:4-dinitroaniline and acting on the sodium salt of ω-nitrotoluene with the 2:4-dinitrobenzenediazonium sulphate so produced. The substance crystallises in yellowish-brown, flat needles, m. p. 152° (decomp.). R. V. S.

Syntheses of Pyrazolones from a Derivative of γ-Pyrone. F. CARLO PALAZZO and RAFFAELE LIVERANI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 55—60. Compare Palazzo, Abstr., 1906, i, 701).—By the action of hydrazine hydrate on ethyl dimethylpyronedicarboxylate the authors have obtained three different nitrogenous compounds, which all belong to the pyrazolone group. When 1 mol. of hydrazine hydrate is boiled with the ester in methyl-alcoholic solution for two minutes, a small quantity (2%) of a compound is obtained, which crystallises in minute needles, m. p. 195—196°, and gives a reddish-violet coloration with ferric chloride. Of this substance no analysis could be made, but it is identical with the product $C_7H_{10}O_3N_2$, from hydrazine hydrate and ethyl acetylmalonate, which is shown to be *3-methyl-5-pyrazolone-4-carboxylate.* When two mol. of hydrazine hydrate are heated in a sealed tube with a concentrated methyl-alcoholic solution of ethyl dimethylpyronedicarboxylate for some hours at 120°, a *substance*, $C_5H_5O_2N_2\cdot OEt$, is obtained in good yield. The compound has m. p. 125—130° (softening considerably at 50—60°), and gives a reddish-brown coloration with ferric chloride. It is suggested that it may be an isomeride of the first-mentioned compound. By the interaction of two mols. of hydrazine hydrate and ethyl dimethylpyronedicarboxylate in methyl-alcoholic solution as before, the mixture being boiled for two hours, a *substance* is produced, which has m. p. 142—145°. It gives a reddish-brown coloration with ferric chloride. The analytical results agree with the formula $C_{11}H_{16}O_4N_4$, but the substance appears to be a mixture, possibly of equimolecular amounts of the two pyrazolones, $C_7H_{10}O_3N_2$ and $C_4H_6ON_2$. R. V. S.

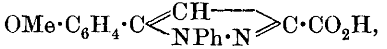
The Pyrazoline Transformation of Unsaturated Hydrazones.

Hugo Bauer and Hedwig Dieterle (*Ber.*, 1911, **44**, 2697—2702).—It has been shown by Auwers (Abstr., 1909, i, 59; 1910, i, 70) that the phenylhydrazones of many unsaturated ketones may be transformed into pyrazoline derivatives by heating them with glacial acetic acid. That the reaction is, however, not a general one has been confirmed by the authors from an examination of the behaviour of unsaturated ketones of the type CHPh:CH·CH:CH·CO·CH:CHR. When R = anisyl or furyl, the action of phenylhydrazine leads directly to the formation of a pyrazoline derivative; the intermediately formed phenylhydrazones could not be isolated. On the other hand, when R = phenyl, the phenylhydrazone is not converted into a pyrazoline derivative, even by prolonged heating with acetic acid.

1-*Phenyl-3-β-styrylvinyl-5-anisylpyrazoline*,



$$CHPh{:}CH\cdot CH{:}CH\cdot C\begin{matrix}-CH_2-\\ N\cdot NPh\end{matrix}CH\cdot C_6H_4\cdot OMe,$$

prepared by heating anisylidenecinnamylideneacetone [*p*-methoxystyryl β-styrylvinyl ketone] with phenylhydrazine in glacial acetic acid solution, forms yellow crystals, m. p. 155—156°; its alcoholic solution has an intense, green fluorescence. When oxidised with aqueous potassium permanganate, it yields benzoic acid and 1-*phenyl-5-anisylpyrazole-3-carboxylic acid*,  $OMe\cdot C_6H_4\cdot C\begin{matrix}CH\text{———}\\ NPh\cdot N\end{matrix}C\cdot CO_2H$, which crystallises from water in white needles, m. p. 178—179°, and yields a *copper* salt, $(C_{17}H_{15}O_3N_2)_2Cu$, crystallising in slender, green needles. The formation of this acid proves that the double linking, adjacent to the anisyl group, is concerned in the pyrazoline formation, and this is confirmed by the behaviour of the two following phenylhydrazones, which do not contain a double linking in this position, and, therefore, are not transformed into pyrazoline derivatives.

ζ-Bromo-η-methoxy-α-phenyl-η-anisyl-$\Delta^{\alpha\gamma}$-heptadien-ε-onephenylhydrazone, CHPh:CH·CH:CH·C(N·NHPh)·CHBr·CH(OMe)·C_6H_4·OMe, obtained from the corresponding ketone (this vol., i, 881) and phenylhydrazine, has m. p. 201—202·5°.

γδζ-Tribromo-η-methoxy-α-phenyl-η-anisyl-Δ^{α}-hepten-ε-onephenylhydrazone, $\mathrm{CHPh{:}CH{\cdot}[CHBr]_2{\cdot}C(N{\cdot}NHPh){\cdot}CHBr{\cdot}CH(OMe){\cdot}C_6H_4{\cdot}OMe}$, also prepared from the corresponding ketone (*loc. cit.*), forms slender, yellow needles, m. p. 181—182°.

Styryl β-styrylvinyl ketonephenylhydrazone,

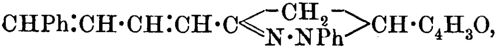
$$\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}C({:}N{\cdot}NHPh){\cdot}CH{:}CHPh},$$

prepared from its components in alcoholic solution, crystallises in yellowish-brown platelets, m. p. 111—112°.

Furfurylidenecinnamylideneacetone [*β-styryl-β′-furyldivinyl ketone*],

$$\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO{\cdot}CH{:}CH{\cdot}C_4H_3O},$$

obtained by the condensation of furfuraldehyde with cinnamylideneacetone (β-styrylvinyl methyl ketone) by means of sodium hydroxide in aqueous alcoholic solution, crystallises in lustrous, golden-yellow leaflets, m. p. 97—98°. It gives an intense red coloration with strong nitric acid, and is transformed by the action of pnenylhydrazine into 1-*phenyl*-3-*β-styrylvinyl*-5-*furylpyrazoline,*



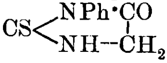
$$\mathrm{CHPh{:}CH{\cdot}CH{:}CH{\cdot}C}\left<\begin{matrix}\mathrm{-CH_2-}\\ \mathrm{N{\cdot}NPh}\end{matrix}\right>\mathrm{CH{\cdot}C_4H_3O},$$

which crystallises in strongly fluorescent, slender, yellow needles, m. p. 165—166°, and is oxidised by aqueous permanganate to benzoic acid and 1-*phenylpyrazole*-3 : 4-*dicarboxylic acid,* m. p. 250—255°.

F. B.

Hydantoins. IV. 2-Thio-1-phenylhydantoins from Some α-Amino-acids. Charles A. Brautlecht (*J. Biol. Chem.*, 1911, 10, 139—146. Compare Wheeler and Brautlecht, this vol., i, 500).—The action of phenylthiocarbimide on a number of α-amino acids has been studied. In the presence of alkali, interaction takes place with the formation of alkali salts of thiohydantoic acids. These readily undergo transformation into the corresponding hydantoins on treatment with hydrochloric acid. Crystalline thiophenylhydantoins could not, however, be obtained from cystine and α-pyrrolidonecarboxylic acid.

These thiophenylhydantoins are characteristic of the α-amino-acids, and should serve for their identification. When warmed with potassium hydroxide, they are hydrolysed to the potassium salts of the thiohydantoic acids. They are desulphurised by digestion in aqueous or dilute alcoholic solutions with silver nitrate, mercuric chloride, etc., and are stable in the presence of boiling hydrochloric acid.



2-Thio-1-phenylhydantoin, $\mathrm{CS}<\begin{matrix}\mathrm{NPh{\cdot}CO}\\ \mathrm{NH{-}CH_2}\end{matrix}$, from glycine has m. p. 240—242°.

2-*Thio*-1-*phenyl*-4-*ethylhydantoin* from α-amino-*n*-butyric acid crystallises in plates, m. p. 190—192°.

2-*Thio*-1-*phenyl*-4-iso*propylhydantoin*, obtained from valine, forms colourless needles, m, p 206—208°.

2-*Thio*-1-*phenyl*-4-*benzylhydantoin* from phenylalanine separates in colourless prisms, m. p. 187°.

Tyrosine gives rise to 2-*thio*-1-*phenyl*-4-p-*hydroxybenzylhydantoin*, colourless or straw-coloured prisms, m. p. 214—216°.

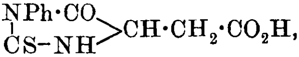
From asparagine 2-*thio*-1-*phenylhydantoin*-4-*acetamide* is obtained; it crystallises in colourless, lenticular prisms, m. p. 234°.

The *potassium* salt of the hydantoic acid,

$$\mathrm{NHPh\cdot CS\cdot NH\cdot CH(CO_2K)\cdot CH_2\cdot CO\cdot NH_2},$$

separates in colourless plates, m. p. 154°.

2-*Thio*-1-*phenylhydantoin*-4-*acetic acid*,



$$\left.\begin{array}{l}\mathrm{NPh\cdot CO}\\ \mathrm{CS{-}NH}\end{array}\right>\mathrm{CH\cdot CH_2\cdot CO_2H},$$

from aspartic acid crystallises in colourless prisms, m. p. 233—234° (decomp.).

2-*Thio*-1-*phenylhydantoin*-4-*propionic acid*, prepared from glutamic acid, separates in microscopic needles, m. p. 169—170°. E. F. A.

Hydantoins. V. Synthesis of 3 : 5-Dichlorotyrosine.

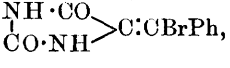
HENRY L. WHEELER, CHARLES HOFFMAN, and TREAT B. JOHNSON (*J. Biol. Chem.*, 1911, **10**, 147—157).—Tyrosine itself does not react smoothly with chlorine, but tyrosinehydantoin reacts with chlorine in glacial acetic acid solution, forming the corresponding *hydantoin* of 3 : 5-*dichlorotyrosine*. The same compound was obtained on reducing 3 : 5-dichlorobenzylidenehydantoin with hydriodic acid, a compound which was prepared by Wheeler and Hoffmann (this vol., i, 498) by condensation of hydantoin with 3 : 5-dichlorobenzaldehyde. Chlorine therefore is substituted in the same positions (3 : 5) in the benzene nucleus of tyrosinehydantoin as are taken by iodine and bromine when they combine with tyrosine. On digestion with barium hydroxide, the hydantoin is converted into 3 : 5-*dichlorotyrosine*. This crystallises with $2H_2O$, dissociates in aqueous solution, and reacts acid to litmus; it does not give a red coloration with Millon's reagent.

Benzylidenehydantoin reacts with chlorine and bromine in acetic acid, forming *a-chloro-* and *a-bromo-benzylidenehydantoin* respectively. The latter is reduced by hydriodic acid, forming benzylhydantoin. Anisylidenehydantoin was not reduced under practically the same conditions.

3 : 5-*Dichlorotyrosinehydantoin* crystallises in rhombohedral prisms, m. p. 202° (decomp.).

3 : 5-*Dichlorotyrosine* separates in rectangular, prismatic crystals, m. p. 252° (decomp.). The *hydrochloride* forms large, prismatic, colourless crystals, m. p. 260—265° (decomp.).

a-Bromobenzylidenehydantoin,



$$\left.\begin{array}{l}\mathrm{NH\cdot CO}\\ \mathrm{CO\cdot NH}\end{array}\right>\mathrm{C{:}CBrPh},$$

crystallises in plates, m. p. 240° to an oil.

a-Thiolbenzylidenehydantoin, prepared by boiling the bromo-compound with potassium hydrosulphide, crystallises in yellow prisms, m. p. 199° (decomp.).

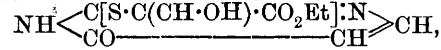
a-Chlorobenzylidenehydantoin also crystallises in plates, m. p. 273° to an oil.

p-*Methoxybenzylhydantoin*, prepared by reduction of anisylidenehydantoin (Wheeler and Hoffman, *loc. cit.*), crystallises in yellow, hexagonal tablets, m. p. 174° to a clear oil. Anisylidenehydantoin could not be reduced with tin and hydrochloric acid; after boiling with zinc and acetic acid, it was recovered unchanged, but in a colourless form. Digestion with sodium hydroxide converts it into *p*-methoxyphenylpyruvic acid. E. F. A.

Pyrimidines. LIII. Condensation of Ethyl Formate and Ethyl Oxalate with Some Pyrimidinethioglycollates. TREAT B. JOHNSON and NORMAN A. SHEPARD (*Amer. Chem. J.*, 1911, 46, 345—361).—The work described was undertaken with the object of obtaining further knowledge of the behaviour of the grouping $-S\cdot CH_2\cdot CO-$. Johnson and Guest (Abstr., 1909, i, 744) have studied the condensation of ethyl formate with ethyl benzylthiolacetate, and Hinsberg (Abstr., 1910, i, 334) has shown that the methylene groups in ethyl thiodiglycollate react readily with α-dicarbonyl compounds.

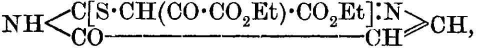
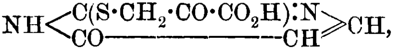
The only pyrimidine derivative of ethyl thiolacetate hitherto described is ethyl 1 : 6-dihydro-6-pyrimidone-2-thiolacetate, which was obtained by Wheeler and Liddle (Abstr., 1909, i, 61) by the action of ethyl chloroacetate on 2-thiouracil. It is now shown that trans-β-*thiocarbaminoacrylic acid*, $NH_2\cdot CS\cdot NH\cdot CH:CH\cdot CO_2H$, which forms lustrous plates and does not melt below 300°, is also produced in this reaction.

Ethyl 1 : 6-dihydro-6-pyrimidone-2-thiolacetate condenses with ethyl formate in presence of sodium ethoxide with formation of *ethyl* 1 : 6-*dihydro*-6-*pyrimidone*-2-α-*thiol*-β-*hydroxyacrylate*,

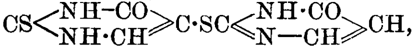


$$\mathrm{NH}<\begin{matrix}\mathrm{C[S\cdot C(CH\cdot OH)\cdot CO_2Et]:N}\\ \mathrm{CO}\text{————————}\mathrm{CH}\end{matrix}>\mathrm{CH},$$

m. p. 138—140°, which crystallises in prisms.

By the condensation of ethyl oxalate with 1 : 6-dihydro-6-pyrimidone-2-thiolacetate, *diethyl* 1 : 6-*dihydro*-6-*pyrimidone*-2-*thioloxalylacetate*,  $\mathrm{NH}<\begin{matrix}\mathrm{C[S\cdot CH(CO\cdot CO_2Et)\cdot CO_2Et]:N}\\ \mathrm{CO}\text{————————}\mathrm{CH}\end{matrix}>\mathrm{CH}$, m. p. 171°, is obtained, which crystallises in stout blocks, and is decomposed by hydrochloric acid with formation of 1 : 6-*dihydro*-6-*pyrimidone*-2-*thiolpyruvic acid*,  $\mathrm{NH}<\begin{matrix}\mathrm{C(S\cdot CH_2\cdot CO\cdot CO_2H):N}\\ \mathrm{CO}\text{——————}\mathrm{CH}\end{matrix}>\mathrm{CH}$, m. p. 200—201° (decomp.); it is also decomposed by potassium hydroxide with production of uracil.

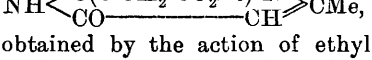
When ethyl 1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate is heated with thiocarbamide in presence of sodium ethoxide, 2(*tetrahydro*-2′-*thio*-6′-*pyrimidonethiol*)-1 : 6-*dihydro*-6-*pyrimidone*,



$$\mathrm{CS}<\begin{matrix}\mathrm{NH-CO}\\ \mathrm{NH\cdot CH}\end{matrix}>\mathrm{C\cdot SC}<\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{N-CH}\end{matrix}>\mathrm{CH},$$

is produced, which crystallises in needles and decomposes at 285—295°. Thiocarbamide also condenses with ethyl 1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate with formation of small quantities of a compound which is probably identical with that just described.

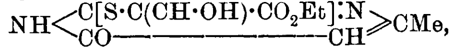
Ethyl 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*-2-*thiolacetate*,



$$\mathrm{NH}<\begin{matrix}\mathrm{C(S\cdot CH_2\cdot CO_2Et):N}\\ \mathrm{CO}\text{——————}\mathrm{CH}\end{matrix}>\mathrm{CMe},$$

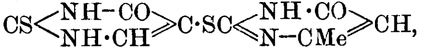
m. p. 145—146°, obtained by the action of ethyl chloroacetate on 2-thio-4-methyluracil, forms colourless needles; the corresponding *acid*, m. p. 192—197° (decomp.), crystallises in colourless prisms; the *potassium* salt is described.

When ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate is heated with ethyl formate in presence of sodium ethoxide, *ethyl* 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*-2-*a-thiol-β-hydroxyacrylate*,



$$NH<\begin{matrix}C[S\cdot C(CH\cdot OH)\cdot CO_2Et]:N\\ CO\text{—————————}CH\end{matrix}>CMe,$$

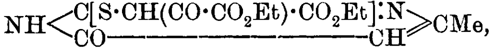
m. p. 106—108°, is produced, which forms colourless crystals; an attempt to reduce this compound with sodium amalgam resulted in the formation of 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetic acid. By the condensation of thiocarbamide with ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate, 4-*methyl*-2(*tetrahydro*-2′-*thio*-6′-*pyrimidonethiol*)-1 : 6-*dihydro*-6-*pyrimidone*,



$$CS<\begin{matrix}NH-CO\\ NH\cdot CH\end{matrix}>C\cdot SC<\begin{matrix}NH\cdot CO\\ N-CMe\end{matrix}>CH,$$

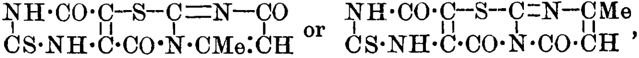
is produced, which forms clusters of prisms, and does not melt below 300°.

Diethyl 4-*methyl*-1 : 6-*dihydro*-6-*pyrimidone*-2-*thioloxalylacetate*,



$$NH<\begin{matrix}C[S\cdot CH(CO\cdot CO_2Et)\cdot CO_2Et]:N\\ CO\text{——————————}CH\end{matrix}>CMe,$$

m. p. 139—140°, obtained by the action of ethyl oxalate on ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate, crystallises in stout, colourless blocks; it condenses with thiocarbamide with formation of a *compound*,



$$\begin{array}{l}NH\cdot CO\cdot C\text{—}S\text{—}C\text{═}N\text{—}CO\\ \vert\qquad\qquad\Vert\qquad\;\vert\qquad\quad\;\vert\\ CS\cdot NH\cdot C\cdot CO\cdot N\cdot CMe:CH\end{array}\quad\text{or}\quad\begin{array}{l}NH\cdot CO\cdot C\text{—}S\text{—}C\text{═}N\text{—}CMe\\ \vert\qquad\qquad\Vert\qquad\;\vert\qquad\quad\;\Vert\\ CS\cdot NH\cdot C\cdot CO\cdot N\cdot CO\cdot CH\end{array},$$

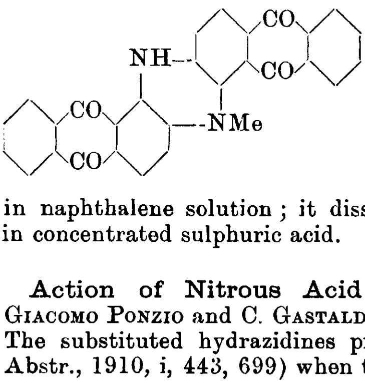
m. p. 164—165°, which crystallises in hexagonal tablets. E. G.

Preparation of Halogenated Derivatives of Indigotin.

BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234961).—When 4 : 4′-dichloroindigotin is suspended in nitrobenzene (or other indifferent liquids), cooled, and treated with chlorine, further halogenation takes place, yielding tri- and tetra-chloro-derivatives. The corresponding bromo-derivatives are obtained when the substance is suspended in dilute sulphuric acid and treated with bromine at a temperature below 5°. F. M. G. M.

[Preparation of Methylindanthren.]

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 234294). — *Methylindanthren* (annexed formula), dark blue needles with metallic lustre, is prepared by boiling 2-bromo-1-aminoanthraquinone with 2-bromo-1-methylaminoanthraquinone in the presence of sodium acetate and cupric chloride in naphthalene solution; it dissolves with a yellowish-brown colour in concentrated sulphuric acid. F. M. G. M.



Action of Nitrous Acid on Substituted Hydrazidines.

GIACOMO PONZIO and C. GASTALDI (*Gazzetta*, 1911, 41, i, 793—796).—The substituted hydrazidines previously described (compare Ponzio, Abstr., 1910, i, 443, 699) when treated with nitrous acid do not yield tetrazoles, but, instead, the hydrogen of the imino-group is displaced by $-NO$, so that ω-aminobenzaldehyde-*p*-nitrophenylhydrazone,

$NH_2\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot NO_2$,

yields *ω-aminobenzaldehydenitroso*-p-*nitrophenylhydrazone*,

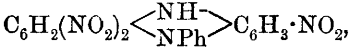
$NH_2\cdot CPh\colon N\cdot N(NO)\cdot C_6H_4\cdot NO_2$.

This nitroso-compound is insoluble in alkali hydroxides, and when boiled with water gives ω-aminobenzaldehyde-*p*-nitrophenylhydrazone and benzoyl-*p*-nitrophenylhydrazine, $COPh\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2$.

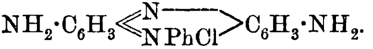
ω-Aminobenzaldehydenitroso-*p*-nitrophenylhydrazone forms small, yellow laminæ, m. p. 127° (decomp.). It gives an emerald-green coloration with concentrated sulphuric acid and phenol. R. V. S.

Preparation of Secondary 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone Citrate. RUDOLF OTTO (D.R.-P. 234631).—Two salts of this base with citric acid have previously been described, and the "citrovanille" employed in pharmacy consists of mixtures of both in varying proportions. The primary salt (a syrup) is prepared from equal molecular proportions of the base and acid, the tertiary, containing 3 mols. of the base, has similar properties, whilst the secondary, *4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone citrate*, $C_6H_8O_7(C_{13}H_{17}ON_3)_2$, has now been prepared by allowing the requisite proportions of the components to react either in warm aqueous solution at 75° or in a fusion without solvent; it crystallises from hot water. F. M. G. M.

Isomeride of *apo*Safranine and the Third Isomeride of Phenosafranine. FRIEDRICH KEHRMANN and JOSÉ RIERA Y PUNTI (*Ber.*, 1911, **44**, 2622—2627).—*2 : 4 : 6 : 5′-Tetranitro-2′-anilinodiphenylamine*, $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_3(NO_2)\cdot NHPh$, brownish-yellow crystals, decomp. above 174°, obtained by warming equal molecular quantities of picryl chloride and 4-nitro-2-aminodiphenylamine in alcoholic solution, is converted in alcoholic suspension by concentrated sodium hydroxide into *1 : 3 : 7-trinitro-10-phenyldihydrophenazine*,

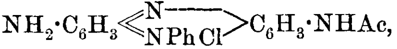


$C_6H_2(NO_2)_2{<}{}^{NH-}_{NPh}{>}C_6H_3\cdot NO_2$, blacki h-violet needles, decomp. above 265°, which dissolves in hot alcoholic sodium hydroxide with a violet colour. When suspended in glacial acetic acid and reduced by stannous chloride and hydrochloric acid, it is reduced to the *triaminophenyldihydrophenazine* (isolated as the yellow *stannichloride*), which loses ammonia by careful warming in faintly alcoholic solution, the subsequent addition of sodium chloride precipitating *2 : 6-diamino-10-phenylphenazonium chloride*,



$NH_2\cdot C_6H_3{\lessdot}{}^{N\text{———}}_{NPhCl}{>}C_6H_3\cdot NH_2$. This salt forms blackish-violet, prismatic crystals with a bronze lustre, yields a violet-blue aqueous solution (so also do other mono-acidic salts), a brown solution in slightly fuming sulphuric acid, and a greenish-blue solution in concentrated sulphuric acid, which changes to magenta-red and finally to violet-blue on sufficient dilution with water; these colour changes indicate the existence of four series of salts, as is the case with phenosafranine itself. This new *iso*-phenosafranine dyes tannined cotton a dirty greenish-blue, the colour changing to red by treatment with dilute hydrochloric acid, and by washing to a blue which is fast to alkalis and soap.

*iso*Phenosafranine chloride and acetic anhydride at the ordinary temperature yield an *acetyl* derivative,



$$NH_2\cdot C_6H_3<\substack{N\text{———}\\NPhCl}>C_6H_3\cdot NHAc,$$

reddish-brown needles, from which by the elimination of the amino-group is obtained the *acetyl* derivative of *iso-apo*safranine chloride, $C_6H_4<\substack{N\text{———}\\NPhCl}>C_6H_3\cdot NHAc$; the corresponding *nitrate*, *ferrichloride*, and *platinichloride* are mentioned. iso-apo*Safranine chloride*, obtained by hydrolysing the preceding acetyl derivative, is an almost black, crystalline powder, which is unstable in solution; the *platinichloride*, $2C_{18}H_{14}N_3,PtCl_6$, is a black, crystalline powder.

*iso*Phenosafranine chloride and acetic anhydride and sodium acetate on the water-bath yield the *diacetyl* derivative,

$$NHAc\cdot C_6H_3<\substack{N\text{———}\\NPhCl}>C_6H_3\cdot NHAc,$$

brownish-red crystals with a bronze lustre; the *platinichloride* is a brownish-red, crystalline substance. C. S.

Third Isomeride of *apo*Safranine. FRIEDRICH KEHRMANN and A. MASSLENIKOFF (*Ber.*, 1911, 44, 2628—2631. Compare preceding abstract).

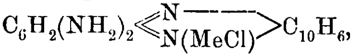
—When the green *iso*phenosafranine chloride (1 : 3-diamino-10-phenylphenazonium chloride) undergoes prolonged treatment at the ordinary temperature with acetic anhydride and acetic acid, it is converted into 3-*amino*-1-*acetylamino*-10-*phenylphenazonium chloride*, $NHAc\cdot C_6H_2(NH_2)<\substack{N\text{———}\\NPhCl}>C_6H_4$, bronze crystals (the *platinichloride*, *dichromate*, *aurichloride*, and *iodide* are described), from which 1-*amino*-10-*phenylphenazonium* salts are obtained by elimination of the amino-group and subsequent hydrolysis; the *nitrate*, *bromide*, *platinichloride*, *dichromate*, *iodide*, and *aurichloride* are described. The *acetyl* derivative, which is prepared best from the bromide, is obtained in small, chocolate-brown crystals, and forms a dark brown, crystalline *platinichloride*. C. S.

Synthesis of Naphthaphenazine Derivatives. FRIEDRICH KEHRMANN and JOSÉ RIERA Y PUNTI (*Ber.*, 1911, 44, 2618—2621).

—2 : 4-*Diaminonaphthaphenazine*, $C_{10}H_6<\substack{N\\N}>C_6H_2(NH_2)_2$, obtained by reducing picryl-β-naphthylamine with the calculated amount of stannous chloride in boiling alcohol and concentrated hydrochloric acid, is purified best by means of the *diacetyl* derivative, yellow leaflets, m. p. 340° (decomp.), and forms red crystals which sublime at 320° with partial decomposition. Its diacetyl derivative does not form an azonium compound with methyl sulphate.

1 : 3-*Diaminonaphthaphenazine*, obtained in a similar manner from picryl-α-naphthylamine, forms dark red crystals and sublimes at 290—300° (decomp.). The *diacetyl* derivative, yellow needles, m. p. 320° (decomp.), easily combines with methyl sulphate in nitrobenzene

at 150°, yielding after hydrolysis with concentrated hydrochloric acid, 1 : 3-*diaminomethylnaphthaphenazonium chloride*,

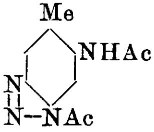


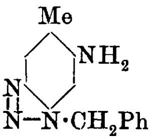
$$C_6H_2(NH_2)_2<\begin{matrix}N\text{———}\\N(MeCl)\end{matrix}>C_{10}H_6,$$

dark red needles; the *platinichloride*, $2C_{17}H_{15}N_4,PtCl_6$, is described.

C. S.

Preparation of Iminoalkyl Derivatives of Azimino-*o*-toluidides. Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 234966).—*Acetylaziminoaceto*-o-*toluidide* (annexed formula), m. p. 222—224°, was prepared by the reduction (iron and acetic acid) and subsequent diazotisation of 5-nitrodiacetyl-*m*-tolylenediamine; the acetyl group in the azimino-ring was then eliminated by boiling with sodium hydroxide, yielding on acidification 4 : 5-*azimino-2-aceto*-o-*toluidide*, a colourless powder, m. p. 235—237°; this was converted into its *benzyl* derivative, the remaining acetyl group removed by heating with sulphuric acid, and the resulting 4 : 5-*benzylazimino*-o-*toluidine* (annexed formula) precipitated with an alkali hydroxide; it forms a crystalline powder, m. p. 161—163°.





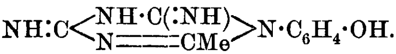
Other alkyl derivatives of this base can be readily prepared in a similar manner.

F. M. G. M.

Diguanides. Georg Cohn (*J. pr. Chem.*, 1911, [ii], **84**, 394—409).—Diguanides of the type $NH{:}C(NHR){\cdot}NH{\cdot}C(NH_2){:}NH$, where R = aryl, are readily obtained in the form of their hydrochlorides by heating dicyanodiamide with the hydrochlorides of aromatic amines in aqueous solution.

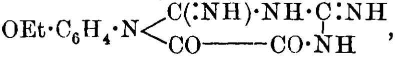
Phenyldiguanide (Lumière and Perrin, Abstr., 1905, i, 249), prepared from aniline hydrochloride and dicyanodiamide, forms a *picrate*, crystallising in yellow needles, m. p. 176—179°, with previous sintering.

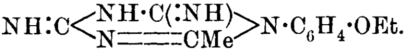
m-*Nitrophenyldiguanide*, $NO_2{\cdot}C_6H_4{\cdot}C_2H_6N_5$, obtained from *m*-nitroaniline, forms amber-yellow prisms or rhombic leaflets, m. p. 147—149°; it crystallises with alcohol in transparent prisms having a colour resembling that of potassium dichromate; it forms a yellow *hydrochloride* and a *picrate*, m. p. 210—211°.

p-Hydroxyphenyldiguanide, $OH{\cdot}C_6H_4{\cdot}C_2H_6N_5$, prepared from *p*-aminophenol hydrochloride, crystallises in spherical aggregates of long, white needles, which become brown at 200° and have m. p. 211°; the hydrochloride has m. p. 203° (compare *loc. cit.*); the *picrate*, m. p. 205—206°, with previous sintering at 203°; when heated with acetic anhydride and sodium acetate, it yields a substance, m. p. 236—237°, which is considered to be an acetyl derivative of the compound  $NH{:}C<\begin{matrix}NH{\cdot}C({:}NH)\\N\text{===}CMe\end{matrix}>N{\cdot}C_6H_4{\cdot}OH$.

p-*Phenetyldiguanide*, $OEt{\cdot}C_6H_4{\cdot}C_2H_6N_5$, crystallises in colourless leaflets, m. p. 170—172° (decomp.); the hydrochloride (Lumière and Perrin, *loc. cit.*) and *picrate*, m. p. 186—189°, are described. When dissolved in concentrated sulphuric acid and the resulting solution treated with water, the hydrochloride yields a substance, m. p. 225—226°, to which the author assigns the formula

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot C(NH_2)\colon NH.$$

Phenetyldiguanide condenses with ethyl oxalate in alcoholic solution, yielding the compound  $OEt\cdot C_6H_4\cdot N{<}\begin{array}{l}C(\colon NH)\cdot NH\cdot C\colon NH\\ CO\text{———}CO\cdot NH\end{array}$, which has m. p. 195—196° (decomp.); it forms *additive* compounds with phenols, and condensation products with formaldehyde and salicylaldehyde. When heated with acetic anhydride and sodium acetate, it yields a *diacetyl* derivative of the triazine base,



$$NH\colon C{<}\begin{array}{l}NH\cdot C(\colon NH)\\ N\text{=====}CMe\end{array}{>}N\cdot C_6H_4\cdot OEt.$$

Ethyl phenyldiguanide-p-carboxylate, $C_2H_6N_5\cdot C_6N_4\cdot CO_2Et$, prepared from ethyl *p*-aminobenzoate, crystallises with one molecule of water in broad-pointed leaflets, m. p. 173°; the anhydrous compound has m. p. 177—178° (decomp.); the *hydrochloride* forms colourless leaflets or prisms; the *picrate* has m. p. 196—197°.

a-Naphthyldiguanide, $C_{12}H_{13}N_5$, forms colourless, iridescent leaflets, m. p. 154—155°, and yields a *hydrochloride* and a *picrate*, m. p. 200—203°.

m-Phenylenebidiguanide, $C_6H_4(C_2H_6N_5)_2$, prepared from *m*-phenylenediamine hydrochloride, has m. p. 165—167° (decomp.), and yields a *picrate*, m. p. 208—210°.

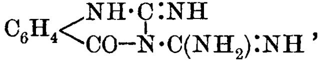
Diphenylbidiguanide, $C_{12}H_8(C_2H_6N_5)_2$, obtained from benzidine (1 mol.) and dicyanodiamide (2 mols.), has m. p. 241°; the *hydrochloride* and *sulphate* are described.

The interaction of benzidine hydrochloride and dicyanodiamide in equimolecular proportions yields *4'-amino-4-diphenylyldiguanide,*

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot C_2H_6N_5,$$

which has m. p. 203—204°, and reacts with nitrous acid to form a diazonium compound which couples with α-naphthol, yielding a purple-red *azo*-dye; the *azo*-dyes obtained from β-naphthol, resorcinol, phenol, salicylic acid, and phenylmethylpyrazolone are also mentioned.

Phenyldiguanide-o-carboxylic anhydride,



$$C_6H_4{<}\begin{array}{l}NH\cdot C\colon NH\\ CO-N\cdot C(NH_2)\colon NH\end{array},$$

prepared from anthranilic acid, is a crystalline powder, m. p. above 280°, and forms a sparingly soluble *hydrochloride.*

Phenylmethyldiguanide, $NMePh\cdot C_2H_5N_4$, obtained from methylaniline, crystallises in hygroscopic needles, which decompose when heated.

The interaction of phenylhydrazine hydrochloride and dicyanodiamide yields phenylguanazole (Pellizari, Abstr., 1892, 356), of which the *hydrochloride* and *picrate*, m. p. 225°, are mentioned.

Many of the diguanides described above give characteristic precipitates with potassium ferrocyanide, ammonium molybdate, and with nickel and cobalt salts.

Quantitative experiments on the precipitation of a large number of dyes by means of the diguanide hydrochlorides are also described.

F. B.

Distribution of Auxochromes in Azo-compounds. HUGO KAUFFMANN and W. KUGEL (*Ber.*, 1911, 44, 2386—2389).—For the study of the effect of the distribution of the auxochromes in azo-compounds (compare Kauffmann and Franck, Abstr., 1906, i, 841), the compounds of the type $N_2[C_6H_3(OMe)_2]_2$, derived from quinol, resorcinol, and catechol, have been compared. These are coloured very differently; the quinol derivative is dark red, that from resorcinol is orange-red or orange, and the catechol derivative is orange-yellow. The rules as to the effect of the positions of the auxochromes therefore apply to azo-compounds. In hydrochloric acid solution the quinol derivative gives a blue, the resorcinol a red, and the catechol a carmine-red coloration.

Resorcinol benzoate couples with diazotised aniline to form p-*benzeneazoresorcinol monobenzoate*, which forms yellow crystals, m. p. 180°, and is hydrolysed to benzeneazoresorcinol, m. p. 169°.

By reduction of nitroresorcinol dimethyl ether with tin and hydrochloric acid, the *hydrochloride* of *aminoresorcinol dimethyl ether* is obtained in long, bluish-white needles. When diazotised, it couples with resorcinol to form 2 : 4-*dimethoxybenzeneazoresorcinol*,

$$C_6H_3(OH)_2\cdot N_2\cdot C_6H_3(OMe)_2,$$

which forms almost black crystals with a green reflex, and is soluble in sodium hydroxide with an orange-yellow coloration, m. p. 186°. Strong hydrochloric acid dissolves it with a dark red, sulphuric acid with a dark blue, coloration.

2 : 4 : 2′ : 4-*Tetramethoxyazobenzene*, $N_2[C_6H_3(OMe)_2]_2$, formed by methylation of the above substance with methyl sulphate, separates in red crystals, m. p. 181°.

3 : 4 : 3′ : 4′-*Tetramethoxyazobenzene* prepared by reduction of nitroveratrole, forms yellow crystals, m. p. 163°.

2 : 5 : 2′ : 5′-Tetramethoxyazobenzene (compare Baessler, Abstr., 1884, 1329) forms dark red crystals, m. p. 142°, soluble in concentrated sulphuric acid with a violet-red, and in hydrochloric acid with a blue, coloration.

E. F. A.

Action of Sodium Sulphite and of Sodium Hydrogen Sulphite on Some Azo-dyes. ROBERTO LEPETIT and E. LEVI (*Gazzetta*, 1911, 41, i, 675—688. Compare Abstr., 1909, i, 569; Nietzki and Helbach, Abstr., 1897, i, 226).—From the reaction between sodium sulphite and nitrobenzeneazosalicylic acid (alizarin-yellow-R) the following substances were isolated: (1) *p*-aminobenzeneazosalicylic acid; (2) *p*-nitroaniline; (3) ammonia; (4) an aminosulphosalicylic acid, to which the formula

$$OH\cdot C_6H_2(NH_2)(CO_2H)\cdot SO_3H,H_2O$$

is ascribed. The last-named substance crystallises in colourless, silky needles (and also in small, compact cubes), which dissolve in alcohol, giving a green, intensely fluorescent solution. The aqueous solution gives a cherry-red coloration with ferric chloride, and reduces ammoniacal silver solutions. Preparation of the substance by sulphonation of aminosalicylic acid shows that the substance is identical with that obtained by Mandt (*Ber.*, 1877, 10, 1701). It was not possible to obtain salts with the heavy metals, but the arsenate crystallises in red needles. An acetyl derivative was obtained in the form of its sodium salt, which crystallises with $1H_2O$. The barium salt also contains $1H_2O$, but is not crystalline.

The action of sodium hydrogen sulphite is more vigorous than that of sodium sulphite, so that, working under the same conditions (in boiling water), after one hour most of the dye is decomposed into *p*-nitroaniline and aminosulphosalicylic acid without formation of aminobenzeneazosalicylic acid.

The reaction between sodium hydrogen sulphite and *p*-aminobenzeneazosalicylic acid (in an autoclave at 130°) proceeds similarly to that just described.

Benzeneazosalicylic acid and sodium sulphite yield (1) a *substance*, which crystallises in small, brown needles, m. p. 140°, which is possibly the hydrazo-compound, $NHPh\cdot N(SO_3H)\cdot C_6H_3(OH)\cdot CO_2H$; (2) aminosulphosalicylic acid.

Benzeneazosalicylic acid is more readily acted on by sodium hydrogen sulphite with formation of the following products: (1) aniline; (2) aminosulphosalicylic acid; (3) a substance which could not be isolated; (4) an *amino*-compound, m. p. 170—173°, which is a benzidine derivative; (5) a *compound*, m. p. 126—128°, which contains sulphur but no nitrogen.

Sodium hydrogen sulphite reacts with diphenylbisazosalicylic acid (chrysamin-G) much less readily than with the preceding compounds. The products isolated were benzidine sulphate and aminosulphosalicylic acid. R. V. S.

Aromatic Nitro-derivatives. II. ROBERTO CIUSA (*Gazzetta*, 1911, **41**, i, 688—697. Compare Abstr., 1907, i, 874).—The present paper deals with the action of picryl chloride on *cyclo*hexanoneazine and on benzaldoxime, and the preparation of *cyclo*hexanonemono- and di-nitrophenylhydrazones is described. The author also finds that trinitro-ψ-cumene is strongly dissociated in formic acid solution, so that a mobile atom of hydrogen is not a necessary condition for the dissociability of aromatic polynitro-derivatives. It is suggested that the power of dissociation depends on the presence either of a free hydrogen atom in the nucleus or of a halogen or nitro-group in the ortho-position with respect to another nitro-group.

2 : 4 : 6 : 4′-Tetranitrohydrazobenzene gives a *potassium* salt, $C_{12}H_6O_8N_6K_2$, which crystallises in small, dark needles with a violet sheen.

2 : 4 : 6 : 4′-Tetranitrohydrazobenzene when heated with concentrated nitric acid yields 2 : 4 : 6 : 4′-*tetranitroazobenzene*,

$$C_6H_2(NO_2)_3N:N\cdot C_6H_4\cdot NO_2,$$

which forms orange-red needles, m. p. 163—164°. It dissolves in alkalis with difficulty, giving a red coloration.

cyclo*Hexanoneazine* (from *cyclo*hexanone and hydrazine hydrate) has b. p. 165°/25 mm., m. p. 35°. On treatment with picryl chloride, it yields cyclo*hexanonetrinitrophenylhydrazone*, $C_6H_{10}:N\cdot NH\cdot C_6H_2(NO_2)_3$, which crystallises in flat, red needles, m. p. 133°, and dissolves in alkali, giving a reddish-brown coloration. cyclo*Hexanone*-2 : 4-*dinitro*-

phenylhydrazone, $C_6H_{10}\!:\!N\cdot NH\cdot C_6H_3(NO_2)_2$, forms golden-yellow scales, m. p. 145°. cyclo*Hexanone*-p-*nitrophenylhydrazone*,

$$C_6H_{10}\!:\!N\cdot NH\cdot C_6H_4\cdot NO_2,$$

crystallises in yellowish-brown needles, m. p. 146°; it is insoluble in water, and may be used to detect *cyclo*hexanone in water.

When α-benzaldoxime is heated with picryl chloride in alcoholic solution for two hours, picramide is obtained.

A nitro-group is eliminated from trinitro-ψ-cumene when treated with alkali, and a *potassium* salt, $C_6Me_3(NO_2)_2\cdot OK$, can be obtained. By the action of dilute hydrochloric acid, this salt is converted into a yellow *substance*. R. V. S.

Hydrazo-compounds. VII. Methylhydrazotoluene, Methyltolidine, and Ethylbenzidine. BERTHOLD RASSOW and ARNO BECKER (*J. pr. Chem.*, 1911, [ii], **84**, 329—351. Compare this vol., i, 820, 821).—N-*Methylhydrazo*-o-*toluene*, $C_6H_4Me\cdot NH\cdot NMe\cdot C_6H_4Me$, is prepared by heating a benzene solution of hydrazo-*o*-toluene with excess of methyl sulphate and magnesium oxide for thirty-six to forty hours in an atmosphere of carbon dioxide; it crystallises in rhombic, rectangular, or almost square plates, m. p. 84°.

N-*Methyl*-o-*tolidine*, $NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot NH_2$, obtained in the form of its *hydrochloride*, $C_{15}H_{18}N_2,2HCl$ (decomp. 260—280°), by the addition of concentrated hydrochloric acid to an alcoholic solution of the preceding compound, has m. p. 85°; it yields an unstable, yellowish-brown *platinichloride*, $C_{15}H_{18}N_2,H_2PtCl_6$, a *picrate*, crystallising in yellow, microscopic needles, which decompose at 184—186°, and a *dibenzoyl* derivative, $NHBz\cdot C_6H_3Me\cdot C_6H_3Me\cdot NMeBz$, m. p. 156°; when heated with salicylaldehyde in alcoholic solution, it forms a *salicylidene* derivative, $NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N\!:\!CH\cdot C_6H_4\cdot OH$, which crystallises in needles, m. p. 120°. It reacts with one or two mols. of nitrous acid, yielding (I) 4-*methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*diazonium chloride*, $NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N_2Cl$, and (II) 4-*methylnitrosoamino*-3 : 3′-*dimethyldiphenyl*-4′-*diazonium chloride*,

$$NO\cdot NMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N_2Cl.$$

4-*Methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-β-*naphthol*,

$$NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N\!:\!N\cdot C_{10}H_6\cdot OH,$$

prepared by coupling the diazonium compound (I) with β naphthol, forms lustrous, dark red crystals, which have m. p. 90—92° and decompose at 120°.

4-*Methylnitrosoamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-β-*naphthol*,

$$C_{20}H_{22}O_2N_4,$$

prepared from (II) and β-naphthol, has m. p. 173°, and is converted into the preceding compound when heated with alcoholic hydrogen chloride.

4-*Methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-p-*dimethylaniline*,

$$NHMe\cdot C_6H_3Me\cdot C_6H_3Me\cdot N\!:\!N\cdot C_6H_4\cdot NMe_2,$$

begins to decompose at 100°, and yields a dark red *hydrochloride*; the *nitroso*-derivative, prepared from (II) and dimethylaniline, forms reddish-yellow, triclinic prisms, which have m. p. 160° and decompose at 180°. It combines with benzenediazonium chloride, yielding 5-*benzeneazo*-4-*methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-p-*dimethylaniline*,

$NPh:N\cdot C_6H_2Me(NHMe)\cdot C_6H_3Me\cdot N:N\cdot C_6H_4\cdot NMe_2$, which decomposes at 180—190°.

Sodium 4-*methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-β-*naphthol*-(3 : 6)-*disulphonate*, $C_{25}H_{21}O_7S_2Na_2$, prepared from the diazonium compound (I) and R-salt, has no definite m. p., and couples with benzenediazonium chloride, yielding *sodium* 5-*benzeneazo*-4-*methylamino*-3 : 3′-*dimethyldiphenyl*-4′-*azo*-β-*naphthol*-(3 : 6)-*disulphonate*,

$NPh:N\cdot C_6H_2Me(NHMe)\cdot C_6H_3Me\cdot N:N\cdot C_{10}H_4(SO_3Na)_2\cdot OH$,

which is dark red and dyes cotton reddish-violet; with diazotised sulphanilic acid it forms a deep bluish-violet *bisazo-dye*.

N-*Ethylbenzidine* $NH_2\cdot C_6H_4\cdot C_6H_4\cdot NHEt$, obtained by heating a benzene solution of hydrazobenzene with ethyl sulphate in the presence of magnesium oxide, crystallises in leaflets or needles, m. p. 73—74°. F. B.

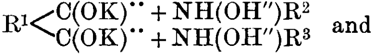
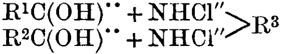
Electrochemistry of Proteins. VII. The Mode of Formation and Ionisation of the Compounds of Proteins with Inorganic Acids and Bases. T. Brailsford Robertson (*J. Physical Chem.*, 1911, **15**, 521—550. Compare this vol., ii, 460).—The author propounds the hypothesis that the combining power of protein for acids and bases resides elsewhere than in the terminal NH_2 and CO_2H groups of the protein chain. The typical group $-CO\cdot NH-$ (alternatively $-C(OH):N-$) is held to be the seat of the amphoteric properties. The main arguments are as follows.

The soluble neutral hydrochloride of edestin contains nine times as much acid as the insoluble hydrochloride. Hence there must be nine or a multiple of nine basic centres in the edestin molecule. On a probable molecular weight of 7000, nine NH_2 groups correspond with more than 10% of the total nitrogen. In caseinogen the maximum combining capacity for alkali is sixteen times the minimum amount required to render the caseinogen soluble. On a probable molecular weight of 17,600 this requires 12½% of the total oxygen to be in the terminal CO_2H groups. Similar calculations made for egg-albumin also lead to percentages which are too high to be consistent with the catenary structure of the protein molecule.

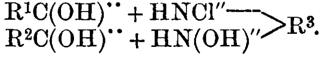
The non-hydrolysable character of the protein salts is presumptive evidence that they are not ordinary amino-salts or carboxylates in the formation of which water is split off. The anions and cations of caseinogen and ovimucoid salts are protein ions, and the dissociation of potassium caseinogenate is not diminished by potassium chloride.

Burgarski and Liebermann showed (Abstr., 1898, i, 716), by potentiometric methods, that as many chlorine as hydrogen ions are removed from circulation when egg-albumin is dissolved in dilute hydrochloric acid. A mixture of ovimucoid hydrochloride with potassium caseinogenate has at first a conductivity equal to the sum of the conductivities of the constituent solutions, and only very slowly deposits caseinogen as a result of the formation of potassium chloride, since the inorganic constituents of the protein salts are combined in a non-dissociable form.

From analysis of the anodic and cathodic solutions after electrolysis of potassium caseinogenate, the loss of caseinogen from the anodal region, is about double the loss from the cathodal region. This is in harmony with the assumption that the positive and negative ions of caseinogen are of about equal mass and mobility. The formula of protein being written $R^1C(OH){:}NR^2$, the ionised salts may be written $R^1C(ONa)^{\cdot\cdot}$ + $HN(OH'')R_2$ and $R^1C(OH)^{\cdot\cdot}$ + $HNCl''R^2$ respectively. The ions are assumed to be bivalent from the electrochemical equivalents.

Kossel has drawn attention to the fact that the combining capacity of a protein for acids is proportional to the diamino-acid content, and the combining capacity for bases is proportional to the dicarboxylic acid content. Hence it is probable that the $-C(OH){:}N-$ groups function only when in contiguous pairs. This leads to the formulæ:  $R^1\left<\begin{matrix}C(OK)^{\cdot\cdot}+NH(OH'')R^2\\ C(OK)^{\cdot\cdot}+NH(OH'')R^3\end{matrix}\right.$ and  $\left.\begin{matrix}R^1C(OH)^{\cdot\cdot}+NHCl''\\ R^2C(OH)^{\cdot\cdot}+NHCl''\end{matrix}\right>R^3$ for the potassium salt and the hydrochloride of protein respectively.

These formulæ are in agreement with the conductivity and freezing-point determinations in the case of ovimucoid dihydrochloride. Ovimucoid monohydrochloride is supposed to be



$$\left.\begin{matrix}R^1C(OH)^{\cdot\cdot}+HNCl''\text{——}\\ R^2C(OH)^{\cdot\cdot}+HN(OH)''\end{matrix}\right>R^3.$$

R. J. C.

Precipitation of Protein by Zinc Sulphate. FRITZ LIPPICH (*Zeitsch. physiol. Chem.*, 1911, **74**, 360—391).—A detailed discussion of the literature leads to the conclusion that the adsorption hypothesis does not explain adequately the formation of metallic albuminates; it is undesirable to extend to proteins the conclusions based on experiments made with inorganic colloidal material.

In a series of experiments the proteins of horse-serum were precipitated by increasing quantities of zinc sulphate, and the amount of protein and zinc salt remaining in the filtrate determined, whence the composition of the precipitate could be calculated. It is found that, under certain conditions, the amount of zinc in the precipitate is independent of the concentration of the protein, and also of the initial concentration of the zinc salt. The power of protein to form a zinc salt increases on dilution, but a maximum is soon reached. The results are not in agreement with the adsorption theory, and the change is better represented as a chemical interaction between an amphoteric and a non-amphoteric electrolyte leading to an equilibrium: $ZnSO_4 + 2Na$ protein $\rightleftharpoons$ $Na_2SO_4 + Zn(\text{protein})_2$. The left-hand side of the equation preponderates so long as protein is present in excess, but the amount of precipitate increases on standing, and especially on dilution. When the amount of metallic salt is increased, a point is reached when a sparingly soluble substance is formed, and the reaction is almost entirely in the sense of the equation from left to right. A still further increase in concentration of the metallic salt causes reaction in the opposite direction, and the precipitate will begin to dissolve. For the full discussion of the results the original should be consulted.

E. F. A.

What is the Cause of the Separation of Albumin in Bottled Beer which has been Subjected to Normal Treatment in Brewery and Cellar? FRITZ EMSLANDER (*Koll. Chem. Beihefte*, 1911, **3**, 47—84).—The conditions favourable to the separation of albumin are discussed with reference to the literature on the subject, and the conclusion is reached that the process is determined primarily by electrochemical effects resulting from the presence of electrolytes. These bring about chemical change in the molecules of albumin, and the transformation is accompanied by alterations in the surface-tension and potential difference between the colloidal particles and the aqueous medium. Coagulation results, and this leads ultimately to turbidity and the deposition of solid substances. H. M. D.

The Hydrolytic Action of Hydrogen Peroxide. CARL NEUBERG and SOICHIRO MIURA (*Biochem. Zeitsch.*, 1911, **36**, 37—43).—Hydrogen peroxide in the presence of a manganese or iron salt will bring about at the ordinary temperature the hydrolysis of a number of compounds of high molecular weight. Egg-albumin after treatment yields 10% of its nitrogen as ammonia when heated with magnesia. Substances of an aldehydic and ketonic nature are also formed. Gelatin under similar conditions gives 10·4% of its nitrogen as amide-nitrogen.

Starch, soluble starch, and glycogen are hydrolysed with formation of reducing and fermentable sugars, which yield mixed phenylosazones. Phenylglucosazone is obtained from the products from soluble starch, and phenylmaltosazone from those from glycogen. Inulin gives lævulose.

Yeast nucleic acid gives 23·2% of its nitrogen as amide-nitrogen, and phosphoric acid is set free. With sodium chondroitin sulphate, sulphuric acid is liberated, whilst lecithin yields fatty acids. W. J. Y.

The Reactions between Ferments and Anti-ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1911, **34**, 485—494. Compare Abstr., 1907, i, 811; ii, 108; 1908, i, 236; ii, 743).—Previous observations that the combination between rennet and anti-rennet of serum is destroyed by acid is confirmed. If acid is allowed to act on serum for some time, the anti-rennet is destroyed. Neither the ferment, anti-ferment, nor the combination are soluble in ether. If rennet solution is shaken, its fermentative action is diminished, and can be neutralised by a smaller quantity of serum. S. B. S.

Action of Oxydases. I. REGINALD O. HERZOG and A. POLOTZKY (*Zeitsch. physiol. Chem.*, 1911, **73**, 247—257. Compare Engler and Herzog, Abstr., 1909, ii, 495).—The peroxydase was prepared from sugar beet, and its action in presence of hydrogen peroxide tested on the leuco-base of brilliant-green, on a mixture of *p*-phenylenediamine and dimethylaniline, and on vanillin. Dyes are formed in the first two cases, and a precipitate in the last. The optimum reaction is shown to depend on the concentration of each of the three reacting substances. The change in the case of brilliant-green can be followed colorimetrically. In addition to the formation of colour there is a bleaching action also brought about by the oxydase. Complete bleaching takes place when the proportion of leuco-base is small compared with that of hydrogen peroxide, provided an excess of enzyme is present. The formation of the dye is much more rapid than the bleaching.

The three possible combinations of mixtures of two of the three reacting substances were prepared and set aside for fourteen hours before the third substance was added. The mixture leuco-base + peroxide reacts the most quickly, that of peroxydase + peroxide is slower, whilst peroxydase + leuco-base shows a marked induction period, and the rate of dye formation is slow. The velocity of the bleaching reaction is much the same for the first and third mixtures, but less for the second. The long induction period indicates that chemical changes, in particular, the formation of additive products, must take place between the components before the formation of colour begins. The experiments indicate that a compound of leuco-base and peroxydase is formed, and that the addition of peroxide displaces the leuco-base and forms a true oxydase from the peroxydase and peroxide. Formation of dye does not take place until the concentration of the active oxydase is sufficient. E. F. A.

Action of Oxydases. II. REGINALD O. HERZOG and A. MEIER (*Zeitsch. physiol. Chem.*, 1911, **73**, 258—265. Compare preceding abstract).—The oxydase extracted from horse-radish was tested against vanillin in presence of hydrogen peroxide, and the amount of dehydrodivanillin formed was weighed. Experiments were made with varying proportions of enzyme and hydrogen peroxide. The filtrate was tested in each case with fresh oxydase solution, and with hydrogen peroxide and guaiacum in order to test whether active peroxydase still remained. The enzyme is destroyed when the relative concentration of hydrogen peroxide is too large; when this is small, the amount of change is approximately proportional to the amount of peroxydase added. The amount of change depends on the proportions of each of the three reacting substances, and the phenomena differ from typical catalysis. The action of peroxydase is classed with the so-called induced reactions. E. F. A.

The Peroxydase of Milk. W. GRIMMER (*Milchw. Zentr.*, 1911, **7**, 395—402).—The peroxydase reaction of fresh milk is shown to be due, not to the presence of inorganic catalysts, but to that of a substance closely connected with the lactalbumin. This is indicated by the similar behaviour of milk-peroxydase and lactalbumin towards precipitating agents and solvents, and, further, by the fact that all compounds which tend to denaturise lactalbumin, such as alcohols, acetone, ether, chloroform, and concentrated acids and alkalis, also lead to the destruction of the enzyme. Putrefaction has the same effect. It is suggested that the enzyme produced in the cells of the mammary gland, and liberated by the destruction of these, is either a protein possessing physical and chemical properties similar to those of lactalbumin, or that it becomes adsorbed by the latter and cannot be separated by ordinary means. H. B. H.

Organic Chemistry.

Catalytic Reactions at High Temperatures and Pressures. XXII. Decomposition of Hexane and *cyclo*Hexane; Isomerisation of *cyclo*Hexane. WLADIMIR N. IPATIEFF and N. DOWGELEWITSCH (*Ber.*, 1911, **44**, 2987—2992).—At ordinary pressures, hexane and *cyclo*hexane are decomposed when passed through an iron tube at 650—700°, the decomposition being accelerated by the presence of alumina; hexane decomposes more readily than *cyclo*hexane. The gases thereby produced consist of saturated hydrocarbons, hydrogen, ethylene, propylene, and probably *iso*butylene, whilst the liquid polymerisation product contains a very small proportion of unsaturated hydrocarbons. No hydrocarbons were obtained which reacted with a nitrating mixture or with permanganate.

The course of reaction is quite different under high pressures, taking place at a much lower temperature. With hexane, at 510°, the increase in pressure takes place so rapidly that an explosion occurs, so that *cyclo*hexane only was used in these experiments. It was heated for four hours at 500—510° in the presence of alumina, at a pressure of 110—120 atmospheres; no reaction takes place at this temperature in the absence of alumina. After removal of the ethylene hydrocarbons from the liquid polymerisation product by means of sulphuric acid, the remaining liquid was divided into eleven fractions, none of which decolorised permanganate. The first three fractions, 45—80°, contained polymethylene hydrocarbons, among which was methyl *cyclo*pentane, but no saturated hydrocarbons. The fractions VI—XI, 125—280°, reacted with a nitrating mixture, and therefore contained benzene hydrocarbons; nitro-compounds were also obtained from fractions VI (125—150°) and VII (150—170°). The higher fractions contain polynuclear hydrocarbons as well as saturated hydrocarbons.

Methyl*cyclo*pentane was isolated by refractionation of the first three fractions, and identified by its physical properties and transformation into the nitro-compound. During its formation from *cyclo*hexane there is also the possibility of hexylene being formed, and this compound was also identified. This isomerisation of *cyclo*hexane takes place only at high pressures and in the presence of alumina; at ordinary pressures, even at 760°, no methyl*cyclo*pentane could be found in the products of decomposition. T. S. P.

Polymerisation of Ethylene Hydrocarbons at High Temperatures and Pressures. WLADIMIR N. IPATIEFF (*Ber.*, 1911, **44**, 2978—2987).—Both ethylene and *iso*butylene when heated in an iron tube under a pressure of about 70 atmospheres (compare Abstr., 1907, i, 5) undergo rapid polymerisation at 380—400°. The liquid polymerisation products thus obtained consist of mixtures of saturated, ethylenic, and polymethylene hydrocarbons. The fractions boiling below 100° consist chiefly of the saturated and ethylene hydrocarbons, whilst the polymethylene compounds are found chiefly in the higher-boiling fractions, the proportion being the greater the higher the boiling point. This holds, however, only for fractions boiling below 250°; above that temperature hydrocarbons are obtained which are poorer in hydrogen than the polymethylene compounds.

The following compounds were identified in the polymerisation product obtained from ethylene: *iso*pentane, hexane, heptane, octane, nonane, amylene, hexylene, nonanaphthene, α-and β-decanaphthene, hendeca-, dodeca-, tetradeca- and pentadeca-naphthenes. In the case of *iso*butylene the polymerisation product also contained some hydrocarbons which reacted with a nitrating mixture and with potassium permanganate, and were insoluble in sulphuric acid (D 1·84).

In the presence of alumina the polymerisation of ethylene gives similar results to those obtained in its absence.

At atmospheric pressure ethylene does not polymerise, even at 600°.

The ethylene hydrocarbons are probably produced by the polymerisation of ethylene itself, or from the polymethylenes by fission of the ring (compare preceding abstract). The saturated hydrocarbons are formed either by the hydrogenisation of the closed-chain hydrocarbons with fission of the ring, or else by fission of the side-chains from the polymethylene nucleus. T. S. P.

Preparation of Sulphurous Acid Derivatives of Unsaturated Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 236386).—When the unsaturated hydrocarbons of general formula $CR_2:CR\cdot CR:CR_2$ (where R is hydrogen, alkyl, or aryl groups) are treated with sulphurous acid, they yield colourless compounds, which when containing a small amount of sulphurous acid are fairly soluble in water, but an increase of the amount renders them insoluble.

When βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene is saturated with sulphur dioxide in aqueous solution, it stiffens to a colourless substance somewhat resembling meerschaum; if shaken for some time with excess of sulphurous acid, an insoluble compound is formed, but if the shaking is interrupted at the right time and the solution carefully evaporated, a *compound* of βγ-dimethylbutadiene with sulphurous acid separates in long needles. The *compound*, prepared from isoprene and sulphurous acid, separates in colourless flakes. F. M. G. M.

α-Iodo-Δ^{δ}-hexene. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1911, **44**, 3062—3065).—The magnesium compound of α-bromo-Δ^{δ}-hexene, $CHMe:CH\cdot[CH_2]_3\cdot MgBr$, obtained by the action of magnesium on αδε-tribromohexane (Braun and Sobecki, this vol., i, 413), is converted by the action of iodine into *α-iodo-Δ^{δ}-hexene*, $CHMe:CH\cdot[CH_2]_2\cdot CH_2I$. This is an almost colourless liquid, b. p. 70—75°/33 mm., and combines with trimethylamine in alcoholic solution, yielding *Δ^{δ}-hexenyltrimethylammonium iodide*, $C_6H_{11}\cdot NMe_3I$, m. p. 110°, which is extremely hygroscopic, and at once forms a yellow oil on exposure to air.

By the exhaustive methylation of α-pipecoline, Merling (Abstr., 1891, 1506) obtained a base, $C_6H_{11}\cdot NMe_2$, which forms a methiodide isomeric with the above compound, and, accordingly, must have the constitution $CH_2:CH\cdot[CH_2]_4\cdot NMe_2$. F. B.

Specific Gravity of Absolute Ethyl Alcohol at 25°. Anton Kailan (*Ber.*, 1911, **44**, 2881—2884).—The author finds the density of absolute ethyl alcohol, prepared by distillation of 99·8% alcohol over calcium, to be D$^{25}_{4}$ 0·78513, which agrees with Winkler's value, 0·78509 (Abstr., 1905, i, 850), within the error of experiment. This necessitates a correction in the water-content of the alcohol used by him in his measurements of the velocity of esterification of organic acids (compare Abstr., 1908, ii, 27, 28, 936), since his previous results were based on Mendeléeff's values for the density of alcohol.

Redeterminations of the velocity of esterification of benzoic acid with hydrogen chloride as catalyst give results in agreement with those obtained by Goldschmidt for alcohol distilled over calcium (Abstr., 1907, ii, 852).

The water-content of alcohol can be determined more accurately by measurement of the density than by measurement of the velocity of esterification, as recommended by Goldschmidt, even when it is less than 0·1%. T. S. P.

Use of Liquid Ammonia in Chemical Reactions. Alkyloxides. E. Chablay (*Compt. rend.*, 1911, **153**, 819—821. Compare Doby, Abstr., 1903, i, 546; Perkin and Pratt, Trans., 1909, **95**, 159).—The preparation of the alkyloxides of alkali earth metals has been realised by bringing about double decomposition between a sodium alkyloxide and the metallic nitrate in liquid ammonia solution. The resulting sodium nitrate, being soluble in the ammonia, can be separated from the alkyloxide. A second method consists in allowing an alcohol to act on a solution of calcium in liquid ammonia, when the action follows the course $2ROH + Ca(NH_3)_4 = Ca(OR)_2 + 4NH_3 + H_2$. A number of barium and strontium alkyloxides have also been prepared in this way. W. O. W.

Catalytic Dehydration of *sec.*- and *tert.*-Pinacolyl Alcohols. François Couturier (*Bull. Soc. chim.*, 1911, [iv], **9**, 898—901).—When these alcohols are dehydrated by Sabatier and Senderens' method, using the apparatus designed by Bouveault (Abstr., 1908, i, 117), the secondary alcohol (methyl*tert.*-butylcarbinol),

$$CMe_3{\cdot}CHMe{\cdot}OH,$$

gives rise to pinacolin, whilst the tertiary alcohol, dimethyl*iso*propylcarbinol, forms $\beta\gamma$-dimethyl-Δ^{α}-butylene with a small amount of $\beta\gamma$-dimethyl-Δ^{β}-butylene (compare Henry, Abstr., 1907, i, 374; 1909, i, 79, and Delacre, Abstr., 1906, i, 921; 1907, i, 459). These results support Delacre's view that *sec.*-pinacolyl alcohol is not readily isomerised, and are in opposition to Henry's results (*loc. cit.*), which indicate that the haloid esters of this alcohol undergo isomerisation when heated (Abstr., 1908, i, 881). T. A. H.

Accessory Products in the Hydrolysis of (I.) Crude Pinacone; (II.) Pure Pinacone. Maurice Delacre (*Bull. Soc. chim.*, 1911, [iv], **9**, 885—889, 889—898).—A detailed revision of the work done by Couturier (Abstr., 1893, i, 244) and by Richard and Langlais (Abstr., 1910, i, 462) on the identification of the by-products formed in the preparation of pinacolin from pinacone.

From 10·3 kilograms of residues from the preparation of pinacolin from crude pinacone, 6·277 kilograms of material boiling at 200—220° were obtained, the remainder, after allowing 2·27 kilograms for residue and loss, being divided into eleven fractions boiling between 140° and 200°. From the portion b. p. 200—220°, two fractions, b. p. 213—214·5° and 214·5—218°, were isolated. The first of these had approximately the composition $C_9H_{14}O$, and gave an oxime, m. p. 161°, and a semicarbazone, m. p. 187°. A portion of this fraction boiling at 214°, on the contrary, gave with hydroxylamine two substances, of m. p. 60° and 88° respectively. The fraction is therefore a mixture, and it is impossible at present to say whether it contains *iso*phorone and deoxymesitylic oxide (Harries and Hubner, Abstr., 1897, i, 549). In the low boiling portion of the residues, di*iso*propenyl (Abstr., 1896, i, 591) and a hydrocarbon, C_7H_{14}, b. p. 60—63°, were found.

In the second paper details are given of a still more exhaustive fractionation of by-products from the preparation of pinacolin from crude pinacone. No mesitylene could be detected, but a substance, $C_9H_{14}O$, b. p. 210° (approx.), giving an oxime, m. p. 75°, and a semicarbazone, m. p. 196°, was obtained; this may be *iso*phorone or a new isomeride of this substance. A similar examination of the by-products resulting from the preparation of pinacolin from pure pinacone gave analogous results. T. A. H.

Autoxidation of Aliphatic Amino- and Polyhydroxy-derivatives. II. Wilhelm Traube (*Ber.*, 1911, **44**, 3141—3145. Compare Abstr., 1910, i, 294).—Cuprammonium oxide and the complex copper salts of aliphatic amino- and hydroxy-compounds are autoxidisable. The experiments with the latter have now been made with barium hydroxide instead of sodium hydroxide, the alkali being saturated with cupric hydroxide and oxidation effected at about 70°. Under these conditions carbon dioxide is formed in considerable quantity, and oxalic acid appears as well as formic acid.

Glycerol is oxidised to the extent of about 20% to carbon dioxide and oxalic acid, $C_3H_8O_3 + O_6 = C_2H_2O_4 + CO_2 + 3H_2O$, and about 80% to formic and oxalic acids, $C_3H_8O_3 + O_5 = C_2H_2O_4 + H_2CO_2 + 2H_2O$.

The oxidation of glyceric acid, barium gluconate, glycollic acid, glycine, and lactic acid has been studied in like manner.

E. F. A.

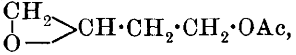
$\alpha\beta\delta$-Trihydroxybutane; its Conversion into Furan Derivatives and Erythritol. Henri Pariselle (*Ann. Chim. Phys.*, 1911, [viii], **24**, 315—410).—This paper gives a detailed, connected account of results already published (Abstr., 1908, i, 496; 1909, i, 282, 691; 1910, i, 353, 463), adding new data regarding certain of the substances described, and giving comparisons of allylcarbinol with allyl alcohol, and of $\alpha\beta\delta$-trihydroxybutane with $\alpha\beta\gamma$-trihydroxybutane and glycerol.

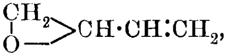
Allylcarbinol, D^{17} 0·848, n_D^{17} 1·421, prepared as described already (Abstr., 1909, i, 282), on treatment with phosphorus tribromide or hydrogen bromide furnishes some $\alpha\gamma$-dibromobutane along with a poor yield of the corresponding *bromide* [*bromo-Δ^α-butylene*],

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2Br,$$

D^0 1·355, D^{17} 1·33, n_D^{17} 1·465, b. p. 97—99°/760 mm., which on treatment with solid potassium hydroxide gives $\Delta^{\alpha\gamma}$-butadiene, $CH_2{:}CH{\cdot}CH{:}CH_2$, identified by conversion into tetrabromobutane, m. p. 117—118° (see below). The acetate has D^0 0·93, D^{15} 0·918, n_D^{15} 1·411, and readily combines with bromine to form γδ-dibromobutyl acetate, D^{18} 1·73, n_D^{18} 1·508, b. p. 135°/16 mm. (compare Wagner, Abstr., 1894, i, 563). Butylcarbinol formal, $CH_2(O{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2)_2$, has D^0 0·897, D^{14} 0·88, n_D^{14} 1·4333 (Abstr., 1909, i, 282).

The methyl ether of allylcarbinol, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, D^0 0·817, D^{20} 0·8, n_D^{20} 1·398, b. p. 68—69°, was prepared by the action of zinc dust in alcohol on γδ-dibromobutyl methyl ether, n_D^{20} 1·5158, b. p. 96°/16 mm. (compare Lespieau, Abstr., 1907, i, 580). γδ-Dibromobutyl ethyl ether, D^0 1·662, D^{20} 1·614, n_D^{20} 1·498, b. p. 98°/12 mm. (compare Abstr., 1910, i, 353), on treatment with hydrogen bromide forms only βδ-dibromobutane, D^{20} 1·80, n_D^{20} 1·507, b. p. 64°/13 mm. (compare Demjanoff, Abstr., 1895, i, 161). The *phenylurethane* of allyl alcohol has m. p. 70° and is crystalline; that of allylcarbinol is a syrup.

αβδ-Tribromobutane, D^0 2·276, D^{18} 2·234, n_D^{18} 1·574, prepared as described already (Abstr., 1908, i, 496), when heated with boiling water or moist silver oxide gives 3-hydroxytetrahydrofuran (Abstr., 1909, i, 691), D^0 1·107, D^{18} 1·07, n_D^{18} 1·4478, MR 21·91 (calc., 21·61), a colourless, syrupy liquid, and with potassium acetate solution yields the triacetin of αβδ-trihydroxybutane, D^0 1·152, D^{19} 1·13, n_D^{19} 1·436, b. p. 150°/11 mm., or 158°/17 mm., which on hydrolysis by baryta gives the trihydric alcohol, D^0 1·21, D^{20} 1·18, n_D^{20} 1·47, b. p. 179°/13 mm. (compare Wagner, *loc. cit.*). This yields a *triphenylurethane*, m. p. 149—152°, in colourless needles, and a *δ-ethyl ether*, D^0 1·08, n_D^{15} 1·45, b. p. 130°/14 mm., of which the *diphenylurethane* is crystalline, and melts at 98—99°. In the formation of this ether, as in that of the methyl ether, some 3-hydroxytetrahydrofuran is formed (Abstr., 1909, i, 691). γδ-Dibromobutyl alcohol, D^0 2·02, D^{15} 1·98, n_D^{15} 1·548, b. p. 114°/11 mm. (compare Wagner, *loc. cit.*, and Abstr., 1909, i, 282), gives a *phenylurethane*, m. p. 70—71°. α-Bromo-Δ^{γ}-butylene oxide with (1) potassium acetate gives the diacetin of αβδ-trihydroxybutane (Abstr., 1909, i, 691), D^0 1·17, D^{16} 1·15, n_D^{16} 1·446, b. p. 161—163°/18 mm.; (2) acetic anhydride and zinc chloride yields *α-bromo-γδ-diacetoxybutane*, $CH_2Ac{\cdot}CHAc{\cdot}CH_2{\cdot}CH_2Br$, D^{20} 1·44, n_D^{20} 1·473, b. p. 140—141°/13—14 mm., a colourless liquid, having an odour like that of ethyl acetate, and (3) with potassium acetate furnishes α-acetoxy-Δ^{γ}-butylene oxide,  $\begin{matrix}CH_2\\|\\O\end{matrix}\!\!>CH{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$, D^{18} 1·12, n_D^{18} 1·446, b. p. 189—192°, a colourless liquid having an odour recalling that of ethyl acetate. α-Ethoxy-Δ^{γ}-butylene oxide, D^0 0·957, D^{18} 0·934, n_D^{18} 1·415 (Abstr., 1910, i, 353), is converted by hydrogen chloride into α-chloro-β-hydroxy-δ-ethoxybutane.

Δ^{α}-Butylene-γδ-oxide,  $\begin{matrix}CH_2\\|\\O\end{matrix}\!\!>CH{\cdot}CH{:}CH_2$, precipitates a solution of magnesium chloride in alcohol and water, polymerises readily, is easily hydrated to form erythrol, from which natural and racemic erythritols may be prepared (compare Abstr., 1910, i, 463), and on treatment wlth bromine in chloroform gives *αβ-dibromo-Δ^γ-butylene oxide*, D^0 2·028, n_{D}^{22} 1·542, b. p. 99°/13—14 mm. The latter with hydrogen bromide in chloroform gives *αγδ-tribromo-β-hydroxybutane*, b. p. 148—150°/14 mm. This in turn reacts with phosphorus pentabromide at 150° to give αβγδ-tetrabromobutane, m. p. 117—119°, crystallising in colourless needles (compare Griner, Abstr., 1893, 237). Ciamician and Magnaghi's form of this substance, m. p. 38—39° (Abstr., 1886, 521), was not obtained. By the action of bromine on erythrol [Δ^α-butylene-γδ-diol], two αβ-dibromo-γδ-dihydroxybutanes, the one crystalline, m. p. 88—89·5°, and probably identical with that of Grimaux and Cloez (Abstr., 1890, 730) and the other liquid, are formed. T. A. H.

Chloro-ethers. VI. αβ-Dichloro-*n*-propyl Ether, αββ′-Trichloro-*n*-propyl Ether, and Tetrachloro-*n*-propyl Ether. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1911, 41, ii, 224—245. Compare Oddo and Mameli, Abstr., 1904, i, 280; 1906, i, 134, 619; and the two following abstracts).—In the present paper the authors continue the study of the above dichloro- and trichloro-ethers, recording new decomposition products and condensations, and describe also a tetrachloro-ether.

In the chlorination of *n*-propyl ether in diffuse light at 25°, in addition to the dichloro-ether, the following substances are produced in small quantities: (1) α-monochloropropaldehyde; (2) a substance, b. p. 144—147°, probably a *monochloropropyl ether*; (3) the trichloro-ether. When the dichloropropyl ether is treated with sulphuric acid at 135—140°, α-chloropropaldehyde, b. p. 85—86°, is obtained (compare Brochet, Abstr., 1896, i, 114). This aldehyde polymerises readily on keeping (although it is stable in a sealed tube); the *polymeride* is a white powder, which does not melt, but is reconverted into the liquid aldehyde at 170—200°. It appears to form a compound with water, but the hydrate could not be obtained in a crystalline state. It also forms an alcoholate with propyl alcohol, but this also was not isolated.

When αβ-dichloro-*n*-propyl ether is boiled with water and the product fractionated, α-chloropropaldehyde and β-chloropropacetal, $\mathrm{CHMeCl{\cdot}CH(OPr)_2}$, are obtained. The action of propyl alcohol also results in the formation of the latter substance.

When αβ-dichloro-*n*-propyl ether is boiled for about one hundred hours, *n-propyl-β-chloropropylene ether*, $\mathrm{CMeCl{:}CH{\cdot}OPr}$, is obtained as a colourless liquid, b. p. 145—146·5°. The action of bromine on this unsaturated compound yields *β-chloro-αβ-dibromopropyl ether*,

$$\mathrm{CMeClBr{\cdot}CHBr{\cdot}OPr},$$

which is a mobile liquid, b. p. 140—142°/20 mm. With pyridine it yields a *compound*, m. p. 216—217°, which gives a *platinichloride*, m. p. also 216—217°.

In view of the above reactions it is shown that the dichloro-ether is αβ-dichloro-*n*-propyl ether, and this is confirmed by its synthesis from α-chloropropaldehyde, propyl alcohol, and hydrogen chloride.

αββ′-Trichloro-*n*-propyl ether is obtained mixed with the tetrachloro-ether by chlorinating *n*-propyl ether or αβ-dichloro-*n*-propyl ether on a boiling brine-bath; it has b. p. 115—120°/5—10 mm. When heated with sulphuric acid it yields α-chloropropaldehyde; with carbamide or urethane it gives the same products as the dichloro-ether. One chlorine atom is removed by silver nitrate, showing that it occupies the α-position, and this is confirmed by its behaviour with pyridine, which yields a compound of which the *platinichloride* (orange-yellow crystals, m. p. 187°) has the composition

$$(C_6H_{11}OCl_3 \cdot C_5H_5N)_2PtCl_4.$$

The constitution of the trichloro-ether follows from these reactions, from its modes of formation, and from its synthesis from β-chloropropaldehyde, allyl alcohol, and hydrogen chloride.

The *tetrachloro-*n*-propyl ether* obtained in the preparation of the trichloro-ether is a colourless, oily liquid, b. p. 157—162°/5—10 mm. With sulphuric acid and with silver nitrate, it behaves like the mono- and di-chloro-ethers. It gives a pyridine compound, of which the *platinichloride*, $(C_6H_{10}OCl_4,C_5H_5N)_2,PtCl_4$, forms orange-yellow crystals, m. p. 187°. R. V. S.

Chloro-ethers. VII. Aldehydic Condensations by means of Halogenated Ethers. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1911, **41**, ii, 246—258. Compare preceding abstract).—Carbamide reacts with dichloroacetaldehyde or its polymeride in aqueous solution, yielding *α-hydroxy-ββ-dichloroethylcarbamide*, which forms crusts of prismatic crystals, m. p. 142° (decomp.). αββ-Trichloroethyl ether and carbamide in presence of sodium acetate yield the same condensation product.

Hydrazine hydrate reacts with dichloroacetaldehyde, with its polymeride, and with αββ-trichloroethyl ether, giving an amorphous, reddish-yellow powder, which does not melt at 300°.

Semicarbazide reacts with the same three ethers, yielding a substance, $C_4H_5O_2N_5$, which is an amorphous, yellowish-white powder.

Phenylhydrazine with dichloroacetaldehyde or αββ-trichloroethyl ether forms glyoxalosazone.

Carbamide and α-chloropropaldehyde yield a white, amorphous substance, m. p. 167—170° (decomp.), which is also formed when carbamide reacts with αβ-dichloro-, αββ'-trichloro-, or tetrachloro-*n*-propyl ether.

Urethane reacts with α-chloropropaldehyde, αβ-dichloro-, αββ'-trichloro- and tetrachloro-*n*-propyl ether, giving in all cases *β-chloropropylidenebisurethane*, $CHMeCl \cdot CH(NH \cdot CO_2Et)_2$, which forms tufts of long, colourless needles, m. p. 122—123°.

Urethane and β-chloro-αβ-dibromo-*n*-propyl ether yield *β-chlorobromopropylidenebisurethane*, $CMeClBr \cdot CH(NH \cdot CO_2Et)_2$, which crystallises in small, transparent prisms, m. p. 113—115°. The above chlorobromo-ether, when treated with carbamide, gives an aldehydic compound crystallising in minute needles, m. p. 183—184°.

R. V. S.

Catalytic Actions of Sulphuric Acid. I. GIUSEPPE ODDO (*Gazzetta*, 1911, **41**, ii, 258—267. Compare preceding abstracts).—When the halogenated ethers and some related substances are dropped on concentrated sulphuric acid at a high temperature, the corresponding aldehydes are formed.

[With EFISIO MAMELI.]—Dichloroacetaldehyde is obtained from any of the following substances when dropped on concentrated sulphuric acid at 140—145°: *αββ*-trichloroethyl ether, dichloroacetaldehyde hydrate, dichloroacetal, and ethyl dichlorovinyl ether (compare Abstr., 1904, i, 280; Wohl and Roth, Abstr., 1907, i, 170).

[With GUIDO CUSMANO.]—*α*-Chloropropaldehyde is obtained by the action of concentrated sulphuric acid at 135—140° on the following substances: *αβ*-dichloro-, *αββ'*-trichloro- and tetrachloro-*n*-propyl ether, di-*n*-propyl-*β*-chloropropylidene ether, and *n*-propyl-*β*-chloropropylene ether.

[With EUGENIA MANTOVANI.]—When ethyl acetoacetate is dropped on sulphuric acid at 155—165°, keten appears to be formed, but is resinified by the acid; at the same time much ethyl acetate is produced. The decomposition of ethyl malonate with sulphuric acid at 200° yields carbon dioxide, ethylene, and ethyl acetate. Ethyl succinate is not acted on below 240—250°, and is then merely hydrolysed, ethyl alcohol and succinic acid being obtained.

R. V. S.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVIII. Chlorothiocarbonates.

MARCEL DELÉPINE (*Bull. Soc. chim.*, 1911, [iv], 9, 901—903. Compare Klason, Abstr., 1887, 1029).—The methyl, ethyl, and propyl esters have been prepared by Klason's method (*loc. cit.*) and are described.

The alcohol (2 mols.) is added gradually to thiocarbonyl chloride at atmospheric temperature, and after twelve to twenty-four hours ether is added, and finally water. The oily layer is separated, washed with water, dried over calcium chloride, and rectified by distillation in carbon dioxide. The yield of the methyl and ethyl esters is about 50% of the theoretical, but is very small in the case of the propyl ester. The esters are pale yellow liquids of pungent ozone-like odour; they fume in the air, owing to oxidation and the liberation of sulphuric acid; they are luminous in the dark, the propyl ester being least luminous. With amines they react according to the equation: $2R_1R_2NH + Cl{\cdot}CS{\cdot}OR' = R_1R_2N{\cdot}CSOR' + R_1H_2NH,HCl$, where R_1 or R_2 may be a hydrogen atom. With secondary amines they give dialkylthiocarbamates (Abstr., 1910, i, 720).

Methyl chlorothiocarbonate, CSCl·OMe, has D_4^0 1·2975, D_4^{22} 1·2686, and b. p. 107—108°. Ethyl chlorothiocarbonate has D_4^0 1·2138, D_4^{15} 1·1955, b. p. 127—128° (compare Klason, *loc. cit.*). *Propyl chlorothiocarbonate*, $CS{\cdot}Cl{\cdot}OPr^{\alpha}$, b. p. 148—151°, reacts with aniline to form propyl phenylthiocarbamate (Orndorff and Richmond, Abstr., 1900, i, 156), which is best obtained by Roschdestvensky's method (Abstr., 1909, i, 300).

T. A. H.

Some Compounds of Organic Salts of Bivalent Metals with Ammonia, Pyridine, and Phenylhydrazine.

HERMANN GROSSMANN and GUSTAV JÄGER (*Zeitsch. anorg. Chem.*, 1911, 73, 48—74).—For the purpose of investigating the influence of the acid radicle on the type of additive compound formed by salts (compare Grossmann and Hünseler, Abstr., 1906, i, 7), the additive compounds of a number of salts of organic acids have been prepared. The ammonia compounds are usually prepared by dissolving the hydrated salt in 25% aqueous ammonia, filtering, and evaporating, first on a water-bath and then in a desiccator over sodium hydroxide in an atmosphere of ammonia.

Ammonia cupric formate, $Cu(HCO_2)_2,3NH_3$, forms large, blue prisms or slender needles, m. p. 154°. The compound is stable in air, but is decomposed by water. *Ammonia cupric chloroacetate*,

$$Cu(CH_2Cl\cdot CO_2)_2,2NH_3,H_2O,$$

forms a blue, crystalline powder, m. p. 180° (decomp.). *Ammonia cupric trichloroacetate*, $Cu(CCl_3\cdot CO_2)_2,5NH_3$, forms dark bluish-violet crystals, which lose ammonia suddenly, becoming grass-green at 94° and melting at 98°. After six weeks in air the crystals contain $3NH_3$. *Ammonia zinc formate*, $Zn(HCO_2)_2,2\frac{1}{2}NH_3$, forms colourless, prismatic needles, m. p. 126^c. *Ammonia zinc acetate*,

$$Zn(C_2H_3O_2)_2,6NH_3,5H_2O,$$

forms colourless needles. *Ammonia cadmium formate*,

$$Cd(HCO_2)_2,3NH_3,3H_2O,$$

forms transparent crystals, m. p. 70°, and loses NH_3 and H_2O in air. *Ammonia cadmium acetate*, $Cd(C_2H_3O_2)_2,4NH_3$, forms transparent cubes, m. p. 141°, and loses NH_3 in air. *Ammonia nickel formate*, $Ni(HCO_2)_2,3NH_3.2H_2O$, is a bright blue, crystalline powder, becoming green at 120° and charring at 360°, three other additive compounds of the salt being also obtained, containing $4NH_3,2H_2O$, $3NH_3,H_2O$, and $2NH_3$ respectively. *Ammonia nickel acetate*, $Ni(C_2H_3O_2)_2,2NH_3$, is a green precipitate; a definite compound could not be obtained from the chloroacetate. *Ammonia nickel trichloroacetate*,

$$Ni(CCl_3\cdot CO_2)_2,3NH_3,3H_2O,$$

forms blue crystals, and becomes green in air, losing $2NH_3$ and $3H_2O$.

Pyridine cupric formate, $Cu(HCO_2)_2,3C_5NH_5$, forms blue needles, m. p. 103°, and loses pyridine in air. Two *pyridine cupric acetates* are obtained, $Cu(C_2H_3O_2)_2,5C_5NH_5$ being bright green, and

$$Cu(C_2H_3O_2)_2.6C_5NH_5$$

dark violet. *Pyridine cupric chloroacetate*,

$$Cu(CH_2Cl\cdot CO_2)_2,2C_5NH_5,2H_2O,$$

forms blue crystals, and a second compound is also obtained. *Pyridine cupric trichloroacetate*, $Cu(CCl_3\cdot CO_2)_2,4C_5NH_5,2H_2O$, forms sky-blue needles. *Pyridine zinc formate*, $Zn(HCO_2)_2,2C_5NH_5$, loses pyridine in air, whilst zinc acetate yields only unstable products. *Pyridine cadmium formate*, $Cd(HCO_2)_2,3C_5NH_5$, has m. p. 94°, and loses pyridine in air. *Pyridine nickel formate*, $Ni(HCO_2)_2,3C_5NH_5$, is a pale green, crystalline powder, which blackens without melting; *pyridine cobalt formate*, $Co(HCO_2)_2,3C_5NH_5$, is pale pink, and is stable in air, but loses pyridine after some months.

Phenylhydrazine zinc formate, $Zn(HCO_2)_2,2C_6H_8N_2$, is a white solid, m. p. 110°, which rapidly darkens in air. *Phenylhydrazine cadmium formate*, $Cd(HCO_2)_2,C_6H_8N_2$, has m. p. 128°; *phenylhydrazine nickel formate*, $Ni(HCO_2)_2,C_6H_8N_2,3H_2O$, a bluish-green, amorphous mass, blackens without melting, a blue product being also obtained, probably containing $2C_6H_8N_2$. *Phenylhydrazine cobalt formate*, $Co(HCO_2)_2,2C_6H_8N_2$, is a pink substance, m. p. 170—172°, which darkens in air. *Phenylhydrazine cobalt acetate*, $Co(C_2H_3O_2)_2,4C_6H_8N_2$ (compare Moitessier, Abstr., 1897, i, 561), is unstable; *phenylhydrazine cobalt chloroacetate*, $Co(CH_2ClCO_2)_2,3C_6H_8N_2$, and *phenylhydrazine cobalt trichloroacetate*, $Co(CCl_3CO_2)_2,6C_6H_8N_2$, m. p. 188°, are pink solids. A tabular summary of the compounds of this series is given. C. H. D.

The Hydrates of Potassium Acetate, their Solubility and Transition Point.

RYUJI ABE (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, 3, 211—215).—The solubility curve of potassium acetate in water has a single break at 41·3°, the stable phase at lower temperatures being $2KC_2H_3O_2,3H_2O$, and at higher temperatures, $2KC_2H_3O_2,H_2O$.

C. H. D.

Aliphatic Nitro-compounds. XI. α-Nitro*iso*butyric Acid.

WILHELM STEINKOPF and ALEXANDER SUPAN (*Ber.*, 1911, 44, 2891—2897).—α-Nitro*iso*butyric acid has been prepared by the following series of operations: α-Hydroxylamino*iso*butyronitrile, obtained by the addition of hydrogen cyanide to acetoxime, was oxidised with potassium permanganate in sulphuric acid to α-nitro*iso*butyronitrile (Piloty, Abstr., 1898, i, 616). This cannot be hydrolysed directly, but on heating with methyl alcohol and hydrochloric acid, it is converted almost quantitatively into the hydrochloride of nitro*iso*butyroiminomethyl ether,

$$NO_2\cdot CMe_2\cdot C(NH)\cdot OMe,HCl.$$

This is decomposed by water into methyl-α-nitro*iso*butyrate, $NO_2\cdot CMe_2\cdot CO_2Me$, a colourless oil, which with ammonia forms α-nitro*iso*butyramide, and when left for some days with concentrated hydrochloric acid is slowly hydrolysed to α-nitro*iso*butyric acid.

When the ammonium salt is treated with sodium nitrite and sulphuric acid, carbon dioxide is eliminated and a blue oil formed, which solidifies to colourless crystals of propyl ψ-nitrol,

$$NO\cdot CMe_2\cdot NO_2.$$

α-Nitro*iso*butyric acid differs from nitroacetic and α-nitropropionic acids in not being hygroscopic. On prolonged keeping, it decomposes to a blue oil mixed with colourless crystals, which melt to a blue liquid, and nitrous acid is liberated. This is a nitroso-compound, but it has not at present been identified. When fused, α-nitro*iso*butyric acid liberates carbon dioxide and forms a colourless oil, which suddenly decomposes, becoming blue and solidifying to a colourless solid. Similar changes are noted on heating in solvents. Possibly the acid decomposes into *sec.-aci*-nitropropane, this into acetone and nitrosyl, which re-unite to a nitroso-alcohol, $NO\cdot CMe_2\cdot OH$.

α-Nitro*iso*butyronitrile is an oil, b. p. 73°/12 mm. *Methyl-α-nitro*iso*butyric acid* has b. p. 73—74°/12 mm. *α-Nitro*isobutyric acid forms crystals, m. p. 95°; the *ammonium*, *sodium*, and *phenylhydrazine* salts have been prepared. E. F. A.

Action of Hydrogen Chloride and Methyl Alcohol on Negatively Substituted Nitriles.

WILHELM STEINKOPF and WIATSCHESLAW MALINOWSKI (*Ber.*, 1911, 44, 2898—2904).—Whilst

Pinner has shown that, in general, both aromatic and aliphatic imino-ether hydrochlorides are obtained by the reaction of nitrile, alcohol, and hydrogen chloride, Steinkopf obtained trichloroacetamide from trichloroacetonitrile (Abstr., 1907, i, 488) and nitroacetamide from nitroacetonitrile (Abstr., 1909, i, 216), instead of the expected imino-ethers. On the other hand, Steinkopf and Supan (preceding abstract) find that α-nitro*iso*butyronitrile gives the normal imino-methyl ether and not the amide. The influence of the negative nitro-group appears to be less when the nitro-group is tertiary.

The behaviour of a number of halogen substituted acetonitriles towards methyl alcohol and hydrogen chloride has now been investigated. Chloro-, bromo- and iodo-acetonitrile give the normal imino-ether hydrochloride; dibromoacetonitrile yields a mixture of imino-ether and dibromoacetamide.

Dichloro-, trichloro-, dichloronitro-, and tribromo-acetonitrile all yield the corresponding amides, no trace of imino-ether being formed.

The primary nitro-group is as active as two or three chlorine atoms; this is probably owing to its reacting in the *aci*-form.

With trichloroacetonitrile and dimethylethylcarbinol only the corresponding amide was obtained. The imino-ether could not be obtained on boiling tribromoacetonitrile with methyl alcohol.

[With ALEXANDER SUPAN.]—ω-*Nitrophenylacetonitrile* was obtained pure in colourless crystals, m. p. 39—40°, from the sodium salt Wislicenus, Abstr., 1902, i, 541). E. F. A.

Oxidation of Hexoic and Heptoic Acids by Dilute Permanganate Solutions.

E. S. PRSCHEVALSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1000—1006).—Oxidation of *n*-hexoic acid with 1% neutral permanganate solution in the cold yields butyric, valeric, oxalic, and succinic acids.

Under similar conditions, *n*-heptoic acid gives oxalic, succinic, propionic, butyric, and valeric acids; further, the action of semicarbazide hydrochloride on that portion of the oxidation products which dissolves readily in ether, water, alcohol, chloroform, and acetone yields two isomeric semicarbazones, $C_8H_{15}O_3N_3$, one, m. p. 138—140°, readily soluble, and the other, m. p 176°, slightly soluble. These represent semicarbazones of a keto-acid, $C_7H_{12}O_3$, which must be regarded as an intermediate product in the oxidation of *n*-heptoic acid. T. H. P.

Preparation of Diglycollic Acid Esters of Phenols and Phenolic Derivatives.

C. F. BOEHRINGER & SÖHNE (D.R.-P. 236045).—Phenolic esters of diglycollic acid prepared from the acid dichloride have been described (Abstr., 1910, i, 732); it is now found that this reaction proceeds smoothly with the acid on gently warming in the presence of phosphorus pentachloride and an indifferent base, the phenyl ester being thus obtained in 90% yield. The o-*tolyl* ester has m. p. 100—101°. F. M. G. M.

Studies on Tautomerism. VI. Colorimetric Method for the Estimation of Enols in Allelotropic Mixtures. LUDWIG KNORR and H. SCHUBERT (*Ber.*, 1911, **44**, 2772—2778. Compare Wislicenus, Abstr., 1900, i, 9, 597).—By colorimetric comparison of the solutions obtained on adding ferric chloride to equilibrium mixtures of tautomeric substances, the amount of enolic form present can be estimated. The maximum coloration is produced when 1 mol. of ferric chloride reacts with the enol, the corresponding equation being $RH + FeCl_3 = FeRCl_2 + HCl$, where R is the enolic residue. Standard solutions of three kinds are employed: (1) when the pure enolic form is available, a solution of it containing an equimolecular quantity of sublimed ferric chloride; (2) solutions of the iron salts of the type FeR_3 (see below), to which 2 mols. of ferric chloride have been added ($FeR_3 + 2FeCl_3 = 3FeCl_2R$), and in addition, to make them identical with those of the first type, 3 mols. of hydrochloric acid; (3) solutions (usually alcoholic) of equilibrium mixtures to which 1 mol. of ferric chloride has been added, the amount of the enolic form present having been determined by comparison with test solutions of one of the first two types. The standard solutions of the third kind often remain unaltered for months. The solutions of types I. and II. also suffer no marked alteration on keeping, unless (as in the case of dibenzoylacetylmethane, for instance) decomposition occurs; hence the enolic forms may be fixed in the form of their iron salts. In some cases (ethyl acetoacetate and especially ethyl benzoylacetate) the addition of hydrochloric acid to the iron salts lessens the intensity of colour of the solution; in other cases (tribenzoylmethane) no change is observed. The standard solutions of the second type have exactly the same degree of coloration as those of type I.

The method has been employed for the study of the diacetylsuccinic ester, mesityl-oxide-oxalic esters, and Claisen's triketones. In the present paper experimental data are given in the case of methyl mesityl-oxide-oxalate. In the fused state at 98° the enolic ester reaches equilibrium (4% enol) after twenty-five hours, whilst the ketonic ester attains to the same equilibrium in two hundred hours. In absolute alcoholic solution at 78° equilibrium is reached (3·7% enol) after twelve days, whilst the ketonic form contains 3·9% enol after twenty days. In absolute alcohol at room temperature, the enolic ester is converted into the equilibrium mixture (4% enol) after eight weeks. Determinations were also made of the equilibria reached in different solvents after fourteen days at 80°.

Some new iron salts have been prepared (compare Hantzsch and Desch, Abstr., 1902, i, 708; also this vol., i, 976). *Ethyl ferriacetoacetate*, $Fe(C_6H_9O_3)_3$ (from an alcoholic solution of ethyl sodioacetoacetate and an ethereal solution of ferric chloride), forms small, compact, red crystals, m. p. 99—100°. The solutions of the salt are orange-coloured, and become cherry-red on addition of ferric chloride.

Ethyl ferriformylphenylacetate, $Fe(C_{11}H_{11}O_3)_3$, is obtained in a crystalline condition by treating an ethereal solution of the ester with an alcoholic solution of sodium ethoxide and ferric chloride in the presence of sodium acetate. R. V. S.

Lactarinic Acid. J. BOUGAULT and CHARLES CHARAUX (*Compt. rend.*, 1911, **153**, 880—881. Compare this vol., i, 835).—Lactarinic acid is identical with ε-*ketostearic acid*,

$$CH_3\cdot[CH_2]_{11}\cdot CO\cdot[CH_2]_4\cdot CO_2H,$$

since it undergoes the Beckmann transformation, giving rise to two compounds, $CH_3\cdot[CH_2]_{11}\cdot NH\cdot CO\cdot[CH_2]_4\cdot CO_2H$ and

$$CH_3\cdot[CH_2]_{11}\cdot CO\cdot NH\cdot[CH_2]_4\cdot CO_2H.$$

These were not isolated, but recognised by the products obtained on hydrolysis. W. O. W.

Synthesis of Fumaric and Maleic Acids from the Acetylene Di-iodides. EDWARD H. KEISER and LEROY MCMASTER (*Amer. Chem. J.*, 1911, **46**, 518—523).—Keiser (Abstr., 1890, 594) has shown that fumaric acid can be produced by the action of potassium cyanide and potassium hydroxide on solid acetylene di-iodide. The same author (Abstr., 1899, i, 398) has also obtained a liquid form of acetylene di-iodide, which he regarded as the *cis*- or maleic form, whilst the solid compound was regarded as the *trans*- or fumaric isomeride.

This view has now been confirmed, and experiments are described which show conclusively that the solid iodide can be converted into fumaric acid and the liquid isomeride into maleic acid. E. G.

Nitrile of Fumaric Acid. EDWARD H. KEISER and J. J. KESSLER (*Amer. Chem. J.*, 1911, **46**, 523—528).—Keiser (Abstr., 1890, 594) and Keiser and McMaster (preceding abstract) have shown that fumaric and maleic acids can be prepared by treating the solid and liquid forms of acetylene di-iodide respectively with potassium cyanide and hydroxide. It is evident that in these syntheses the nitriles of the acids must be formed, but they could not be isolated.

Attempts have therefore been made to prepare the nitriles by heating fumaramide and ammonium maleate with phosphoric oxide. Fumaronitrile has been produced in this way, but maleonitrile could not be obtained.

Fumaramide is prepared (1) by treating ethyl bromosuccinate with dilute ammonia, and (2) by the action of 50% ammonia solution on dimethyl fumarate. When an intimate mixture of fumaramide and phosphoric oxide is heated on a sand-bath at about 120°, *fumaronitrile*, m. p. 96°, b. p. 186°/760 mm., is obtained as a sublimate of slender needles. The nitrile has a pleasant, pungent odour, sublimes readily even below 100°, and is decomposed by alkali hydroxide with formation of alkali cyanide. E. G.

Hydrogenation of Crotonaldehyde in Presence of Nickel. ROGER DOURIS (*Bull. Soc. chim.*, 1911, [iv], **9**, 922—925).—On reduction by Sabatier and Senderens' method (Abstr., 1905, i, 333), crotonaldehyde furnishes butyraldehyde and butyl alcohol with a small quantity of a syrupy substance, b. p. 115—119°/18 mm., which may contain an octyl alcohol.

n-*Butylidenediurethane*, $CHPr^a(NH\cdot CO_2Et)_2$, m. p. 130°, obtained by condensing butyraldehyde with urethane in presence of hydrochloric acid, crystallises in rosettes of colourless needles. n-*Butyl phenylthiocarbamate*, $NHPh\cdot CS\cdot O\cdot C_4H_9$, m. p. 53°, obtained by Roschdestvensky's method (Abstr., 1910, i, 107) or by the action of phenylthiocarbimide on *n*-butyl alcohol in presence of sodium hydroxide, crystallises in long, colourless needles. T. A. H.

Ethylation of Acetone. ERNST ZERNER (*Monatsh.*, 1911, **32**, 677—686).

—By the action of sodamide and halogen alkyls on ketones, alkyl derivatives of these are obtained. Haller and Bauer (Abstr., 1909, i, 108) have thus prepared methyl and mixed methyl ethyl derivatives of acetone. Acetone itself yields only condensation products, particularly *iso*phorone, when treated with sodamide and ethyl bromide. Accordingly, dipropyl ketone was used as the starting-point for the preparation of ethyl derivatives of acetone. In ethereal solution no action takes place, but in benzene prolonged boiling suffices to cause interaction. About half of the dipropyl ketone is recovered unchanged, and the operation has to be repeated several times. Other products are not formed in any quantity, and the ketones are separated and purified by fractional distillation. The process is repeated in order to pass to the more alkylated ketones.

The ethylacetones described do not mix with water and have a camphor-like odour; only hexaethylacetone resembles the fruity odour of dipropyl ketone. The corresponding alcohols have a sharp, peppermint-like odour.

Triethylacetone [γ-ethylheptane-δ-one], perhaps already obtained by Geuther and Frölich (Abstr., 1880, 622), has b. p. 174·5—175·5°/741 mm. On reduction it yields *triethyl*iso*propyl alcohol* [*γ-ethylheptane-δ-ol*], which has b. p. 80—81°/10 mm. The *oxime* obtained by heating the ketone with Crismer's salt formed slender needles, m. p. 90—91°.

sym-Tetraethylacetone [γε-diethylheptane-δ-one] has b. p. 206—207·5°/771 mm. (Herzig and Zeisel, Abstr., 1894, i, 74). It does not form an oxime or phenylhydrazone. *Tetraethyl*iso*propyl alcohol* [*γε-diethylheptane-δ-ol*], obtained on reduction, has b. p. 99—101°/13 mm.; it reacts with phenylcarbimide, forming the *phenylurethane*, m. p. 72—73°.

Pentaethylacetone [*γγε-triethylheptane-δ-one*] has b. p. 237·5—238·5°/761 mm.; *pentaethyl*iso*propyl alcohol* [*γγε-triethylheptane-δ-ol*] has b. p. 125—127°/18 mm., and forms a *phenylurethane*, m. p. 71—72°. The mixture of the phenylurethane with that of the γε-diethylheptane-δ-ol shows a depression of 18° in the m. p.

Hexaethylacetone [*γγεε-tetraethylheptane-δ-one*] has b. p. 274—275°/759 mm., and crystallises in plates, m. p. 44°. The corresponding *hexaethyl*iso*propyl alcohol* [*γγεε-tetraethylheptane-δ-ol*] has b. p. 159—161°/18 mm. The *phenylurethane* forms a butter-like substance, which is not characteristic. E. F. A.

An Intermediate Product of Alcoholic Fermentation. HANS VON EULER and A. FODOR (*Biochem. Zeitsch.*, 1911, **36**, 401—410).

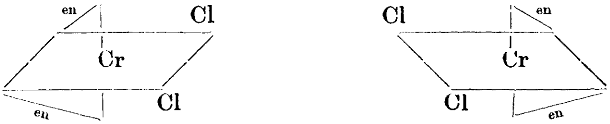
—The authors fail to confirm Boyson-Jenssen's statement that dihydroxy-

acetone can be isolated as an intermediate product of fermentation by yeast. They describe their method for preparing hexosephosphoric acid ester, and their results obtained with this substance agree in the main with those of Harden and Young. They have found indications that in addition to the hexosediphosphoric acid, a triosemonophosphoric acid is also formed (compare Young, Abstr., 1910, i, 12; Lebedeff, *ibid.*, 716; this vol., i, 837).
S. B. S.

Decomposition of Dextrose by Dilute Sulphuric Acid. Hermann Ost and Th. Brodtkorb (*Chem. Zeit.*, 1911, **35**, 1125—1126. Compare Ost and Wilkening, Abstr., 1910, i, 364).—Dextrose is converted by dilute sulphuric acid under pressure at high temperatures chiefly into humin substances, formic acid, and lævulic acid; for example, about 8% of the dextrose is destroyed by heating a 5% solution of the sugar with a 2% solution of sulphuric acid for twenty-four hours at 100°, whilst 100 grams of dextrose heated with 2% sulphuric acid at 140° for seven hours yield about 16 grams of formic acid, 32 grams of lævulic acid, and 13 grams of humin substances.
W. H. G.

The Behaviour of Invert Sugar in Alkaline Solution in Presence of Hydrogen Peroxide. Adolf Jolles (*Biochem. Zeitsch.*, 1911, **36**, 389—393).—In following the polarisation changes when invert sugar is treated with hydrogen peroxide in alkaline solutions, it is found that the rotation sinks gradually to 0°, then becomes dextrorotatory, the dextrorotation then reaches a maximum, and again decreases. The explanation of this result is that lævulose is more readily oxidised than dextrose, and is more rapidly destroyed.
S. B. S.

Mirror Image Isomerism with Chromium Compounds. I. Alfred Werner (*Ber.*, 1911, **44**, 3132—3140).—The author has succeeded in resolving salts of the 1 : 2-dichlorodiethylenediaminechromium series into their optical isomerides, in accordance with the configurations:



These salts present a case of molecular asymmetry I, similar to that observed with the 1 : 2-dinitrodiethylenediaminecobalt salts (this vol., i, 838). Owing to the fact that the aqueous solutions of these salts are not very stable, readily giving chloro-aquo- and diaquo-salts, their resolution with silver bromocamphorsulphonate did not afford much hope of success. It was found, however, that when *d*-ammonium *α*-bromocamphorsulphonate was added to a freshly-prepared saturated solution of 1 : 2-dichlorodiethylenediaminechromic chloride, violet crystals of l-*dichlorodiethylenediaminechromic* d-*α-bromocamphorsulphonate* were deposited after a short time in a pure condition. From the mother liquor, any racemate could then be precipitated as dithionate, and then, on the addition of potassium platinochloride, the *d*-isomeride obtained as the platinochloride, from which the nitrate could be prepared by decomposition with silver nitrate. Similar results were obtained with *l*-ammonium α-bromocamphorsulphonate, d-*dichlorodiethylenediaminechromic* l-α-*bromocamphorsulphonate* being first deposited.

It is noteworthy that the *l*-dichloro-salts and *d*-bromocamphorsulphonic acid, and the *d*-dichloro-salts and *l*-bromocamphorsulphonic acid, give the least soluble salts, which is the opposite to what was observed with the cobalt salts.

The active salts are not different in colour from the inactive, but the active chlorides and dithionates are more soluble than the corresponding racemates.

The optical rotation observed are as follows (I):

	I.		II.	
	[α].	[M].	[α].	[M].
Chloride …………	−140°	−415·1°	−182°	−552·4°
	+140	+415·1	+184	+558
Bromide …………	−130	−419·9	−176	−571
	+124	+400·5	+168	+554
Iodide ……………	−120	−366	−164	−511
	+122	+372	+164	+511

They are much less than those of the corresponding dichlorodiethylenediaminecobalt salts (II.) (details are to be given later).

Racemisation takes place rapidly in aqueous solution, being complete at 0° after three hours in a 0·5% solution; in hydrochloric acid solution the velocity of racemisation is much slower, and at the same time the rotation of the chloride is much diminished.

Racemic 1:2-dichlorodiethylenediaminechromic chloride, $[Cl_2Cr\,en_2]Cl$, is best prepared as follows: Potassium chromium oxalate,

$$[Cr(C_2O_4)_3]K_3,$$

is heated with a 10% solution of ethylenediamine until a red salt begins to deposit from the dark violet solution. After cooling, the salt, which has the formula $[C_2O_4Cr\,en_2][(C_2O_4)_2Cr\,en]$, is collected, well washed with cold water, rubbed into a paste with concentrated hydrochloric acid, and kept until a portion when dried on a porous plate leaves a yellow residue of oxalatodiethylenediaminechromic chloride, $[C_2O_4Cr\,en_2]Cl$. This is collected and carefully heated with concentrated hydrochloric acid until solution is complete. The cherry-red solution so obtained is put into a crystallising dish, and alcohol added gradually, with vigorous stirring, until a violet salt begins to deposit. On keeping, a thick, violet paste of the required racemate is formed, which is well washed with alcohol and ether to remove oxalic acid, and may then be used for the resolution.

l-*Dichlorodiethylenediaminechromic* d-*bromocamphorsulphonate*,

$$[Cl_2Cr\,en_2]SO_3\cdot C_{10}H_{14}OBr,$$

forms small, shining, violet crystals, and has $[\alpha] = -35^\circ$, $[M] = -193\cdot55^\circ$. The corresponding d-l-*salt* has $[\alpha]_D = +32^\circ$, and $[M]_D = +176\cdot9^\circ$. The solutions rapidly undergo racemisation. The active 1:2-*dichlorodiethylenediaminechromic chlorides*, $[Cl_2Cr\,en_2]Cl,H_2O$, were obtained from the bromocamphorsulphonates by treatment with concentrated hydrochloric acid; they form small, violet needles. The *bromides*, $[Cl_2Cr\,en_2]Br$, were prepared from the chlorides and hydrobromic acid, and crystallise in small, reddish-violet needles. The *nitrates*, $[Cl_2Cr\,en_2]NO_3$, were obtained from the chlorides and nitric acid as violet, crystalline powders. T. S. P.

Chemico-Crystallographic Examination of the Platinichlorides, Platinibromides, Stannichlorides, and Stannibromides of Quaternary Ammonium Bases. A. RIES (*Zeitsch. Kryst. Min.*, 1911, **49**, 513—617).—The quaternary ammonium bases, the salts of which have been examined, are those containing the groups NMe_4, NMe_3Et, NMe_3Pr^{α}, NMe_3Pr^{β}, NMe_2Et_2, $NMeEt_3$, $NMe_3{\cdot}C_4H_9$, $NMe_3{\cdot}CH_2Pr^{\beta}$, NMe_2EtPr^{α}, NEt_4, $NMe_3{\cdot}CH_2{\cdot}CHMeEt$, $NMe_3{\cdot}CH_2{\cdot}CH_2Pr^{\beta}$, $NMeEt_2Pr^{\alpha}$, $NMe_2Pr^{\alpha}{}_2$, NEt_3Pr^{α}, $NMeEtPr^{\alpha}{}_2$, $NMePr^{\alpha}{}_3$, $NEt_2Pr^{\alpha}{}_2$, $NEt_3{\cdot}C_4H_9$, $NEt_3{\cdot}CH_2Pr^{\beta}$, $NMeEtPr^{\alpha}{\cdot}CH_2Pr^{\beta}$, $NEtPr^{\alpha}{}_3$, $NPr^{\alpha}{}_4$, $NPr^{\alpha}{}_3{\cdot}CH_2Pr^{\beta}$, $NMe(CH_2Pr^{\beta})_3$, $NEt(CH_2Pr^{\beta})_3$, $NPr^{\alpha}(CH_2Pr^{\beta})_3$, and $N(CH_2Pr^{\beta})_4$. The crystallographic properties of the platini-chlorides and -bromides, and stanni-chlorides and -bromides of these bases are described; their m. p.'s or points of decomposition are stated; in many cases the densities of the several modifications of any one salt have been determined by the floating method in acetylene tetrabromide and toluene, and the transition temperatures of the modifications have been ascertained.

After a detailed comparison of the preceding physical constants, the author states the following generalisations:

(1) The m. p.'s decrease, and the transition temperatures (of the several modifications) increase, as the molecular weights of the tetra-alkylammonium platinichlorides increase.

(2) In the case of two isomeric salts, the one containing one or more *iso*alkyl groups has a lower m. p. and a higher transition temperature (for corresponding modifications) than that containing normal alkyl groups.

(3) The temperatures, at which the corresponding point systems of two or more isomeric and metameric salts undergo transition into the more highly symmetric analogous point systems, are higher the less is the symmetry of the molecule corresponding with the point system.

(4) The region of stability of the different modifications is dependent on the molecular weight and the symmetry of the molecule.

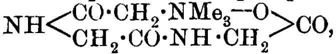
Experiments on the morphotropic relations of the salts with regard to their topic axis show that the platinichloride, platinibromide, and stannichloride of a given tetra-alkylammonium base form isomorphous mixtures in all proportions.

An outstanding feature of the author's experiments is the regular shifting at high temperatures of the region of stability of the polymorphous modifications of members of homologous series. The paper concludes with a discussion of the question whether this regularity is characteristic of all salts of members of the families in the periodic table. A consideration of the transition temperatures of the modifications of the nitrates of the alkali metals, of the halides of mercury, of the carbonates of the magnesium-barium group and so forth, indicates that the answer to the question is in the affirmative.

C. S.

Methylated Polypeptides. Betaine of Diglycylglycine.

EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1911, **75**, 19—29. Compare this vol., i, 528).—*Trimethyldiglycylglycine*, $OH\cdot NMe_3\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$ or



$$NH<\begin{matrix}CO\cdot CH_2\cdot NMe_3—O\\ CH_2\cdot CO\cdot NH\cdot CH_2\end{matrix}>CO,$$

obtained from chloroacetylglycylglycine and trimethylamine, is isolated in the form of the *platinichloride*, which forms orange-yellow, prismatic crystals, m. p. 181° (corr., decomp.).

The *ethyl* ester, prepared by decomposition of the platinichloride with hydrogen sulphide and treatment of the hydrogen chloride of the base with ethyl alcohol and hydrogen chloride, yields a *platinichloride*, crystallising in slender, lustrous, bright orange-yellow plates. The *platinichloride* of the corresponding *methyl* ester, prepared in the same way, crystallises in six-sided prisms, m. p. 180°. Analysis showed it to be partly hydrolytically decomposed. When prepared by dissolving the platinichloride of the base in methyl alcohol and saturating with dry hydrogen chloride, it was obtained in yellow needles, m. p. 215·5—216·5° (corr., decomp.).

Trimethyldiglycylglycine when hydrolysed with boiling concentrated hydrochloric acid for fifteen hours gives betaine hydrochloride and glycine hydrochloride, the resolution being complete. Trimethyl-*dl*-leucylglycine when boiled for two hours with fuming hydrochloric acid is recovered almost unchanged.

Hydrolysis leading to the formation of betaine took place on attempting to methylate chloroacetylalanine with trimethylamine, and a similar behaviour was shown by chloroacetyl-*l*-tyrosine. Betaine was obtained further on attempting to methylate glycylglycine with methyl iodide. When attempting to methylate polypeptides with methyl iodide and potassium hydroxide, products containing iodine and potassium were usually obtained; these probably represent potassium iodide additive products.

E. F. A.

Preparation of Iodo-fatty Acid Compounds and their Behaviour in the Animal.

EMIL ABDERHALDEN and PAUL HIRSCH [and M. GUGGENHEIM] (*Zeitsch. physiol. Chem.*, 1911, **75**, 38—56).—*Iodoacetylglycine*, $CH_2I\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, prepared by the reaction of glycine with iodoacetyl chloride in *N*-sodium hydroxide, sinters at 130°, and begins to melt at 142°, m. p. 160°, decomp. 165°.

dl-*a-Iodopropionylglycine*, $CHMeI\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, from glycine and *a*-iodopropionyl chloride, sinters and begins to melt at 60°, m. p. 80°, decomp. 135°. The *ethyl* ester crystallises in needles, which sinter at 45°, m. p. 60°, and give up iodine at 225°. dl-*a-Iodopropionyl*-dl-*alanine*, $CHMeI\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, crystallises in needles, which sinter at 155°, m. p. 180—190°, decomp. 194°. The *ethyl* ester forms yellow needles, which sinter at 50°, m. p. 52—60°, decomp. 234° with liberation of iodine.

Di-iodoelaidyl chloride, $C_{17}H_{33}I_2\cdot COCl$, is obtained as a brownish-red mass by the action of thionyl chloride on di-iodoelaidic acid. With glycine, *di-iodoelaidylglycine*, $C_{17}H_{33}I_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, is obtained. The amorphous, colourless product sinters at 52°, m. p. 57°. The *ethyl* ester, prepared by interaction of the chloride with glycine ester, is crystalline, m. p. 82°, after sintering at 70°.

Di-iodoelaidylalanine sinters at 54°, m. p. 64°; it has $[\alpha]_D^{20}$ $-4\cdot9°$. The corresponding ester was only obtained as a syrup.

Di-iodoelaidyl-di-iodotyrosine,

$$C_{17}H_{33}I_2\cdot CO\cdot NH\cdot CH(CH_2\cdot C_6H_2I_2\cdot OH)\cdot CO_2H,$$

sinters at 92°, m. p. 170°.

Iodobehenyl chloride, $C_{21}H_{42}I\cdot COCl$, from iodobehenic acid and thionyl chloride, could not be distilled. It couples readily with amino-acids. *Iodobehenylglycine* is an amorphous, faintly yellow-coloured, fatty mass; it sinters at 50°, m. p. 70°, decomp. 170—180°.

Ethyl di-iodobrassidate (lipoiodin), $C_8H_{17}\cdot CHI\cdot CHI\cdot C_{11}H_{22}\cdot CO_2Et$, sinters at 32°, m. p. 40°, decomp. 220—230°, liberating iodine.

The physiological experiments indicate that iodine administered as di-iodoelaidic acid is slowly but completely excreted. The iodine of di-iodoelaidylglycine was in ten days only 50% excreted. The resorption was complete, but in the case of the ethyl ester it was less complete. Most of the iodine is in the fæces; in some experiments none was present in the urine.

Di-iodo-*l* tyrosine and di-iodoelaidyl-*l*-tyrosine are badly resorbed; ethyl di-iodobrassidate is better resorbed. E. F. A.

α-Aminobutyric Acid. EMIL ABDERHALDEN (*Zeitsch. physiol.*, 1911, **74**, 509—510).—Polemical. Koelker (this vol., i, 773) has not mentioned that Abderhalden, Chang, and Wurm (this vol., i, 526) have previously studied the behaviour of *dl*-α-aminobutyric acid towards yeast. E. F. A.

Alkylation of Commercial Cyanamide Salts. WILHELM TRAUBE and ALFRED ENGELHARDT (*Ber.*, 1911, **44**, 3149—3152. Compare Traube and Wedelstaedt, Abstr., 1900, i, 389).—The relatively pure disodium cyanamide, and likewise the crude commercial calcium cyanamide, react very readily with halogen alkyl and with dialkyl sulphate in presence of water or alcohol, forming disubstituted cyanamides. These are converted into secondary amines without difficulty, and it is easy to separate the ammonia formed at the same time. This affords a very convenient method of preparing secondary amines in quantity. Dimethyl-, diethyl-, di-*iso*amyl-, and dibenzyl cyanamide have been prepared in the manner described: from calcium cyanamide and methyl sulphate, 70—80% of the theoretical quantity of dimethylamine is obtained. Dimethylcyanamide has b. p. 163·5° (corr.); *diethylcyanamide*, b. p. 78°/16 mm.; *di-isoamylcyanamide*, b. p. 134°/14 mm.; *dibenzylcyanamide* forms transparent, rhombic plates, m. p. 53·5° (corr.). E. F. A.

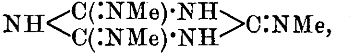
Acylation and Alkylation of Cyanamide. OTTO DIELS and RICHARD GOLLMANN (*Ber.*, 1911, **44**, 3158—3165).—Cyanamide can be acylated with ethyl chlorocarboxylate by the Schotten-Baumann method without difficulty, ethyl cyaniminodicarboxylate,

$NC\cdot N(CO_2Et)_2$,

being formed. With phosphoric oxide, the formation of cyano*iso*cyanate [carbimidonitrile] was expected; actually carbethoxyl *iso*cyanate [ethyl carbimidecarboxylate], $CO:N\cdot CO_2Et$, is formed, identical with the substance prepared by Diels and Wolf (Abstr., 1906, i, 237) by the action of phosphoric oxide on ethyl nitrogentricarboxylate.

Ammonia converts the diacylated cyanamide into the crystalline ammonium salt of the monoacyl compound, $NC\cdot N(NH_4)\cdot CO_2Et$. Dilute acids form ethyl allophanate; concentrated acids cause the addition of water and the formation of ethyl *as*-carbamidedicarboxylate,

$NH_2\cdot CO\cdot N(CO_2Et)_2$.

By the interaction of methyl sulphate and cyanamide, the monomethylcyanamide initially formed is polymerised to iso*trimethylmelamine*,  $NH<\begin{matrix}C(:NMe)\cdot NH\\C(:NMe)\cdot NH\end{matrix}>C:NMe$, but dimethylcyanamide is very readily obtained in this manner. It is easily converted into dimethylcarbamide.

Ethyl cyanoiminodicarboxylate, $NC\cdot N(CO_2Et)_2$, forms long, lustrous, silky prisms, with a burning taste, m. p. 33° (Bässler, Abstr., 1878, 214).

Methyl cyanoiminodicarboxylate, $NC\cdot N(CO_2Me)_2$, crystallises in lustrous, octahedra, m. p. 96—97°.

Ethyl carbimidecarboxylate (Diels and Wolf, *loc. cit.*) is a transparent, mobile liquid, b. p. 115—116°/781 mm.

Methyl carbimidecarboxylate, $CO:N\cdot CO_2Me$, is a transparent, mobile liquid of intensely biting odour, b. p. 97—98°; it decomposes on keeping to a colourless, crystalline compound, probably a polymeride.

Methyl phenylallophanate, $NHPh\cdot CO\cdot NH\cdot CO_2Me$, prepared by the interaction of methyl carbamidecarboxylate with aniline, crystallises in long needles, m. p. 143—144°.

The *ammonium* salt of *ethyl cyaniminocarboxylate*,

$CN\cdot N(NH_4)\cdot CO_2Et$,

forms lustrous, compact, octahedral crystals, m. p. 107—108°.

Ethyl as-*carbamidedicarboxylate*, $NH_2\cdot CO\cdot N(CO_2Et)_2$, crystallises in lustrous prisms, m. p. 86—87°, of faintly sweet taste. The corresponding *methyl* ester separates in slender, colourless needles, m. p. 137—138° (decomp.).

Dimethylcyanamide has b. p. 52°/14 mm.

as-*Dimethylcarbamide*, $NH_2\cdot CO\cdot NMe_2$, forms large, compact, lustrous prisms, m. p. 181—182°; it tastes sweet. E. F. A.

Synthesis of δ-Guanidinovaleric Acid. DANKWART ACKERMANN, R. ENGELAND, and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1911, **57**, 179—182).—δ-Aminovaleric acid and cyanamide were set aside in concentrated aqueous solution for some weeks, when a crystalline crust of *δ-guanidonovaleric acid*, $CO_2H\cdot[CH_2]_4\cdot NH\cdot C(NH_2):NH$, separated. This forms short, stunted, hard crystals, m. p. 265—266°, after previously becoming brown and sintering. When evaporated with concentrated hydrochloric acid, the *chloride* is obtained in long, lustrous needles, m. p. 170—171°. The *aurichloride* forms broad, lustrous plates, m. p. 120—122°. The *platinichloride* is very soluble and not characteristic. E. F. A.

Hypobromous [Acid and] Amides. Étienne Boismenu (*Compt. rend.*, 1911, **153**, 678—680. Compare François, Abstr., 1909, i, 13, 140).—A description of the preparation of certain bromo-amides by the action of hypobromous acid on the amides.

Bromoformamide, H·CO·NHBr, is best prepared by the action of bromine on a solution of formamide in ethyl acetate in presence of silver oxide. It is thus obtained in crystals, m. p. 87—88° (decomp.). W. O. W.

A New Derivative of Carbamide, Chlorocarbamide. Auguste Béhal and A. Detœuf (*Compt. rend.*, 1911, **153**, 681—683. Compare Chattaway, Trans., 1909, **95**, 464).—Carbamide absorbs chlorine at 15°, forming a mixture of monochlorocarbamide and carbamide hydrochloride. The former may be isolated in a state of purity by adding carbamide (60 grams) to water (13 grams), cooling in ice, and passing chlorine until the weight increases by 32 grams. The clear liquid is cooled in methyl chloride for thirty minutes, the chlorocarbamide filtered in a vacuum, and washed with a previously prepared solution of the same substance.

Chlorocarbamide, $NH_2 \cdot CO \cdot NHCl$, occurs in crystals, m. p. 71° (decomp.). It is soluble in five parts of water at the ordinary temperature, giving a neutral solution which slowly loses nitrogen, at the same time becoming acid and forming biuret. The substance behaves towards saturated organic compounds as a chlorinating or as an oxidising agent, or sometimes as hypochlorous acid, forming additive compounds. With unsaturated substances, it effects addition of hypochlorous acid or of chlorocarbamide, but sometimes brings about oxidation. The reactions are progressive, and their course can be followed by titration. W. O. W.

Ethyl Azodicarboxylate. Otto Diels and Paul Fritzsche (*Ber* 1911, **44**, 3018—3027).—Ethyl azodicarboxylate reacts normally with piperidine in cold petroleum, yielding the *dipiperidide,*

$$N_2[CO \cdot C_5NH_{10}]_2,$$

m. p. 134—135° (decomp.), golden-yellow prisms, but forms with aniline an additive *compound,* $C_{12}H_{17}O_4N_3$, m. p. 138°, of unknown constitution, although probably it is a hydrazine derivative, since it crystallises in colourless plates and prisms. A similar colourless *compound,* $C_{14}H_{21}O_4N_3$, m. p. 75—76°, is obtained with dimethylaniline.

Acting as a mild oxidising agent in consequence of its tendency to yield ethyl hydrazinedicarboxylate, ethyl azodicarboxylate very smoothly converts quinol into *p*-benzoquinone.

Reacting in methyl-alcoholic solution at 0°, hydrazine hydrate and methyl chlorocarbonate yield hydrazine hydrochloride and *methyl hydrazinecarboxylate hydrochloride,* $CO_2Me \cdot NH \cdot NH_2,HCl$, m. p. 160°.

The *base*, $C_2H_6O_2N_2$, m. p. 63°, b. p. 108°/12 mm, colourless prisms, has a faint, alkaline reaction, is volatile with steam, yields a *benzylidene* derivative, $CO_2Me\cdot NH\cdot N\colon CHPh$, m. p. 146°, and with aqueous potassium cyanate at 0°, the *semicarbazide*, $CO_2Me\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 169—170°, and reacts with methyl chlorocarbonate in ether to form *methyl hydrazinedicarboxylate*, $CO_2Me\cdot NH\cdot NH\cdot CO_2Me$, m. p. 131°. This ester, which is very stable and resists the attack of strong acids or bases, is also formed by the action of warm aqueous potassium hydroxide on methyl hydrazinecarboxylate hydrochloride. *Methyl azodicarboxylate*, $N_2[CO_2Me]_2$, b. p. 96°/25 mm., is prepared by the action of fuming nitric acid on methyl hydrazinedicarboxylate in nitric acid, D 1·4, at 0°, and behaves like the ethyl ester. C. S.

Dehydrogenation by Catalysis. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 3121—3125; *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1220—1222).—Heated palladium black, prepared by reducing ammonium palladochloride by means of formic acid in presence of alkali, serves as an excellent catalyst for the dehydrogenation of *cyclo*hexane and methyl*cyclo*hexane, which lose all the six hydrogen atoms of the ring and yield hydrogen and benzene or toluene, with no trace of the tetrahydro- or dihydro-derivative of the aromatic hydrocarbon. This action commences at about 170°, and proceeds very rapidly at 200—300°.

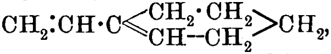
At lower temperatures, the reverse change occurs, passage of hydrogen and benzene over the freshly-prepared palladium black heated at 100—110° resulting in the hydrogenation of the benzene. Under these conditions, the temperature of equilibrium is about 200°, since, above this temperature, in spite of the presence of excess of hydrogen, dehydrogenation occurs.

The catalytic decomposition of *cyclo*hexane hydrocarbons under the influence of palladium seems to be specific, as neither hexane, nor *cyclo*pentane, nor methyl*cyclo*pentane undergoes similar dehydrogenation, at any rate below 300°. This reaction hence serves to distinguish between five- and six-carbon atom rings. T. H. P.

Selective Catalysis: A New Tetrahydrobenzene [*cyclo*Hexene]. NICOLAI D. ZELINSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1222—1224).—Dehydrogenation of *cyclo*hexene (prepared by the action of oxalic acid on *cyclo*hexanol) under the influence of palladium proceeds more energetically than that of *cyclo*hexane (compare preceding abstract), the products being hydrogen and benzene. The *cyclo*hexene employed in this experiment showed a continuous absorption spectrum, whilst another preparation, obtained by the action of quinoline on iodo*cyclo*hexane, was found to exhibit more or less marked selective absorption. The latter *cyclo*hexene only underwent partial dehydrogenation in presence of palladium, the benzene formed being mixed with a new *cyclo*hexene, C_6H_{10}, b. p. 77·5—78° (corr.), D_4^{20} 0·8005, n_D^{20} 1·4416, the increment of the molecular refraction being 1·58; it has a fatty, aromatic odour, and is a saturated hydrocarbon, as it reacts with neither permanganate nor bromine. T. H. P.

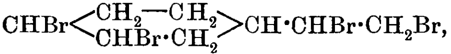
Isomerisation of Unsaturated Cyclic Hydrocarbons, C_8H_{12}. (Mlle.) V. I. Egorova (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1116—1124).—*cyclo*Hexylacetylene, $C_6H_{11}\cdot C\vdots CH$, best prepared by the method of Darzens and Rost (Abstr., 1909, i, 899), has D_0^0 0·8602, D_0^{20} 0·8424, n_D^{20} 1·4597.

cyclo*Hexylidene-ethylene*, $CH_2\!:\!C\!:\!C_6H_{10}$, obtained on heating *cyclo*hexylacetylene with alcoholic potassium hydroxide for ten hours at 140°, is a liquid, b. p. 138—141°, D_0^0 0·8682, D_0^{20} 0·8508, n_D 1·4826, and, when heated with sodium in a sealed tube, gives the sodium derivative of *cyclo*hexylacetylene (Darzens and Rost, *loc. cit.*).

1-*Vinyl*-Δ¹-cyclo*hexene*,  $CH_2\!:\!CH\cdot C{<}{\begin{matrix}CH_2\cdot CH_2\\ CH\text{—}CH_2\end{matrix}}{>}CH_2$, prepared by heating *cyclo*hexylidene-ethylene with benzoic acid in a sealed tube for ten hours at 170°, is a liquid, b. p. 143—145°, D_0^0 0·8862, D_0^{20} 0·8701, n_D^{20} 1·49060, and, although it contains a conjugated linking, shows no optical exaltation (compare Auwers and Eisenlohr, Abstr., 1910, ii, 365); it does not react with sodium. T. H. P.

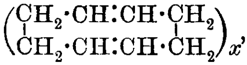
Polymerisation of Diethylene Hydrocarbons. III. Divinyl. Sergius V. Lebedeff and (Mlle.) N. A. Skavronskaja (*J Russ. Phys. Chem. Soc.*, 1911, **43**, 1124—1131).—This paper is largely a repetition of one already published (this vol., i, 26).

4-Ethenyl*cyclo*-Δ¹-hexene (*loc. cit.*) gives with bromine 1-*αβ-di bromoethyl*-3 : 4-*dibromo*cyclo*hexane*,



$$CHBr{<}{\begin{matrix}CH_2\text{—}CH_2\\ CHBr\cdot CH_2\end{matrix}}{>}CH\cdot CHBr\cdot CH_2Br,$$

m. p. 69·5—70·5°. When oxidised with permanganate it yields *β*-carboxyadipic acid (butane-*αβδ*-tricarboxylic acid), m. p. 111—113° (compare Guthzeit and Engelmann, Abstr., 1902, i, 742; Leuchs and Möbis, Abstr., 1909, i, 361).

The polymeride obtained, together with the above dimeride, on heating divinyl, yields an ozonide (*loc. cit.*) identical with that given by di*cyclo*octadiene (compare Harries, Abstr., 1908, i, 254). The conclusion is hence drawn that the polymeride has the structure  $\left(\begin{matrix}CH_2\cdot CH\!:\!CH\cdot CH_2\\ |\qquad\qquad\quad |\\ CH_2\cdot CH\!:\!CH\cdot CH_2\end{matrix}\right)_x$, and is de-polymerised by the action of ozone.

T. H. P.

Benzene Problem. Ernst Mohr (*Ber.*, 1911, **44**, 2971).—Pauly has recently suggested (this vol., i, 986) that the existence of the aromatic hydrocarbon, $C_{13}H_9$, decides for the centric formula for benzene in place of the Kekulé formula. It is doubtful, however, whether this criterion can be accepted, since the hydrocarbon, $C_{13}H_9$, does not conform with the law of even numbers of atoms, and is therefore analogous to triphenylmethyl and the radicle of diphenyl nitrogen, NPh_2, rather than with benzene, naphthalene, and anthracene.

T. A. H.

A New Hypothesis on Benzene. Aníbal Chacón (Pamphlet, pp. 43).—See this vol., ii, 1080.

[Orientation in the Benzene Nucleus.] JULIUS OBERMILLER (*Ber.*, 1911, **44**, 3179—3180).—A renewed claim for priority over Holleman (compare Abstr., 1910, i, 826; also Holleman and Caland, this vol., i, 849). E. F. A.

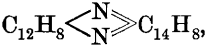
Oxidation of Amino-acids by Alloxan, Isatin, and *p*-Benzoquinone. WILHELM TRAUBE (*Ber.*, 1911, **44**, 3145—3148).—It was first shown by Strecker that alloxan oxidises aliphatic α-amino-acids to the aldehyde of the next lower carbon series with liberation of crabon dioxide and ammonia. Hurtley and Wootton (Trans., 1911, **99**, 288) have shown that dimethylalloxan behaves similarly. It is now found that alloxan likewise oxidises anilinoacetic acid to benzaldehyde and carbon dioxide, the solution becoming red. The amount of benzaldehyde produced was determined quantitatively by means of the phenylhydrazone.

Besides alloxan, isatin, *p*-benzoquinone and toluquinone are shown to oxidise the amino-acid to aldehyde, whereas naphthaquinone and anthraquinone, parabanic acid, and chloroanil are without action. Fatty aromatic amines, for example, benzylamine, are in like manner oxidised to aldehydes by alloxan and isatin, but *p*-benzoquinone is without effect. Purely fatty amines, for example, *iso*amylamine, are not oxidised by alloxan. E. F. A.

Acenaphthene. II. FRANZ SACHS and GERHARDT MOSEBACH (*Ber.*, 1911, **44**, 2852—2862. Compare Abstr., 1910, i, 726).—The importance recently acquired by acenaphthene for technical purposes renders desirable an extension of the accurate knowledge of its substitution products. 4-Acetylaminoacenaphthene in glacial acetic acid at 0° is converted by concentrated nitric acid into 2-*nitro*-3-*acetylaminoacenaphthene*, $NHAc\cdot C_{12}H_8\cdot NO_2$, m. p. 253°, yellow needles, in which the ortho-relation of the substituents is proved by the fact that the compound in aqueous alcohol is reduced by sodium hyposulphite to the *iminoazole*,

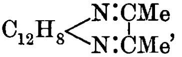
$C_{12}H_8{<}\begin{smallmatrix}-N-\\ NH\end{smallmatrix}{>}CMe$

(*nitrate*, $C_{14}H_{12}N_2,HNO_3$, m. p. 320°; *platinichloride*, $2C_{14}H_{12}N_2,H_2PtCl_6$; *chloride*, $C_{14}H_{12}N_2,HCl$), and also by the fact that the 2-*nitro*-3-*aminoacenaphthene*, m. p. 222—224°, red prisms, obtained by its hydrolysis by alcohol and concentrated hydrochloric acid, is reduced by stannous chloride and hydrochloric acid to 2 : 3-*acenaphthylenediamine*, m. p. 140—142°, almost colourless needles, which condenses with phenanthraquinone and with diacetyl to form the *azines*,



$C_{12}H_8{<}\begin{smallmatrix}N\\ N\end{smallmatrix}{>}C_{14}H_8$

m. p. 293°, yellow needles, and

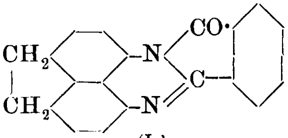


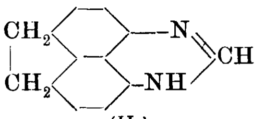
$C_{12}H_8{<}\begin{smallmatrix}N:CMe\\ |\\ N:CMe\end{smallmatrix}$

m. p. 200°, respectively.

2-Nitro-3-acetylaminoacenaphthene is converted by boiling alcoholic sodium hydroxide into the *sodium* salt of 2-nitro-3-hydroxyacenaphthene, $ONa\cdot C_{12}H_8\cdot NO_2,H_2O$, dark red crystals. 2-*Nitro*-3-*hydroxyacenaphthene* itself has m. p. 148°, crystallises in yellowish-red needles, and is reduced by sodium hyposulphite in aqueous alcohol to 2-*amino*-3-*hydroxyacenaphthene*, m. p. 159°.

Quincke's 3 : 4-dinitroacenaphthene is obtained best by heating a finely-divided suspension of acenaphthene in glacial acetic acid with concentrated nitric acid at 80° for twenty minutes. Its reduction to 3 : 4-acenaphthylenediamine is conveniently effected by an excess of stannous chloride and hydrochloric acid. The *peri*-position of the two amino-groups is proved by the preparation of the following substances. *Phthalo-aceperinone* (formula I), m. p. 290°, red needles, from the diamine and phthalic anhydride at about 200°; *aceperimidine* (formula II), m. p. 285°, greenish-brown crystals, from the diamine and formic acid in boiling alcohol; *acenaphthylene*-3 : 4-*thiocarbamide*, $C_{12}H_8{<}\substack{NN\\NH}{>}CS$, colourless crystals, from the diamine and carbon disulphide in alcohol. C. S.


(I.)


(II.)

Cholesterol. XIII. Cholesterylamine. Adolf Windaus and J. Adamla (*Ber.*, 1911, **44**, 3051—3058).—In their attempts to prepare cholesterylamine, the authors obtained *cholesterylurethane*, $C_{27}H_{45}O\cdot CO\cdot NH_2$, m. p. 212—213°, by heating cholesterol and carbamide at 220°. *Cholesterylamine*, $C_{27}H_{45}\ NH_2$, m. p. 98°, is obtained by heating cholesteryl chloride and alcoholic ammonia at 180° in the presence of a little ammonium iodide. The *hydrochloride*, *sulphate*, *platinichloride*, and *picrate*, m. p. 274—275° (decomp.), are described. The *acetyl* and the *benzoyl* derivatives have m. p. 243—244° and 236° respectively. The reduction of cholestenoneoxime by sodium and boiling alcohol yields a mixture of stereoisomeric bases (*picrate*, decomp. 253°; *platinichloride*, decomp. 252°; *benzoyl* derivative, m. p. 203°). The acetylated mixture has been separated by fractionation into three individual substances; one, identical with the preceding acetyl derivative, has m. p. 243—244°, another, *β-acetylcholesterylamine*, has m. p. 216—217°, and constitutes the chief ingredient of the acetylated mixture, whilst the third, *γ-acetylcholesterylamine*, has m. p. 190°. C. S.

Synthesis of Aromatic and Hydroaromatic Alcohols Containing the Allyl Group. Ippolyt Matschurevitsch (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 973—990).—The author has prepared a number of tertiary alcohols by the interaction of allyl bromide (or iodide), magnesium, and a carbonyl compound in ethereal solution (compare Javorsky, Abstr., 1908, i, 753).

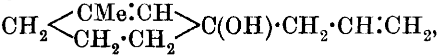
o-4-*Xylylmethylallylcarbinol*, $C_6H_3Me_2\cdot CMe(OH)\cdot CH_2\cdot CH{:}CH_2$, prepared from *o*-4-xylyl methyl ketone, allyl bromide, and magnesium, is a colourless, viscous liquid with an aromatic odour, b. p. 144—144·5°/19·5 mm., $D_4^{21\cdot5}$ 0·97258, $n_D^{21\cdot5}$ 1·52752.

m-4-*Xylylmethylallylcarbinol*, prepared from *m*-4-xylyl methyl ketone, is a pleasant-smelling, colourless, viscous liquid, b. p. 139—139·5°/14·5 mm., $D_4^{21\cdot5}$ 0·97675, $n_D^{21\cdot5}$ 1·52882.

p-2-*Xylylmethylallylcarbinol*, prepared from *p*-2-xylyl methyl ketone, is a liquid, b. p. 138—139°/22·5 mm., $D_4^{21\cdot5}$ 0·97774, $n_D^{21\cdot5}$ 1·52925.

1-*Allyl*cyclo*hexane*-1-*ol*, $OH\cdot C_6H_{10}\cdot CH_2\cdot CH:CH_2$, prepared from *cyclo*hexanone, is a liquid, b. p. 95—97°/27·5 mm., D_4^{22} 0·93410, n_D^{22} 1·47564.

1-*Methyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*,



$$CH_2<\begin{matrix}CMe:CH\\CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CH:CH_2,$$

prepared from 1-methyl-Δ^1-*cyclo*hexene-3-one, is a liquid, b. p. 99·5—100°/16·5 mm., D_4^{22} 0·95510, n_D^{22} 1·49923.

1 : 3-*Dimethyl*-5-*allyl*-Δ^3-cyclo*hexene*-5-*ol*,

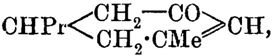
$$OH\cdot C_6H_6Me_2\cdot CH_2\cdot CH:CH_2,$$

prepared from 1 : 3-dimethyl-Δ^3-*cyclo*hexene-5-one, forms a fibrous, crystalline, fatty mass, m. p. 28—31°, b. p. 108—108·5°/17·5 mm.

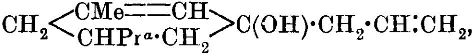
1-*Methyl*-5-*ethyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*,

$$OH\cdot C_6H_6MeEt\cdot CH_2\cdot CH:CH_2,$$

has b. p. 120—122°/13·5 mm., D_4^{22} 0·91795, n_D^{22} 1·48731.

1-*Methyl*-5-*propyl*-Δ^1-cyclo*hexene*-3-*one*,  $CHPr<\begin{matrix}CH_2—CO\\CH_2\cdot CMe\end{matrix}>CH$, obtained by condensing ethyl acetoacetate and *n*-butaldehyde in presence of diethylamine to ethyl $\alpha\gamma$-diacetyl-β-propylglutarate, $CO_2Et\cdot CHAc\cdot CHPr^\alpha\cdot CHAc\cdot CO_2Et$, and treating the latter with alkali, is a colourless liquid, b. p. 242—244°, 128—129°/37 mm., $D_4^{22\cdot5}$ 0·9267.

1-*Methyl*-5-*propyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*,



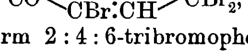
$$CH_2<\begin{matrix}CMe{=\!=}CH\\CHPr^\alpha\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CH:CH_2,$$

prepared from the preceding compound, is a crystalline, waxy mass, m. p. 34—37°, b. p. 135—136°/29 mm., $D_4^{22\cdot5}$ 0·9225.

1-*Methyl*-5-iso*propyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*, $C_{13}H_{22}O$, forms a waxy mass, m. p. 26—29°, b. p. 127—128°/25·5 mm., $D_4^{22\cdot5}$ 0·9175, $n_D^{22\cdot5}$ 1·48905.

1-*Methyl*-5-iso*butyl*-3-*allyl*-Δ^1-cyclo*hexene*-3-*ol*, $C_{14}H_{24}O$, prepared from the corresponding hexenone, was obtained as a crystalline, waxy mass, m. p. 50—52·5°, b. p. 140—142°/38 mm. T. H. P.

Bromination of Phenol. J. G. DINWIDDIE and JOSEPH H. KASTLE (*Amer. Chem. J.*, 1911, **46**, 502—503).—It is well known that when bromine is added to an aqueous solution of phenol, tribromophenol and tribromophenol bromide are the only compounds produced. It is now shown that if bromine is added to solutions of phenol in glacial acetic acid, chloroform, carbon tetrachloride, or carbon disulphide, substitution takes place with the formation of a dibromophenol, probably the 2 : 4-derivative.

It is suggested that the peculiar behaviour of phenol in aqueous solution is due to its tendency to form quinonoid derivatives. Tribromophenol bromide,  $CO<\begin{matrix}CBr:CH\\CBr:CH\end{matrix}>CBr_2$, is first produced, and reacts with phenol to form 2 : 4 : 6-tribromophenol. The mechanism of these reactions is discussed. E. G.

Isomerism and Polymorphism. II. EINAR BIILMANN (*Ber.*, 1911, **44**, 3152—3157).—Polemical (compare Hantzsch, Abstr., 1910, i, 474; this vol., i, 715; Biilmann, this vol., i, 367).

Hantzsch's contention as to the persistence of the individuality of the homochromoisomerides is based on what is probably only a retention of the inoculation nuclei.

Polymorphism is a very general property. Methylcoumarinic acid has been obtained in a new modification, m. p. 86°, in addition to that, m. p. 91—92°. E. F. A.

The Reactivity of Benzene Substituents and the Acidity of Aromatic Acids in their Dependence on Orientating Influences. The Structure of Benzene. JULIUS OBERMILLER (*J. pr. Chem.*, 1911, [ii], **84**, 449—459). The author finds that the removal of the sulphoxyl group from *o*-phenolsulphonic acid by heating with hydrochloric acid at 100°, takes place more readily than with the para-compound, whilst the meta-acid, when subjected to the same treatment, remains intact.

The mobility of the sulphoxyl group thus increases as the latter approaches the hydroxyl group, as represented in Claus's diagonal formula for benzene. The view is expressed that the increase in the reactivity of the hydrogen atoms of a side-chain is coincident with an increase in its acid character. The acidity of the side-chain should accordingly be greater the less firmly it is attached, and with position-isomeric compounds increase in the order meta, para, ortho. This is confirmed by the behaviour of the sulphanilic acids and, to some extent, by the phenolsulphonic acids.

It is shown that the acidity of the hydroxyl group of the isomeric phenolsulphonic acids, as judged by the ease with which the dimagnesium salts are hydrolysed, diminishes in the order ortho, para, meta, whereas from measurements of the hydrogen ion concentration of the sodium salts the order of acidity is meta, para, ortho. This discrepancy is referred by the author to differences in the condition of the benzene ring. F. B.

Reactivity of Aromatic Bromo-compounds. II. Formation of Aromatic Disulphides of the Types R·S·R′·S·R and R·S·R′·S·R″. ÉDOUARD BOURGEOIS and A. FOUASSIN (*Bull. Soc. chim.*, 1911, [iv], **9**, 938—944. Compare Abstr., 1896, i, 17).—When *p*-dibromobenzene reacts with lead derivatives of the thiophenols, the two reactions represented by the following equations occur: (1) $2C_6H_4Br_2 + PbS_2R_2 = PbBr_2 + 2Br{\cdot}C_6H_4{\cdot}SR$, (2) $2Br{\cdot}C_6H_4{\cdot}SR + PbS_2R_2 = PbBr_2 + 2RS{\cdot}C_6H_4{\cdot}SR$. The first of these reactions takes place more rapidly than the second, and even if dibromobenzene is employed in large excess, some disulphide is always formed. The velocity of the second reaction increases with greater complexity of the thiophenol employed. Reaction begins at 180—185°, but only becomes practicable at 200°. Above 225° secondary actions occur. The two substances were heated together in an autoclave at 225°, and the resulting products extracted with ether or carbon disulphide and, after removal of the solvent, fractionally distilled to separate the bromosulphide from the disulphide.

p-Bromodiphenyl sulphide (*loc. cit.*) reacts with the lead derivative of thiophenol to form *diphenyl* p-*phenylene disulphide*, $C_6H_4(SPh)_2$, m. p. 81·5°, b. p. 265°/14 mm., which crystallises in colourless spangles from hot alcohol.

p-*Bromophenyl* p-*tolyl sulphide*, $C_6H_4Br\cdot S\cdot C_6H_4Me$, m. p. 82·5°, b. p. 200·5°/14 mm., crystallises in pearly leaflets. *Di*-p-*tolyl* p-*phenylene disulphide*, $C_6H_4Me\cdot S\cdot C_6H_4\cdot S\cdot C_6H_4Me$, m. p. 99°, b. p. 285°/14 mm., crystallises in prismatic needles.

p-*Bromophenyl a-naphthyl sulphide*, m. p. 73°, b. p. 247°, forms large, prismatic needles. *Di-a-naphthyl* p-*phenylene disulphide*, m. p. 148·5°, b. p. above 360°/14 mm. (decomp.), forms colourless, rhombic tablets.

p-*Bromophenyl β-naphthyl sulphide*, m. p. 114·5°, b. p. 253°/14 mm., forms rhombic crystals. *Di-β-naphthyl* p-*phenylene disulphide*, m. p. 185°, b. p. above 360°/14 mm. (decomp.), is nearly insoluble in neutral solvents.

Phenyl p-*tolyl* p-*phenylene disulphide*, m. p. 55·5°, b. p. 272°/14 mm., obtained by heating *p*-bromodiphenyl sulphide with the lead derivative of tolyl mercaptan, is colourless and crystalline. T. A. H.

Reactivity of Aromatic Bromo-compounds. III. Action of Bromonitrobenzenes on Phenylmercaptides. ÉDOUARD BOURGEOIS and P. HUBER (*Bull. Soc. chim.*, 1911, [iv], **9**, 944—947).—It is known that *o*- and *p*-bromonitrobenzenes are more highly reactive than their meta-isomeride, and in confirmation of this, it is found that the two former, although they do not react with the lead derivative of thiophenol, give with the sodium derivative the corresponding nitrodiphenyl sulphides; with *m*-bromonitrobenzene, on the other hand, the nitro-group appears to undergo reduction with the formation of a red substance, m. p. 125·5°, which may be Gabriel's *m*-dibromoazobenzene (this Journ., 1877, i, 307).

4-Nitrodiphenyl sulphide, m. p. 54·4°, b. p. 240°/25 mm., or 262·5°/50 mm., or 288·2°/100 mm., forms pale yellow, prismatic needles or hexagonal tablets (Kehrmann and Bauer, Abstr., 1897, i, 27), and on oxidation gives 4-nitrodiphenylsulphone (Ullmann and Pasdermadjian, Abstr., 1901, i, 383).

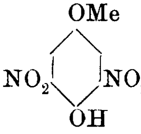
2-*Nitrodiphenyl sulphide*, m. p. 80·2°, forms pale orange-coloured crystals from alcohol mixed with ether. On oxidation it furnishes 2-nitrodiphenylsulphone (*loc. cit.*), which is colourless, but becomes brown on exposure to light. T. A. H.

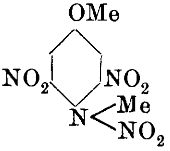
The Two Forms of Decahydro-β-naphthol (a Particular Case in Stereochemistry). LUIGI MASCARELLI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 223—227).—Leroux (Abstr., 1905, i, 278) described decahydro-β-naphthol as having m. p. 75°, b. p. 238°. Ipatieff gave m. p. 99—100°, b. p. 242—244°. By recrystallisation of a product obtained by the latter, the author has isolated two substances, A and B, which have the same composition and molecular weight, and are both stable towards permanganate. a-*Decahydro*-

β-naphthol forms flat, transparent crystals, m. p. 75°; b-*decahydro-β-naphthol* forms colourless, prismatic crystals, m. p. 103°, and is generally less soluble than its isomeride. From the consideration of the stereochemistry of monosubstituted decahydronaphthalenes it appears that four different decahydro-β-naphthols may exist, forming two pairs of enantiomorphs, and the two products above described are to be regarded as the two corresponding racemic mixtures. The stereoisomerism is due to the different positions which may be occupied by the hydrogen atoms attached to the carbon atoms 9 and 10. These two carbon atoms, although asymmetric, must necessarily have opposite configurations, and therefore the possible stereoisomerides are those due to the carbon atom to which the substituent is attached, regard being had to th edifferent situations of the two hydrogen atoms attached to the carbon atoms 9 and 10 with which a given configuration of it can be associated. R. V. S.

Constitution of Weselsky and Benedikt's Dinitroquinol Methyl Ether. Preparation of Some Methyl Derivatives of the Dinitro-*p*-anisidines. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Arch. Sci. Phys. Nat.*, 1911, [iv], **32**, 343—346; *Bull. Soc. chim.*, 1911, [iv], **9**, 925—928; *J. pr. Chem.*, 1911, [ii], **84**, 554—558. Compare Abstr., 1881, 1139; this vol., i, 123).—The authors have determined the constitution (I) for Weselsky and Benedikt's dinitroquinol methyl ether, and (II) for a nitroamine previously described by one of them (this vol., i, 123) with m. p. 125°.

Starting with 2 : 6-dinitro-*p*-anisidine, by the action of methyl sulphate at 100°, 2 : 6-*dinitrodimethyl*-p-*anisidine*, m. p. 150°, was obtained. This substance with hot nitric acid yields a *nitroamine*, m. p. 139—140°, different from their original one; thus their *nitroamine*, m. p. 125°, is that of 3 : 5-*dinitromethyl*-p-*anisidine* (II), and since by boiling with sodium hydroxide solution it yields Weselsky and Benedikt's ether, the latter must have the constitution (I).


(I.)


(II.)

The authors were unsuccessful in attempts to methylate 3 : 5-dinitro-*p*-anisidine, but succeeded in methylating the corresponding 2 : 3- and 2 : 5-compounds, which, however, unlike the 2 : 6-compound, only yielded monomethyl derivatives.

2 : 3-*Dinitromethyl*-p-*anisidine* crystallises in deep red needles, m. p. 156°.

2 : 5-*Dinitromethyl*-p-*anisidine* crystallises in dull red, felted needles, m. p. 201—202°. W. G.

Some Derivatives of Hydroxyquinol. VI. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 183—190. Compare this vol., i, 305).—The present paper deals with the products of the condensation of benzoyl chloride, anisyl chloride, and phenylacetyl chloride, respectively, with hydroxyquinol trimethyl ether in the presence of aluminium chloride.

Benzoyl chloride and hydroxyquinol trimethyl ether yield a mixture of 2 : 4 : 5-trimethoxybenzophenone and 2-hydroxy-4 : 5-dimethoxybenzophenone. 2 : 4 : 5-*Trimethoxybenzophenone*, $C_{16}H_{16}O_4$, forms pale yellow needles, m. p. 97°. Its *phenylhydrazone*, $C_{22}H_{22}O_3N_2$, crystallises in colourless scales, m. p. 178—179°, and gives a yellowish-green coloration with concentrated sulphuric acid. 2-*Hydroxy*-4 : 5-*dimethoxybenzophenone*, $C_{15}H_{14}O_4$, forms yellowish-green, flat, prismatic crystals, m. p. 106—107°. Its alcoholic solution gives a yellowish-green coloration with ferric chloride. On methylation, it yields the above trimethyl ether. The *acetyl* derivative, $C_{17}H_{16}O_5$, crystallises in slightly yellow needles, m. p. 108—110°, and dissolves in concentrated sulphuric acid, giving an orange-yellow coloration. When treated with hydrobromic acid in glacial acetic acid (compare Stoermer, Abstr., 1908, i, 190), both the trimethoxy- and the dimethoxy-derivatives yield 2 : 4-*dihydroxy*-5-*methoxybenzophenone*, $C_{14}H_{12}O_4$, which forms small, yellow needles, m. p. 183—185°, and in alcoholic solution gives a yellowish-green coloration with ferric chloride. All three methoxybenzophenones dissolve in concentrated sulphuric acid with production of an orange-yellow coloration. The positions of the methoxy- and hydroxy-groups are assigned on the basis of analogies and regularities to be found in the literature, and the constitutions of the following substances are arrived at in a similar manner.

Anisyl chloride and hydroxyquinol trimethyl ether give a mixture of 2 : 4 : 5 : 4′-tetramethoxybenzophenone and 2-hydroxy-4 : 5 : 4′-trimethoxybenzophenone. 2 : 4 : 5 : 4′-*Tetramethoxybenzophenone*, $C_{17}H_{18}O_5$, is a yellowish-white, crystalline powder, m. p. 122—124°, and gives an orange-yellow coloration with sulphuric acid. Its *phenylhydrazone*, $C_{23}H_{24}O_4N_2$, has m. p. 173—174°, and dissolves in concentrated sulphuric acid, with production of a green coloration. 2-*Hydroxy*-4 : 5 : 4′-*trimethoxybenzophenone*, $C_{16}H_{16}O_5$, crystallises in small, yellow needles, m. p. 127—128°, and dissolves in concentrated sulphuric acid, producing an orange coloration. The alcoholic solution gives a yellowish-green coloration with ferric chloride.

The products of the reaction between phenylacetyl chloride and hydroxyquinol trimethyl ether are 2 : 4 : 5-trimethoxy- and 2-hydroxy-4 : 5-dimethoxy-deoxybenzoin. 2 : 4 : 5-*Trimethoxydeoxybenzoin*, $C_{17}H_{18}O_4$, crystallises in colourless leaves, m. p. 76—77°, and gives an orange coloration when dissolved in concentrated sulphuric acid. Its *phenylhydrazone*, $C_{23}H_{24}O_3N_2$, is a yellow, crystalline powder, m. p. 142—143°; it gives a yellowish-green coloration with concentrated sulphuric acid. 2-*Hydroxy*-4 : 5-*dimethoxydeoxybenzoin*, $C_{16}H_{16}O_4$, forms colourless leaves, m. p. 94°; it dissolves in concentrated sulphuric acid with production of a yellowish-green coloration, and its alcoholic solution gives a green coloration with ferric chloride. R. V. S.

Benzyl Orthothioformate. JOHN A. SMYTHE (*Proc. Univ. Durham Phil. Soc.*, 1911, **4**, 75—83. Compare Dennstedt, Abstr., 1879, 318; 1880, 646).—A white, crystalline solid, m. p. 103°, produced in small quantities when hydrogen chloride acts on benzyl mercaptan in the presence of glacial acetic acid, is proved to be identical with Dennstedt's benzyl orthothioformate. Its formation is due to the presence of formic acid as an impurity in the acetic acid employed; the yield is equivalent to the amount of formic acid present. This indicates a ready method of preparing the thio-ester by the action of hydrogen chloride on an solution of benzyl mercaptan (1 mol.) dissolved in glacial acetic acid containing sodium formate (3 mols.). The reaction under these conditions is reversible:

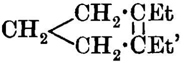
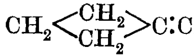
$$H\cdot CO_2H + 3CH_2Ph\cdot SH \rightleftharpoons CH(S\cdot CH_2Ph)_3 + 2H_2O.$$

The thio-ester can be accurately estimated by means of standard iodine solution under certain conditions. The reaction takes place in two stages; in the first, hydrochloric acid acts as a catalyst. The second stage, although reversible, proceeds almost completely, as the velocity of reaction is very great.

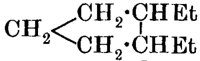
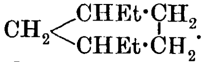
$$CH(S\cdot CH_2Ph)_3 + 2H_2O \rightleftharpoons H\cdot CO_2H + 3CH_2Ph\cdot SH,$$
$$2CH_2Ph\cdot SH + I_2 \rightleftharpoons (C_6H_5\cdot CH_2)_2S_2 + 2HI.$$

W. G.

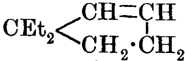
Transformations of *cyclo*Butyldiethylcarbinol. Nicolai M. Kijner (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1149—1157).—As it has been found that all the transformations of *cyclo*butyldimethylcarbinol are accompanied by isomerisation of the four-membered into a five-membered ring, it is necessary to reconsider the transformations undergone by *cyclo*butyldiethylcarbinol (compare Kijner and Amosoff, Abstr., 1905, i, 772). If, with the latter, the changes are similar to those occurring with the former, the action of oxalic acid on *cyclo*butyldiethylcarbinol should give 1 : 2-diethyl-Δ^1-*cyclo*pentene, whilst the action of alcoholic potassium hydroxide on the iodo- or bromo-derivative corresponding with the alcohol should yield 1 : 1-diethyl-Δ^2-*cyclo*pentene. In the latter case it is, indeed, found that the resulting product is an unsaturated hydrocarbon, C_9H_{16}, which differs from that given with oxalic acid, and yields oxidation products in complete agreement with the conclusion that it is 1 : 1-diethyl-Δ^2-*cyclo*pentene. It is hence to be assumed that the action of hydrobromic (or hydriodic) acid on the alcohol is accompanied by isomeric change of the carbon ring, and so gives rise to 1 : 1-diethyl-2-bromo*cyclo*pentane.

[With W. Amosoff.]—1 : 2-*Diethyl*-Δ^1-cyclo*pentene*,  $CH_2<\begin{matrix}CH_2\cdot CEt\\ \| \\ CH_2\cdot CEt\end{matrix}$, formed by the action of oxalic acid on *cyclo*butyldiethylcarbinol and previously given as  $CH_2<\begin{matrix}CH_2\\ CH_2\end{matrix}>C:CEt$ (*loc. cit.*), has b. p. 151·5—152°/774 mm., and is also obtained as a by-product in the synthesis of the carbinol itself. In the reaction with oxalic acid there is no isomeric change of the tertiary into secondary alcohol, such as occurs with *cyclo*butyldimethylcarbinol. Reduction of this hydrocarbon with concentrated sulphuric acid yields (1) a saturated hydrocarbon, C_9H_{18} (*loc. cit.*), isomeric with that obtained by reducing *cyclo*butyldiethylcarbinol with hydriodic acid, and (2) an unsaturated *dimeride* of 1 : 2-diethyl-Δ^1-*cyclo*pentene, $C_{18}H_{32}$, b. p. 295—300°, or 168—173°/15 mm.

The two hydrocarbons of the formula C_9H_{18} have probably the structures:


and


[With S. VOZNESENSKY.]—1 : 1-*Diethyl*-Δ^2-cyclo*pentene*,



has b. p. 143·5—144·5°/754 mm., D_0^{20} 0·8084, n_D 1·4455, and gives a green coloration with concentrated sulphuric acid and alcohol. On oxidation with permanganate, it yields an *acid*, $C_9H_{16}O_4$, which crystallises from light petroleum in needles, m. p. 85°, and forms an *anhydride*, $C_7H_{14}<\begin{smallmatrix}CO\\CO\end{smallmatrix}>O$, m. p. 10—11°, D_4^{20} 1·1077, n_D 1·4689, an *anilido-acid*, $CO_2H\cdot C_7H_{14}\cdot CO\cdot NHPh$, crystallising from aqueous methyl alcohol in slender needles, m. p. 142°, and an *anil*, $C_7H_{14}<\begin{smallmatrix}CO\\CO\end{smallmatrix}>NPh$, separating from benzene in silky needles, m. p. 163°. On reduction with sulphuric acid, 1 : 1-diethyl-Δ^2-*cyclo*pentene gives 1 : 2-diethyl*cyclo*pentane.

2-*Bromo*-1 : 1-*diethyl*cyclo*pentane*, $C_9H_{17}Br$, has b. p. 105—106°/24 mm., D_0^{20} 1·2005, n_D 1·4895, and, on reduction with a copper-zinc couple, gives 1 : 1-*diethyl*cyclo*pentane*, $C_5H_8Et_2$, b. p. 150·5°/757 mm., D_0^{20} 0·8028, n_D 1·4388. T. H. P.

Syntheses in the Fatty Aromatic Series. II. JULIUS VON BRAUN [with H. DEUTSCH and O. KRUBER] (*Ber.*, 1911, **44**, 2867—2881. Compare Abstr., 1910, i, 843).—At the present time there are, for the conversion of an alcohol into the next higher homologue, three practical methods, represented by the following schemes: (i) $R\cdot OH \longrightarrow RCl \longrightarrow R\cdot CN \longrightarrow R\cdot CO_2H \longrightarrow R\cdot CO_2Et \longrightarrow R\cdot CH_2\cdot OH$, (ii) $R\cdot OH \longrightarrow RBr \longrightarrow R\cdot MgBr \xrightarrow{(CH_2O)_3} R\cdot CH_2\cdot OH$, (iii) $R\cdot OH \longrightarrow RCl \longrightarrow R\cdot CN \longrightarrow R\cdot CH_2\cdot NH_2 \longrightarrow R\cdot CH_2\cdot NHBz \xrightarrow{PCl_5} R\cdot CH_2Cl \longrightarrow R\cdot CH_2\cdot OH$. All these methods are efficacious for the conversion of γ-chloropropylbenzene into δ-phenylbutyl alcohol method (ii) giving the best result. For the synthesis of yet higher alcohols, however, only methods (i) and (iii) are practicable, the latter being the more convenient, since larger quantities can be manipulated at a time. In this way derivatives of phenylheptane have been prepared.

Ethyl γ-phenylbutyrate, $CH_2Ph\cdot CH_2\cdot CH_2\cdot CO_2Et$, b. p. 130—131°/10 mm., is reduced by sodium and alcohol to *δ-phenylbutyl alcohol*, $CH_2Ph\cdot[CH_2]_2\cdot CH_2\cdot OH$, b. p. 140°/14 mm., in 70% yield; the alcohol, which has a strong, unpleasant odour, forms a *phenylurethane*, $C_{17}H_{19}O_2N$, m. p. 51—52°, and is converted by concentrated hydrobromic acid at 100° into *δ-bromobutylbenzene*, b. p. 131—133°/12 mm. *ε-Phenylamyl alcohol*, $CH_2Ph\cdot[CH_2]_3\cdot CH_2\cdot OH$, b. p. 155°/20 mm., can be prepared in less than 50% yield from this bromide, magnesium, and trioxymethylene, but is obtained quantitatively by converting ε-chloroamylbenzene into *ε-phenylamyl acetate*, $CH_2Ph\cdot[CH_2]_4\cdot OAc$, b. p. 155°/12 mm., by boiling acetic acid and potassium acetate and hydrolysing the ester by alcoholic alkali; it has an extremely pleasant, but not very persistent, odour of citron.

ε-Phenylhexonitrile, $CH_2Ph\cdot[CH_2]_4\cdot CN$, b. p. 160—164°/13 mm., prepared from ε-iodoamylbenzene and potassium cyanide in boiling aqueous alcohol, yields by hydrolysis *ε-phenylhexoic acid*, b. p. 180—190°/17 mm. (*ethyl* ester, b. p. 161—163°/13 mm.), and by reduction with sodium and alcohol, *ζ-phenylhexylamine*,

$$CH_2Ph\cdot[CH_2]_5\cdot NH_2,$$

b. p. 144—146°/15 mm., which absorbs moisture and carbon dioxide; it forms a *picrate*, m. p. 99—100°, *benzoyl* derivative, m. p. 59—61°, *platinichloride*, m. p. 216—220° (decomp.), *aurichloride*, m. p. 71—72°, and quaternary *methiodide*, $CH_2Ph\cdot[CH_2]_5\cdot NMe_3I$, m. p. 172°.

ζ-Chlorohexylbenzene, $CH_2Ph\cdot[CH_2]_5\cdot Cl$, b. p. 142—146°/15 mm., prepared by fusing the preceding benzoyl derivative with phosphorus pentachloride, has a pleasant odour less intense than that of ε-chloroamylbenzene, and is converted into the almost odourless *ζ-iodohexylbenzene*, b. p. 168—173°/15 mm., by sodium iodide in the usual manner. *ζ-Phenylhexyl alcohol*, b. p. 160—161°/13 mm., obtained by the reduction of ethyl ε-phenylhexoate, has a not particularly pleasant odour, less intense than that of the phenylamyl alcohol, forms an *acetate*, b. p. 166—168°/13 mm., and is converted by concentrated hydrochloric acid at 120° into the preceding chlorohexylbenzene, and by hydrobromic acid at 125° into *ζ-bromohexylbenzene*, b. p. 160—161°/17 mm.

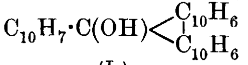
ζ-Phenylheptonitrile, $CH_2Ph\cdot[CH_2]_5\cdot CN$, b. p. 173—178°/15 mm., obtained from iodohexylbenzene and potassium cyanide, has a very intense, persistent odour, and yields by hydrolysis *ζ-phenylheptoic acid*, b. p. 205—210°/17 mm. (*amide*, m. p. 89°), from the *ethyl* ester, b. p. 175—177°/16 mm., of which is obtained *η-phenylheptyl alcohol*,

$$CH_2Ph\cdot[CH_2]_6\cdot OH,$$

b. p. 170—172°/15 mm. This alcohol has a pleasant odour of roses, which is less intense than that of the phenylhexyl alcohol (attention is particularly called to the alternating intensity of the odour of these homologous alcohols); its *acetate* has b. p. 188—190°/24 mm. *η-Phenylheptylamine*, b. p. 159—160°/16 mm., obtained by the reduction of the preceding nitrile, forms a *picrate*, m. p. 120—122°, *platinichloride*, m. p. 210—213° (decomp.), *aurichloride*, m. p. 103°, and quaternary *methiodide*, $CH_2Ph\cdot[CH_2]_6\cdot NMe_3I$, m. p. 164°. By the distillation of its oily *benzoyl* derivative with phosphorus pentachloride is obtained *η-chloroheptylbenzene*, b. p. 159—164°/17 mm.; the corresponding *bromide* and *iodide* have b. p. 170—175°/15 mm. and 179—184°/17 mm. respectively. The iodide combines with trimethylamine to form the preceding methiodide.

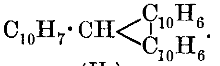
β-Chloroethylbenzene is conveniently obtained by reducing benzyl cyanide with sodium and alcohol, and distilling the benzoyl derivative of the resulting β-phenylethylamine (which need not be isolated) with phosphorus pentachloride; the yield is 65—70%. C. S.

Trinaphthylmethane Compounds. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1022—1039).—Further investigation of the alcohol described by Schmidlin and Massini (Abstr., 1909, i, 563) as tri-α-naphthylcarbinol and of the hydrocarbon, regarded as tri-α-naphthylmethane, obtained by the author by reduction of the carbinol (this vol., i, 436), shows that these compounds are really α-naphthyldi-αα-naphthafluoryl alcohol (I) and α-naphthyldi-αα-naphthafluorene (II) respectively:



$$C_{10}H_7\cdot C(OH){<}\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix}$$

(I.)

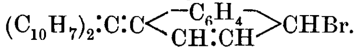


$$C_{10}H_7\cdot CH{<}\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix}.$$

(II.)

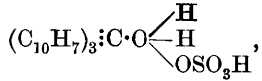
This stable carbinol, described by Schmidlin and Massini, is found to be formed as a result of the oxidising action of atmospheric oxygen on the unstable tri-α-naphthylcarbinol, with which it has no reactions in common, thus: $C_{31}H_{22}O + O_2 = C_{31}H_{20}O + H_2O_2$. This oxidation may also be carried out by means of neutral permanganate solution. These constitutions of the two compounds and that of the reduction product of the stable carbinol referred to above are confirmed by the previous and also by new analytical results.

Contrary to the opinion of Schmidlin and Massini, the yellow colour of the bromo-derivative (see below) of α-naphthyldi-αα-naphthafluoryl alcohol is probably due to its paraquinonoid structure,



$$(C_{10}H_7)_2{:}C{:}C{<}\begin{matrix}-C_6H_4-\\ CH{:}CH\end{matrix}{>}CHBr.$$

Also the red colour of the solution of this alcohol in sulphuric acid may be due to the formation of an oxonium compound,



$$(C_{10}H_7)_3{:}C\cdot O{<}\begin{matrix}H\\ H\\ OSO_3H\end{matrix},$$

and the blue colour obtained on heating this solution to loss of water and formation either of a carbonium salt, $(C_{10}H_7)_3{:}C\cdot OSO_3H$, or, more probably, of a complex compound of the type

$$(C_{10}H_7)_3{:}C\cdot O\cdot SO_3H,(H_2SO_4)_x.$$

Di-α-naphthyl ketone, obtained by the oxidation of di-α-naphthylcarbinol with sulphuric acid and potassium dichromate, forms large, yellow prisms, m. p. 98°. In view of the higher melting point (104°) of the colourless compound obtained by Schmidlin and Massini (Abstr., 1909, i, 561), it is regarded as possible that this ketone exhibits polymorphism.

Tri-α-naphthylcarbinol, $C_{31}H_{22}O$, prepared by the interaction of di-α-naphthyl ketone and magnesium α-naphthyl bromide in presence of ether, forms compounds with both ether and benzene, the former showing the greater inclination to oxidise in the air; both these compounds dissolve with some difficulty in sulphuric acid, giving pale yellow solutions, whilst the stable carbinol dissolves readily and forms an intense red solution. The amount of the solvent in the dry benzene compound cannot be determined by analysis. The carbinol free from solvent forms drusy masses of large, colourless prisms, m. p. 140—160° (decomp.). The hydroxyl group of tri-α-naphthylcarbinol is readily replaceable by halogens; thus the action of hydriodic acid in the cold on an acetic acid solution of the carbinol gives *iodotri-α-naphthylmethane*, $CI(C_{10}H_7)_3$, which crystallises in slender, unstable, white needles, decomposing at 159°; the corresponding *bromo*-derivative forms slender, white needles, m. p. 178° (decomp.).

α-Naphthyldi-αα-naphthafluoryl alcohol, obtained by oxidation of tri-α-naphthylcarbinol, crystallises from acetic acid in yellow prisms, m. p. 165°, and does not give the reaction for hydroxyl. α-Naphthyldi-αα-naphthafluoryl bromide, $C_{31}H_{19}Br$, forms an intensely lemon-yellow, crystalline powder, decomposing at 215—218°, and gives a deep blue solution with concentrated sulphuric acid. Reduction of the bromide with hydriodic acid yields α-naphthyldi-αα-naphthafluorene, m. p. 191°, identical with that obtained by reduction of α-naphthyldi-αα-naphthafluoryl alcohol (compare this vol., i, 436). T. H. P.

Preparation of Cholesteryl Ethers. OTTO DIELS and PAUL BLUMBERG (*Ber.*, 1911, **44**, 2847—2851).—The following cholesteryl ethers have been prepared by heating magnesium and cholesteryl chloride with the corresponding alcohol; the numbers in parenthesis denote the temperature and time of heating. *Methyl ether*, $C_{27}H_{45}\cdot OMe$, m. p. 84° (125°, twelve hours); *ethyl ether*, $C_{27}H_{45}\cdot OEt$, m. p. 88—90°, long needles (140°, eighteen hours); *propyl ether*, $C_{27}H_{45}\cdot OPr^{\alpha}$, m. p. 99·5—100·5°, long prisms (140—150°, six hours); benzyl ether, m. p. 114—115° (Obermüller gives 78°) (170°, seven hours).

An attempt to prepare α-cholestyl methyl ether from magnesium, α-cholestyl chloride, and methyl alcohol (140°, eight hours) led to the formation of a *hydrocarbon*, $C_{27}H_{46}$, m. p. 56°, leaflets or prisms. C. S.

Some Ethers of Cholesterol. WILHELM STEINKOPF and ERWIN BLÜMMER (*J. pr. Chem.*, 1911, [ii], **84**, 460—472).—When heated with ethyl iodide, the potassium derivative of cholesterol yields ethylene and cholesterol; with cholesteryl chloride it forms cholesterol and cholesterylene (compare Lindenmeyer, *J. pr. Chem.*, 1863, [i], **90**, 321).

By heating cholesteryl chloride with zinc dust or zinc oxide, Mauthner and Suida (Abstr., 1896, i, 425) obtained a substance which they considered to be cholesteryl ether. The authors have repeated these experiments, and find that the product consists of cholesterylene together with a small quantity of a substance, m. p. 210—225°.

Cholesteryl phenyl ether, $C_{27}H_{45}\cdot OPh$, obtained by heating cholesteryl chloride with sodium phenoxide, crystallises in lustrous, silvery leaflets, m. p. 157·5°, and has, in chloroform solution, $[\alpha]_D - 34·89°$; the p-*tolyl ether*, prepared in a similar manner, has m. p. 154·5°, $[\alpha]_D - 32·95°$ in chloroform solution. The benzyl ether, obtained by heating the potassium derivative of cholesterol with benzyl chloride at 100°, forms small, white needles, m. p. 118·5°, $[\alpha]_D - 26·02°$ (compare preceding abstract).

Cholesteryl p-*methylbenzyl ether*, $C_{27}H_{45}\cdot O\cdot CH_2\cdot C_6H_4Me$, prepared from ω-bromo-*p*-xylene in a similar manner, exists in several solid and liquid crystalline modifications. It melts at 129—130° to a turbid, opalescent liquid, which becomes clear at 141·5°; on cooling, the liquid again becomes turbid, and acquires a deep violet colour, which then passes successively into blue, green, red, and pink, solidification finally taking place at 130°; in chloroform solution it has $[\alpha]_D - 26·32°$. The m-*methylbenzyl ether* melts at 93—94° to a turbid liquid, which becomes isotropic at 125°, and shows the same colour changes as the preceding compound; in chloroform solution it has $[\alpha]_D - 31\cdot76^\circ$. A microcrystallographic examination of the two last-mentioned ethers is given by Lehmann. F. B.

l-Phytosterols. II. TIMOTHÉE KLOBB (*Ann. Chim. Phys.*, 1911, [viii], **24**, 410—421. Compare Abstr., 1910, i, 31; ii, 1100; 1911, i, 199).—The phytosterols of *Matricaria chamomilla, Tilia europea, Linaria vulgaris,* and *Verbascum thapsus* are described.

The oily matter left after the deposition of hydrocarbon by the acetone extract of *Matricaria chamomilla* (Abstr., 1910, ii, 1100) on treatment with potassium hydroxide in alcohol yields to ether a small amount of unsaponifiable matter, which after solution in hot alcohol deposits a mixture (m. p. 120—131°, $\alpha_D - 29\cdot3^\circ$) of needles and hexagonal lamellæ. This mixture gives the colour reactions of the *l*-phytosterols, and in addition a purple coloration with sulphuric acid containing nitrous acid. Acetic anhydride converts it into a mixture of acetyl derivatives, m. p. 150—175°, crystallising in lamellæ and flattened prisms. The mixture on bromination separates into a *substance*, $C_{36}H_{63}OAc,Br_4$, m. p. 158—160°, crystallising in hexagonal lamellæ, and a *product*, $C_{36}H_{43}OAc,Br_2$, m. p. 115—118°, which crystallises from benzene, on addition of alcohol, in microscopic granules.

[With J. GARNIER, in part.]—The unsaponifiable matter from the flowers of *Tilia europea* contains a phytosterol, $C_{27}H_{46}O$, $\alpha_D - 29\cdot7^\circ$, m. p. 126°, crystallising in hexagonal lamellæ, and giving normal colour reactions; the *benzoyl* derivative, m. p. 140°, and the *acetyl* derivative, m. p. 118—119°, crystallise in hexagonal lamellæ. The second of these gives a *dibromo*-compound, $C_{26}H_{43}OAc,Br_2$, m. p. 115—120°, which separates from benzene on addition of alcohol in microscopic granules.

The phytosterol, $C_{26}H_{44}O$, obtained from *Linaria vulgaris* (Abstr., 1907, ii, 123), gives a *benzoyl* derivative, $\alpha_D - 14\cdot55^\circ$, m. p. 142°, crystallising in nacreous, rectangular lamellæ, and an *acetyl* derivative, $\alpha_D - 38\cdot61^\circ$, m. p. 117—130°, which crystallises simultaneously in hexagonal lamellæ and short prisms, and may be a mixture.

[With R. EHRWEIN.]—The flowers of *Verbascum thapsus* treated by the general process (Abstr., 1910, ii, 1100) furnish *verbasterol*, $\alpha_D - 3^\circ 3'$, m. p. 142—144°, containing carbon 82·05% and hydrogen 11·89%, and crystallising in pearly, hexagonal lamellæ. On treatment with acetic anhydride two *substances* are formed; the *one* has m. p. 169—171°, and the *other*, m. p. 108—110°. It is impossible at present to say whether in this and the previous case the two acetyl derivatives are isomerides derived from the same phytosterol, or whether the original substance is a mixture and is resolved into its components by acetylation. T. A. H.

3:4-Dihydroxybenzyl-methyl and -dimethyl Amines. MARC TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 928—932).—These two bases, which are closely related to adrenaline and exhibit a similar but far weaker physiological action, are described.

3 : 4-*Dimethoxybenzyl alcohol* (*veratryl alcohol*), D^{16} 1·180, b. p. 169°/14 mm., obtained by the action of potassium hydroxide on veratraldehyde, is a viscous liquid; the *acetate*, b. p. 170—175°/13 mm., is a thick liquid; the *benzoate*, D^0 1·203, m. p. 36—37°, b. p. 233—236°/12 mm., crystallises on long keeping; the *phenylurethane*, m. p. 118°, is crystalline.

3 : 4-*Dimethoxybenzyl chloride*, m. p. 48°, is crystalline, and when heated with methylamine in a closed tube furnishes 3 : 4-*dimethoxybenzylmethylamine*, b. p. 135—140°/12 mm., the *hydriodide* of which has m. p. 170—171°. On demethylation, the base yields 3 : 4-*dihydroxybenzylmethylamine*, m. p. 179°, the *hydrochloride* of which has m. p. 182°.

When heated with dimethylamine in a closed tube, or when treated with this substance in dilute ethereal solution, 3 : 4-dimethoxybenzyl chloride yields 3 : 4-*dimethoxybenzyldimethylamine*, D^0 1·0578, b. p. 132—137°/12 mm., or 236—239°/760 mm., as a colourless liquid. This gives a *hydriodide*, m. p. 174°, a *methiodide*, m. p. 179°, and with acid anhydrides or chlorides furnishes the corresponding acyldimethylamines and dimethoxybenzyl esters. On demethylation of the parent base, 3 : 4-*dihydroxybenzyldimethylamine* is obtained, yielding a *hydrochloride*, m. p. 183°, which may also be prepared by the action of phosphorus pentachloride on 3 : 4-*methylenedioxybenzyldimethylamine*, D^0 1·101, b. p. 125°/13 mm. The latter was obtained by heating piperonyl chloride (Decker and Koch, Abstr., 1905, i, 473) with dimethylamine in a closed tube. The *hydrochloride* has m. p. 223°, the *hydriodide*, m. p. 135°, and the *methiodide*, m. p. 233°.

Piperonyl alcohol furnishes an *acetate*, m. p. 48°, and a phenylurethane, m. p. 102·5°. T. A. H.

2:3- and 3:4-Dihydroxybenzylamines. René Douetteau (*Bull. Soc. chim.*, 1911, [iv], 9, 932—938. Compare preceding abstract).—These substances were prepared with a view to comparing their physiological action with that of adrenaline.

2 : 3-*Dimethoxybenzylamine*, D^0 1·1243, b. p. 137°/11 mm., obtained by reduction of 2 : 3-dimethoxybenzaldoxime (Noelting, Abstr., 1910, i, 176), is a colourless, oily liquid; the *hydrochloride*, m. p. 159°, is crystalline; the *picrate*, m. p. 205°, forms golden-yellow needles; the *methiodide* has m. p. 174°; the *acetyl* derivative, m. p. 94°, b. p. 210—211°/10 mm., is crystalline, and when treated with sodium in boiling benzene and then submitted to the action of methyl iodide furnishes 2 : 3-*dimethoxyphenylacetomethylamide*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot NMeAc,$$

D^0 1·1506, b. p. 202—205°/13 mm. (approx.), as a pale yellow, viscous liquid. When heated with acetic anhydride at 150—160° this decomposes, furnishing the initial amide (compare Tiffeneau, this vol., i, 778).

2 : 3-*Dihydroxybenzylamine hydriodide*, m. p. 149°, obtained by the action of hydriodic acid on the dimethyl ether referred to above, is crystalline, and on treatment with silver chloride yields the *hydrochloride*, m. p. 186°; both salts give a green coloration with ferric chloride.

3 : 4-*Dimethoxybenzylamine*, b. p. 154—158°/12 mm. (approx.), prepared like its isomeride, is a colourless oil; the *hydrochloride*, m. p. 257°, the *picrate*, m. p. 169°, and the *methiodide*, m. p. 228°, were obtained crystalline. On demethylation by hydriodic acid, 3 : 4-*dihydroxybenzylamine hydriodide*, m. p. 205°, is produced, from which the *hydrochloride*, m. p. 172°, is obtained by agitation with silver chloride. T. A. H.

1-Amino*cyclo*pentane-1-carboxylic Acid. NICOLAI D. ZELINSKY and G. STADNIKOFF (*Zeitsch. physiol. Chem.*, 1911, **75**, 350—351. Compare Abstr., 1906, i, 425).—1-Amino*cyclo*pentane-1-carboxylic acid has been obtained by the interaction of *cyclo*pentanone, ammonium chloride, and potassium cyanide in aqueous alcoholic solution, and subsequent hydrolysis of the nitrile so formed by means of hydrochloric acid. It separates from water in monoclinic crystals containing $1H_2O$, decomp. 320°. The *copper* salt was analysed. H. W.

Naphthenic Acids. I. PETROFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1198—1201).—Crude naphthenic acid from Baku naphtha was carefully purified from neutral substances and then converted into methyl esters, of which the three following were isolated: (1) b. p. 161—163°/748 mm.; the acid from this has b. p. 211—213°, which corresponds with that of Markownikoff's heptanaphthenic acid (Abstr., 1893, i, 93); (2) b. p. 169—171°/748 mm., the acid from which has b. p. 218—220°, corresponding with that of Colman and Perkin's 1-methylpentamethylene-2-carboxylate (Trans., 1888, **53**, 185), and (3) $C_7H_{13}\cdot CO_2Me$, b. p. 177—178°/736 mm., D_0^0 0·9455, $D_{21\cdot7}^{21\cdot7}$ 0·9295, $n_D^{21\cdot7}$ 1·43005.

Reduction of ester (3) by Bouveault and Blanc's method (Abstr., 1903, i, 597) yields the *alcohol*, $C_8H_{15}\cdot OH$, as a colourless, viscous liquid with a pleasant odour, b. p. 183—184°/756 mm., or 103—104°/35 mm., D_0^0 0·8943, $D_{23\cdot5}^{23\cdot5}$ 0·8808, $n_D^{23\cdot5}$ 1·44541.

The alcohol was converted through the xanthate into the naphthylene, b. p. about 108°, which contained an admixture of toluene, and hence was not analysed.

When the ester (3) was heated in a sealed tube with concentrated ammonia solution at 150°, it was converted into a mixture of two amides, which after several fractional crystallisations showed m. p. 117° and 160° respectively, but it is possible that the separation was not complete; it is probable that these two amides are *cis*- and *trans*-isomerides. Two other fractions, b. p. 192° and 200°, were also separated, and are being investigated. T. H. P.

***o*-Amino-*p*-sulphobenzoic Acid and its Derivatives, with Special Reference to their Fluorescence. II.** JOSEPH H. KASTLE and R. L. HADEN (*Amer. Chem. J.*, 1911, **46**, 508—518).—It has been shown in an earlier paper (this vol., i, 200) that when disilver *o*-amino-*p*-sulphobenzoate is treated with ethyl iodide, *o*-ethylamino-*p*-sulphobenzoic acid is produced. In one experiment, a small quantity of a sulphur-yellow compound was obtained, which has now been found to be diethyl *o*-ethylamino-*p*-sulphobenzoate,

$$CO_2Et\cdot C_6H_3(NHEt)\cdot SO_3Et,$$

m. p. 151—153° (uncorr.); it crystallises in yellow needles, and on hydrolysis is converted into *o*-ethylamino-*p*-sulphobenzoic acid.

When *o*-amino-*p*-sulphobenzoic acid (1 mol.) is heated with its disilver salt (1 mol.), an acid silver salt,

$$CO_2H\cdot C_6H_3(NH_2)\cdot SO_3H,CO_2Ag\cdot C_6H_3(NH_2)\cdot SO_3Ag,2H_2O,$$

is formed, which on being treated with ethyl iodide is converted into a mixture of diethyl *o*-ethylamino-*p*-sulphobenzoate and the original amino-acid.

Comparison has been made of the fluorescence in various solvents of *o*-amino-*p*-sulphobenzoic acid, *o*-ethylamino-*p*-sulphobenzoic acid, and the diethyl ester of the latter. The substitution of an ethyl group for a hydrogen atom of the carboxyl or amino-group has the effect of increasing the blue tint of the fluorescence; thus, in a mixture of equal volumes of water and alcohol, *o*-amino-*p*-sulphobenzoic acid shows a pinkish-purple fluorescence, and the ethylamino-acid a pure blue, whilst the diethyl ester of the latter gives a yellow solution with a pure blue fluorescence.

o-Aminoterephthalic acid exhibits a reddish-blue fluorescence in dilute aqueous and alkaline solutions, and a pure blue fluorescence in acetone solutions. Aqueous solutions of the mono- and di-ethyl esters show a pure blue fluorescence. E. G.

Isomerism of the Three *allo*-Cinnamic Acids. JULIUS MEYER (*Ber.*, 1911, **44**, 2966—2970).—Evidence is adduced in support of Biilmann's (Abstr., 1909, i, 155, 382; 1910, i, 346) view of the relationship of the three acids as opposed to Stobbe's explanation of their isomerism (this vol., i, 859).

Biilmann's observation that any one of the three acids may be obtained by inoculating the melted substance with the required acid is confirmed (Abstr., 1909, i, 155) and extended by the observation that a supersaturated solution behaves similarly. A spontaneously crystallised fusion of one form can be converted into a second form by inoculation, and the rate of this transformation descends in the following order, $42° \rightarrow 68° > 42° \rightarrow 58° > 58° \rightarrow 68°$. The velocity of crystallisation is greatest for the 68° acid and least for the 42° acid. The heat developed in the change of one form into either of the other two is too small to be measured. The spontaneously crystallised fusion may consist of all three acids, and no difference in behaviour could be observed whichever form was melted in the first instance. Solutions of all three acids at the same concentration and temperature have the same electrical conductivity (compare Biilmann, Abstr., 1910, i, 346), but the solubility in water is least for the 68° acid and greatest for the 42° acid. All these observations are in harmony with Biilmann's view that the *allo*-cinnamic acids are polymorphous modifications of *cis*-cinnamic acid. T. A. H.

Transformations of *cis*-Cinnamic Acid. HUGO R. KRUYT (*Ber.*, 1911, **44**, 3108—3115. Compare Stobbe, this vol., i, 859). To explain Stobbe's results (*loc. cit.*), Tammann's theory of the mechanism of spontaneous crystallisation must be extended to the equilibrium solid–solid. The maximum rate of crystallisation occurs at a much higher temperature than that of the formation of crystalline nuclei. When a liquid is undercooled and warmed again slightly, no crystallisation takes place at the lower temperature, but it sets in rapidly on warming, owing to the marked formation of nuclei at the lower temperature. Stobbe's results are criticised in detail, and shown to be fully in agreement with this hypothesis. E. F. A.

Compounds of 3:5-Dinitro-4-hydroxybenzoic Acid with Hydrocarbons. II. OTTO MORGENSTERN (*Monatsh.*, 1911, **32**, 711—746. Compare Abstr., 1910, i, 482).—It is sought by physical chemical measurements to establish the composition of the coloured compounds of 3 : 5-dinitro-4-hydroxybenzoic acid with aromatic hydrocarbons previously described (Abstr., 1910, i, 482). Measurements have been made of the equilibrium between hydrocarbon and acid in alcoholic solution.

If two molecules of acid combine with one of hydrocarbon $(c_1^2.c_2)/c_3$ = a constant, c_1, c_2, and c_3 being the concentrations of free acid, free hydrocarbon, and of the compound of the two respectively.

The values of c_1, c_2, and c_3 were determined experimentally in two ways. In the first a small proportion of hydrocarbon was added to the saturated solution of acid; in the second a little acid was added to the saturated hydrocarbon solution. The results show that in the second series the expression $(c_1^2.c_2)/c_3$ was not a constant, but that equilibrium was obtained between an equal number of molecules of acid and hydrocarbon, or, in other words, $(c_1.c_2)/c_3$ = a constant. The first series in which acid was in excess pointed to the formation of a compound 2 acid + hydrocarbon as assumed.

Two series of compounds are thus proved to exist in the case of phenanthrene, retene, and fluorene with dinitrohydroxybenzoic acid.

The *compound* acid + phenanthrene crystallises in yellow needles, m. p. 180° (decomp.).

The *compound* acid + fluorene is a yellowish-white powder, m. p. 210—214° (decomp.).

The analogous retene *compound* forms yellow plates, m. p. 220° (decomp.). E. F. A.

Studies on Tautomerism. V. Enolic Forms of Methyl Benzoylacetate and Acetylacetone. LUDWIG KNORR (*Ber.*, 1911, **44**, 2767—2772. Compare Meyer, this vol., i, 833).—The enolic forms of methyl benzoylacetate and acetylacetone can be isolated by the methods previously given in the case of ethyl acetoacetate (this vol., i, 516), with the difference that in these cases the enolic and not the ketonic forms crystallise out on strongly cooling solutions of the equilibrium mixtures. Methyl benzoylacetate when dissolved in a mixture of ether and light petroleum deposits at −78° acicular crystals, which can be collected, washed, and dried in the apparatus previously described. The freshly prepared substance has m. p. about 40° (bath previously heated), and gives an intense coloration with alcoholic ferric chloride solution. It has $n_D^{12.5}$ 1·5620, whilst the equilibrium mixture has $n_D^{12.5}$ 1·5418. These properties indicate that it is the enolic form of the ester, and, in fact, the same substance is obtained (but it is not so pure) by treating an aqueous solution of the pure sodium salt (see below) with the calculated quantity of normal sulphuric acid at 0°. The production of the ketonic form takes place fairly rapidly. The crystals liquefy gradually even in a desiccator, and the oil attains to the refractive index of the equilibrium mixture in the course of hours or days according to the name of the containing vessel.

The sodium and iron salts of the enolic ester were also prepared. The *sodium* salt, $C_{10}H_9O_3Na$, is obtained in small laminæ by mixing at 0° a methyl-alcoholic solution of sodium methoxide with the equivalent quantity of the ester dissolved in ether. The *sodium* salt of ethyl benzoylacetate, $C_{11}H_{11}O_3Na$, is similarly prepared. The *ferric* salt of methyl benzoylacetate, $Fe(C_{10}H_9O_3)_3$, is prepared by mixing at 0° a methyl-alcoholic solution of the ester with an ethereal solution of ferric chloride, and the salt is washed with water until the chlorine reaction disappears. After recrystallisation, it forms red needles, m. p. 188° (previously sintering). From the reaction in dilute ethereal solution of molecular quantities of ferric chloride and the ester, an *iron* salt containing chlorine is obtained. It forms compact, yellow, hygroscopic crystals, which on analysis yield numbers corresponding fairly well with the formula $FeCl_2(C_{10}H_9O_3),3H_2O$. It dissolves in water and alcohol, with production of the deep reddish-violet coloration characteristic of the iron reaction.

[With HERMANN FISCHER.]—The enolic form of acetylacetone has been isolated by strongly cooling solutions of the equilibrium mixture. The crystalline substance has m. p. $-9°$, n_D^{15} 1·4609. At the ordinary temperature the substance rapidly changes into the allelotropic mixture of diketone and enol-ketone (n_D^{15} 1·4550); at 15° the transformation is complete in twenty minutes By withdrawal of the enolic isomeride with copper hydroxide, preparations containing much of the ketonic form have also been obtained. R. V. S.

General Additive Reaction between Alkylidene-urethanes and β-Dicarboxylic Compounds.

G. BIANCHI and ROBERT SCHIFF (*Gazzetta*, 1911, **41**, ii, 81—93).—When a concentrated alcoholic solution of equimolecular quantities of ethyl acetoacetate and urethane are treated with a corresponding quantity of benzaldehyde and a few drops of concentrated hydrochloric acid, the mixture becomes solid in a few minutes (formation of benzylidenediurethane), then liquefies, and finally solidifies two days later. The substance produced (compare Schiff and Bertini, Abstr., 1897, i, 493) is the additive product, *ethyl urethanobenzylacetoacetate*, $CO_2Et·CHAc·CHPh·NH·CO_2Et$, which is a white, microcrystalline powder, m. p. 96—97°. When slightly warmed with concentrated sulphuric acid, it gives a red coloration. The analogous compounds described were similarly prepared, and the reaction appears to be a general one.

Ethyl urethanobenzylbenzoylacetate,

$$CO_2Et·CHBz·CHPh·NH·CO_2Et,$$

is a white, minutely crystalline powder, m. p. 97°.

Urethanobenzylacetylacetone, $CHAc_2·CHPh·NH·CO_2Et$, forms a white, crystalline powder, m. p. 101°; its alcoholic solution gives a red coloration with ferric chloride when warmed.

Ethyl urethanocinnamylacetoacetate, $CHPh{:}CH{\cdot}CH(NH{\cdot}CO_2Et){\cdot}CHAc{\cdot}CO_2Et$, is a white, microcrystalline powder, m. p. 92—93°.

Urethanocinnamylacetylacetone, $CHPh{:}CH{\cdot}CH(CHAc_2){\cdot}NH{\cdot}CO_2Et$, is a white, microcrystalline powder, m. p. 107°, and gives an intense red coloration with ferric chloride.

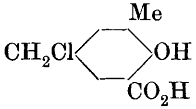
Urethanoanisylacetylacetone, $OMe{\cdot}C_6H_4{\cdot}CH(CHAc_2){\cdot}NH{\cdot}CO_2Et$, is a white, crystalline powder, m. p. 98°; with ferric chloride it gives an intense red coloration.

Urethanosalicylacetylacetone, $OH{\cdot}C_6H_4{\cdot}CH(CHAc_2){\cdot}NH{\cdot}CO_2Et$, is a white, crystalline powder, m. p. 128—130°, and gives a red coloration with ferric chloride.

All the compounds described are very stable towards mineral acids. R. V. S.

Preparation of Unsymmetrical Substituted Diphenylmethane Derivatives. ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. JOH. RUD. GEIGY (D.R.-P. 236046).—When 2-hydroxy-*m*-toluic acid is treated with chloromethyl alcohol (or analogous reagents) in the presence of fuming hydrogen chloride, condensation takes place in the para-position to the hydroxyl group.

2-*Hydroxy*-3-*methyl*-5-*chloromethylbenzoic acid* (annexed formula) is a colourless, crystalline powder, m. p. 197°; when heated with water it furnishes, in part, 2-*hydroxy*-3-*methyl*-5-*hydroxymethylbenzoic acid*, $CO_2H{\cdot}C_6H_2Me(OH){\cdot}CH_2{\cdot}OH$, hard prisms, m. p. 186°; in part, the *anhydro*-compound an amorphous, colourless, insoluble, infusible powder.



2-*Hydroxy*-5-*diethylaminobenzyl*-3-*methylbenzoic acid* is prepared by heating 2-hydroxy-3-methyl-5-chloromethylbenzoic acid with diethylaniline, first at 70°, and subsequently at 100°; the *sodium* salt forms glistening leaflets, and the free acid crystallises in tablets, m. p. 171°.

2-*Hydroxy*-5-*ethylaminotolylmethyl*-3-*methylbenzoic acid*, glistening prisms, m. p. 184°, is prepared from 2-hydroxy-3-methyl-5-hydroxymethylbenzoic acid (or its anhydro-compound) and ethyl-*o*-toluidine in the presence of hydrogen chloride at 110—120°; the *sodium* salt forms glistening leaflets.

2-*Hydroxy*-5-*methylaminobenzyl*-3-*methylbenzoic acid*, leaflets, m. p. 193°; 2-*hydroxy*-5-*dimethylaminobenzyl*-3-*methylbenzoic acid*, glistening, silvery scales, m. p. 195°; 2-*hydroxy*-5-*dimethylaminotolylmethyl*-3-*methylbenzoic acid*, glistening, pearly leaflets, m. p. 167°; 2-*hydroxy*-5-*diethylaminochlorobenzyl*-3-*methylbenzoic acid*, prisms, m. p. 152°, and 2-*hydroxy*-5-*diethylaminodichlorobenzyl*-3-*methylbenzoic acid*, needles, m. p. 230°, were also prepared. F. M. G. M.

Action of Sodium Amalgam on Naphtholcarboxylic Acids. HUGO WEIL (*Ber.*, 1911, 44, 3058—3062).—When reduced with sodium amalgam in aqueous solution in the presence of boric acid and sodium hydrogen sulphite, α-naphthol-2-carboxylic acid yields 1-hydroxy-2-naphthaldehyde (Bezdzik and Friedländer, Abstr., 1909, i, 416).

β-Naphthol-3-carboxylic acid is reduced, under similar conditions, to tetrahydronaphthaldehyde, and β-naphthoic acid to β-naphthaldehyde, whilst α-naphthoic acid remains unchanged.

[With WALTER HEERDT.]—4-Sulphoxyl-α-naphthol-2-carboxylic acid is converted into 1-hydroxy-2-naphthaldehyde, the sulphoxyl group being eliminated during the reduction.

4-Bromo-α-naphthol-2-carboxylic acid, obtained by brominating α-naphthol-2-carboxylic acid in glacial acetic acid solution (compare Schmitt and Burkhard, Abstr., 1888, 59), is reduced by sodium amalgam to *4-bromo-1-hydroxy-2-naphthaldehyde*. This crystallises in yellow needles, m. p. 112°, yields a *phenylhydrazone*, m. p. 159°, and condenses with primary aromatic amines, yielding anils; the *compound*, $C_{17}H_{12}ONBr$, obtained from aniline, forms orange-yellow needles, m. p. 161°; the *compounds*, $C_{18}H_{14}ONBr$, formed by condensation with *o*- and *p*-toluidine crystallise in yellowish-red needles, m. p. 188° and 171° respectively; the *compound* from α-naphthylamine has m. p. 196°.

4-Chloro-α-naphthol-2-carboxylic acid, $C_{11}H_7O_3Cl$, prepared by chlorinating α-naphthol-2-carboxylic acid in glacial acetic acid solution, has m. p. 228°. It is reduced by sodium amalgam to *4-chloro-1-hydroxy-2-naphthaldehyde*, which crystallises in yellow needles, m. p. 103°, and yields an *oxime*, m. p. 194°, and a *phenylhydrazone*, m. p. 153°; the *azine*, $C_{22}H_{14}O_2N_2Cl_2$, forms yellow needles, m. p. 179°. The aldehyde yields a *sodium* salt, crystallising in yellow leaflets, and condenses with aniline, yielding the *anil*, $C_{17}H_{12}ONCl$, which crystallises in yellow needles, m. p. 157°; with α-naphthylamine it forms the *compound*, $C_{21}H_{14}ONCl$, reddish-yellow leaflets, m. p. 188°; the *compounds*, $C_{18}H_{14}ONCl$, obtained by condensation with *o*- and *p*-toluidine are orange-yellow, and have m. p. 183° and 164° respectively. F. B.

Addition of Hydrogen Bromide to Cinnamylidenemalonic Acid, Cinnamylideneacetic Acid, and Phenylbutadiene.

C. N. RIIBER (*Ber.*, 1911, 44, 2974—2978).—The addition of hydrogen bromide (1 mol.) to methyl cinnamylidenemalonate (compare Hinrichsen, Abstr., 1904, i, 1012) and to methyl cinnamylideneacetate in the αβ-position (contrary to the predictions of Thiele's theory) has been proved as follows. Ethereal solutions of the respective esters are treated with hydrogen bromide; the solution of the additive compound is treated with magnesium and subsequently with water, the resulting product being finally oxidised by potassium permanganate. In both cases benzoic and succinic acids are obtained. The reaction between α-phenyl-$\Delta^{\alpha\gamma}$-butadiene and ethereal hydrogen bromide yields, in addition to a small quantity of a crystalline *substance*, $C_{10}H_9Br,2HBr$, m. p. 146°, an unstable *oil*, $CHPh{:}CH{\cdot}CHBrMe$, which reacts with ethereal zinc methyl at 100° to form a *hydrocarbon*, $C_{11}H_{14}$, b. p. 84—86°/13 mm., from which benzoic and *iso*butyric acids are obtained by oxidation with potassium permanganate. C. S.

[Preparation of Derivatives of Anthraquinonecarboxylic Acids and of Anthraquinoneacridones.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 237236 and 237237).—Condensation products of chloro- and amino-anthraquinones have previously been described; it is now found that similar condensations take place with halogen- or nitro-anthraquinonecarboxylic acids (or bases) in the presence of condensing agents, such as aluminium chloride, sulphuric acid, or copper.

1-*Anilinoanthraquinone-2-carboxylic acid* is prepared by heating 1-nitro- or 1-chloro-anthraquinone-2-carboxylic acid with aniline at 120—130° in the presence of copper powder and anhydrous sodium acetate; it forms glistening, brown leaflets, m. p. 297—298°; the *sodium* salt, glistening, violet-black needles, gives a deep violet solution in water, and when heated at 50—60° with phosphorus pentachloride in benzene solution with aluminium chloride furnishes an *anthraquinoneacridone* as a violet-red powder.

p-*Toluidino-1-anthraquinone-2-carboxylic acid*, a violet powder, is similarly obtained with *p*-toluidine.

4′-*Chloro-1-anilinoanthraquinone-2-carboxylic acid*, a carmine-red powder, is furnished by the employment of *p*-chloroaniline.

1-*Naphthylamino-1-anthraquinone-2-carboxylic acid* is a violet powder, and the *product* from 1-chloroanthraquinone-2-carboxylic acid (2 mols.) and 4 : 4′-diaminodiphenylmethane (1 mol.), a violet-red powder, all of which furnish the corresponding *anthraquinoneacridone* on treatment with phosphorus pentachloride.

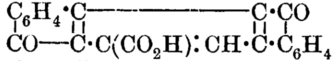
The colours of the solutions given by these substances in various solvents and other tinctorial properties are described in the original.

The second patent describes the preparation of 1-*anilinoanthraquinone-2-carboxyl chloride*, glistening, reddish-brown leaflets, by the action of phosphorus pentachloride on a benzene solution of the foregoing acid at 50—60°; this, by heating at 200° with trichlorobenzene until the evolution of hydrogen chloride ceases, yields the anthraquinoneacridone in violet-red needles.

1-*Naphthylaminoanthraquinone-2-carboxyl chloride*, a reddish-brown powder, is obtained by treating the corresponding acid with thionyl chloride, and on boiling with xylene furnishes the anthraquinoneacridone.

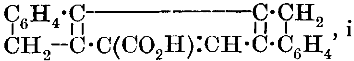
F. M. G. M.

Oxidation of Phthalacene. D. MAROTTA (*Gazzetta*, 1911, 41, ii, 59—63).—The oxidation of the methyl group of phthalacene (compare Errera, Abstr., 1908, i, 183) can be effected by means of nitric acid, and 3 : 4 : 5 : 6-dibenzoylenebenzoic acid,



$$\begin{array}{l} C_6H_4\cdot C\text{———————}C\cdot CO \\ CO\text{—}C\cdot C(CO_2H)\colon CH\cdot C\cdot C_6H_4 \end{array},$$

is produced. From this, on reduction, 3 : 4 : 5 : 6-dibenzylenebenzoic acid,

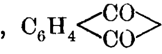


$$\begin{array}{l} C_6H_4\cdot C\text{———————}C\cdot CH_2 \\ CH_2\text{—}C\cdot C(CO_2H)\colon CH\cdot C\cdot C_6H_4 \end{array},$$

is obtained. 3 : 4 : 5 : 6-*Dibenzoylenebenzoic acid* is prepared by heating phthalacene with dilute nitric acid (D 1·035) in a sealed tube for five hours at 200°. In this way nitration is avoided, but the reaction must be completed by opening the tube, decanting the liquid, adding more acid, and then re-heating at 200° for five hours. The substance is an orange-red powder, m. p. 299—300°. The *potassium* salt, $C_{21}H_9O_4K,3H_2O$, can be prepared, but is very readily hydrolysable. From it the *silver* salt is obtained, and from this the *ethyl* ester, $C_{20}H_9O_2{\cdot}CO_2Et$, which forms silky, yellow needles, m. p. 230°.

3 : 4 : 5 : 6-*Dibenzylenebenzoic acid* is obtained by heating the above acid with hydriodic acid and phosphorus in a sealed tube for five hours at 200°; it forms minute, pale yellow needles, m. p. above 300°. The alkali salts can be hardly isolated on account of their hydrolysability. From the *silver* salt the *ethyl* ester (brown crystals, m. p. 136—137°) was prepared. R. V. S.

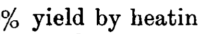
Derivatives of Phthalic Acid Containing Sulphur and Nitrogen.

ARNOLD REISSERT and HERMANN HOLLE (*Ber.*, 1911, **44**, 3027—3040).—Thiophthalic anhydride,  $C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}S$, m. p. 114°, is conveniently prepared by triturating phthalic anhydride and crystallised sodium sulphide in a mortar, adding water, and pouring the mixture into dilute hydrochloric acid; the product is freed from phthalic acid by repeated extraction with aqueous sodium carbonate. It is converted into phthalide by reduction with 8% sodium amalgam.

Ethyl thiolphthalate, $CO_2Et{\cdot}C_6H_4{\cdot}CO{\cdot}SEt$, b. p. about 194°/10 mm., is obtained by treating thiophthalic anhydride with cold alcoholic sodium ethoxide, and adding ethyl iodide. In a similar manner the isomeric esters, $CO_2R{\cdot}C_6H_4{\cdot}CO{\cdot}SR'$ and $CO_2R'{\cdot}C_6H_4{\cdot}CO{\cdot}SR$, have been prepared; thus (S)-*methyl ethyl thiolphthalate*,

$$CO_2Et{\cdot}C_6H_4{\cdot}CO{\cdot}SMe,$$

b. p. 209°/16 mm., D 1·1923, is obtained by adding methyl iodide to thiophthalic anhydride in alcoholic sodium ethoxide, and yields phthalic acid, ethyl alcohol, and methyl mercaptan by hydrolysis, whilst *methyl* (S)-*ethyl thiolphthalate*, $CO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}SEt$, b. p. 209°/16 mm., D 1·1906, is prepared by adding ethyl iodide to the anhydride in methyl-alcoholic sodium methoxide, and yields phthalic acid, methyl alcohol, and ethyl mercaptan by hydrolysis. When chloro-2 : 4-dinitrobenzene in methyl alcohol is added to a cold methyl-alcoholic solution of sodium methoxide and thiophthalic anhydride, and the mixture is subsequently boiled, tetranitrodiphenyl sulphide and (S)-2 : 4-*dinitrophenyl methyl thiolphthalate*, $CO_2Me{\cdot}C_6H_4{\cdot}CO{\cdot}S{\cdot}C_6H_3(NO_2)_2$, m. p. 121°, yellow prisms, are obtained. *Methyl dithiolphthalate*, $C_6H_4(CO{\cdot}SMe)_2$, m. p. 124°, yellowish-brown leaflets or needles, is obtained by the addition of methyl sulphate to the liquid produced by the trituration of thiophthalic anhydride and crystallised sodium sulphide.

Thiophthalanil,  $C_6H_4{<}\begin{smallmatrix}CO\\CS\end{smallmatrix}{>}NPh$, m. p. about 144°, long, red needles, is obtained in 80% yield by heating phthalanil and phosphorus pentasulphide in boiling xylene containing a little aniline as a sulphur-carrier, and is purified best by conversion into thiophthalanilic acid by alcoholic sodium hydroxide, the acid being reconverted into the anhydride by boiling with water. The hydrolysis of thiophthalanil by *N*-sodium hydroxide and alcohol, and the subsequent oxidation of the product by potassium ferricyanide, yields *benzthiazole*-1-o-*benzoic acid*,

$CO_2H\cdot C_6H_4\cdot C{<}\begin{smallmatrix}S\\N\end{smallmatrix}{>}C_6H_4$, m. p. 189°, the *methyl* ester of which has m. p. 73°; the *hydrochloride*, $C_{14}H_9O_2NS,HCl$, and the *copper* and *calcium* salts are described, the latter yielding 1-phenylbenzthiazole by distillation.

Iminophthalanil, $C_6H_4{<}\begin{smallmatrix}CO\text{——}\\C(:NH)\end{smallmatrix}{>}NPh$, m. p. 170°, yellow needles, obtained from thiophthalanil and carbamide at 140—150°, dissolves in alkalis and in dilute acids, and yields *methyliminophthalanil*, $C_6H_4{<}\begin{smallmatrix}CO\text{——}\\C(:NMe)\end{smallmatrix}{>}NPh$, m. p. 145°, with methyl sulphate in alkaline solutions, and *benzyliminophthalanil*, m. p. 120°, with benzyl chloride and alcoholic sodium ethoxide. *Oximinophthalanil*,

$$C_6H_4{<}\begin{smallmatrix}CO\text{——}\\C(:NOH)\end{smallmatrix}{>}NPh,$$

m. p. 246° (decomp.), prepared from thiophthalanil, hydroxylamine sulphate, and sodium carbonate in alcoholic solution, is very stable, and has a strongly acidic, but no basic, character. The bromination of iminophthalanil in chloroform yields *bromoiminophthalbromoanil dibromide*, $C_6H_4{<}\begin{smallmatrix}CO\text{——}\\C(:NBr_3)\end{smallmatrix}{>}N\cdot C_6H_4Br$, brown needles, which reddens at 180°, loses bromine, and yields *bromoiminophthalbromoanil*, $C_{14}H_8ON_2Br_2$, m. p. 242°, colourless leaflets. C. S.

Compounds of the Propane Series. II. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 3084—3091. Compare this vol., i, 644).—When heated at 200° and then distilled under diminished pressure, α-phthaliminoisobutyryl chloride loses carbon monoxide and hydrogen chloride, yielding *β-phthaliminopropylene*, $C_8H_4O_2:N\cdot CMe:CH_2$. This crystallises from alcohol in lustrous, hexagonal needles, m. p. 105—106°, and is hydrolysed by dilute acids to phthalic acid and acetone. It combines with bromine, forming *αβ-dibromo-β-phthaliminopropane*,

$$C_8H_4O_2:N\cdot CMeBr\cdot CH_2Br,$$

which forms lustrous, glassy needles, m. p. 86—89°, and, in the presence of moisture, decomposes into phthalimide and bromoacetone. When heated above its m. p. under diminished pressure, the dibromo-compound loses hydrogen bromide and yields a mixture of two isomeric *bromo-β-phthaliminopropylenes*, $C_8H_4O_2:N\cdot C:C_2H_3Br$, of which the one crystallises in leaflets or needles, m. p. 150—151°, whilst the other forms flat needles, m. p. 90—91°, with previous sintering at 86°. The interaction of bromine and *phthaliminoisobutyryl bromide* (obtained from phthaliminoisobutyric acid and phosphorus pentabromide) yields *dibromo-β-phthaliminopropylene*, $C_8H_4O_2:N\cdot C_3H_3Br_2$, which crystallises in lustrous needles, m. p. 169—170°; the same compound is obtained by the interaction of bromine and phthaliminoisobutyryl chloride.

Tribromo-β-phthaliminopropylene, $C_8H_4O_2:N\cdot C_3H_2Br_3$, obtained by the action of phosphorus and excess of bromine on phthaliminoisobutyric acid, crystallises in stout needles, resembling gypsum, m. p. 106—107°. It is hydrolysed by potassium hydroxide in aqueous alcoholic solution to a *dibasic acid*, $C_{11}H_9O_5N$. This crystallises in small needles, which become brown at 135° and decompose at

141—144°; the *silver* salt, $C_{11}H_7O_5NAg_2,1\frac{1}{2}H_2O$, and *barium* salt, $C_{11}H_7O_5NBa,3H_2O$, are described.

It is suggested that the above-mentioned tribromo-compound has the constitution $C_8H_4O_2{:}N\cdot C(CHBr_2){:}CHBr$ or

$$C_8H_4O_2{:}N\cdot C(CH_2Br){:}CBr_2,$$

whilst the dibasic acid has probably the formula

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH(CO_2H){:}CH_2.$$

When phthaliminocyclopropane (*loc. cit.*) is heated with excess of bromine on the water-bath, it yields a *tribromo*-derivative, $C_{11}H_6O_2NBr_3$, which crystallises in colourless needles, m. p. 162—163°, with previous softening at 159°, and is isomeric with the above tribromo-β-phthaliminopropylene. F. B.

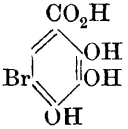
Preparation of 2:4-Diamino*iso*phthalic Acid and Derivatives.

Marston Taylor Bogert (D.R.-P. 236848).—Diacetyl-*m*-xylylene-4:6-diamine, m. p. 295° (compare Morgan, Trans., 1902, **81**, 93), when oxidised with potassium permanganate in the presence of magnesium sulphate yields 4:6-*diacetylamino*iso*phthalic acid*, colourless needles, m. p. 276°, which on hydrolysis with concentrated hydrochloric acid furnishes 4:6-*diamino*iso*phthalic acid hydrochloride* as yellow needles; the free *acid* is a colourless powder, m. p. 235° (decomp.); the *bisacetylanthranil* of the acid is crystalline, m. p. 283°, and forms with aniline (2 mols.) a condensation *product*, colourless needles, m. p. 315°. F. M. G. M.

Trihydroxybenzoic Acids.

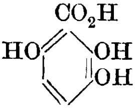
Franz von Hemmelmayr (*Monatsh.*, 1911, **32**, 773—791).—The influence of the position of the hydroxyl groups on the entry of bromine, and on the chemical behaviour of the substitution compounds obtained, has been studied in the case of the trihydroxybenzoic acids.

Phloroglucinolcarboxylic acid does not form a substitution compound, but on treatment with bromine, carbon dioxide is eliminated, and ultimately di- or tri-bromophloroglucinol is formed.



Pyrogallolcarboxylic acid forms a monobromo-derivative, which in view of the fact that it can be esterified, is considered to have the annexed constitution. Further treatment with bromine causes the elimination of carbon dioxide and subsequent formation of di- or tri-bromopyrogallol. The former is probably identical with a substance described by Einhorn (Abstr., 1904, i, 238).

The hydroxyquinolcarboxylic acid described by Thiele and Jäger (Abstr., 1901, i, 701) cannot be esterified by alcohol and hydrogen chloride. Accordingly, the annexed constitutional formula is the most probable. Only one bromine atom could be introduced, further action again causing elimination of the carboxylic group and formation of a dibromohydroxyquinol. The monobromo-compound could not be esterified.



The rate of elimination of carbon dioxide on boiling with water has been determined for each of these compounds; in general, the entry of the bromine atom doubles the rate of decomposition.

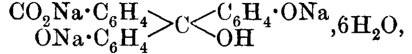
Dibromophloroglucinol forms colourless, lustrous needles, m. p. 171—172°; it dissolves in sodium carbonate or in ammonia with an orange-yellow coloration. *Dibromophloroglucinyl triacetate* forms colourless needles, m. p. 128—129°.

Monobromopyrogallolcarboxylic acid forms colourless or slightly yellow needles, which on heating sinter, decomp. 230°. The *barium* salt forms crystalline plates; the methyl ester separates in colourless needles, m. p. 135°. *Dibromopyrogallol* forms bunches of brown needles, which sinter at 160°, decomp. 173°. *Tribromopyrogallol* forms yellowish-brown plates, decomp. 180—186°.

The *barium* salt of hydroxyquinolcarboxylic acid separates in brown crystals. *Monobromohydroxyquinolcarboxylic acid* forms feather-like groups of needles, decomp. 199°. *Dibromohydroxyquinol* forms large, colourless, prismatic crystals.

E. F. A.

Preparation of Tribasic Phenolphthalates. PHILIP A. KOBER and J. THEODORE MARSHALL (*J. Amer. Chem. Soc.*, 1911, **33**, 1779—1783).—In an earlier paper (this vol., i, 300), tripotassium phenolphthalate was described. An account is now given of the preparation of this salt and the corresponding trisodium salt,



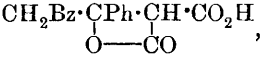
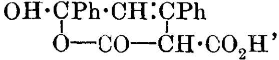
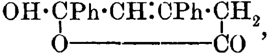
$$\begin{matrix}CO_2Na\cdot C_6H_4\\ ONa\cdot C_6H_4\end{matrix}>C<\begin{matrix}C_6H_4\cdot ONa\\ OH\end{matrix},6H_2O,$$

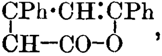
which crystallises in rhombohedra, and is more soluble, but less stable, than the potassium salt. Of the three alkali atoms in these salts, two are readily displaced by the action of weak acids, such as acetic and carbonic acids, whilst the third, probably that attached to the carboxyl group, is more resistant, but is easily displaced by mineral acids.

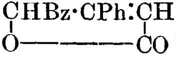
E. G.

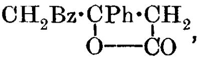
Unsaturated δ-Ketonic Acids. ELMER P. KOHLER (*Amer. Chem. J.*, 1911, **46**, 474—502).—Unsaturated δ-lactonic acids have now been prepared for the first time. They can be readily obtained by the methods used for preparing the corresponding saturated compounds, or by introducing bromine into saturated ketonic acids and eliminating hydrogen bromide from the product.

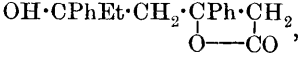
Methyl γ-benzoyl-β-phenylethylmalonate can be obtained in good yield by the condensation of methyl malonate with phenyl styryl ketone in presence of piperidine; on hydrolysis, it yields the free acid. The *ethyl* ester, $CH_2Bz\cdot CHPh\cdot CH(CO_2Et)_2$, m. p. 65°, forms friable needles, and, on bromination, yields two stereoisomeric *ethyl γ-bromo-γ-benzoyl-β-phenylethylmalonates*, m. p. 88° and 43°, the former crystallising in needles and the latter in large prisms or tablets. The methyl ester similarly yields two *bromo*-derivatives, m. p. 113° and 87°, crystallising in needles and prisms respectively; on the addition of bromine to solutions of these compounds in carbon tetrachloride, two isomeric *methyl αγ-dibromo-γ-benzoyl-β-phenylethylmalonates*, m. p. 132° and 94°, are produced, which crystallise in needles and large tablets respectively.

Methyl γ-benzoyl-β-phenylvinylmalonate, $CHBz\!:\!CPh\cdot CH(CO_2Me)_2$, m. p. 94°, obtained by the action of potassium hydroxide on the methyl γ-bromo-γ-benzoyl-β-phenylethylmalonates, forms large, transparent prisms or tablets; it does not combine with bromine, but yields a *bromo*-derivative, m. p. 141°, which crystallises in prisms or tablets. When methyl γ-benzoyl-β-phenylvinylmalonate is hydrolysed with potassium hydroxide, *mono-* and *di-potassium* salts are produced, which on treatment with acids yield *γ-benzoyl-β-phenylbutyrolactonic acid*,  $\begin{array}{l}\mathrm{CH_2Bz\cdot CPh\cdot CH\cdot CO_2H}\\ \quad\mathrm{O{-\!\!-\!\!-}CO}\end{array}$, which crystallises from water in small, lustrous pyramids containing $2H_2O$. When heated the hydrated acid melts at about 100°, then loses water, re-solidifies, and finally melts and decomposes at about 170°. The product of hydrolysis of the unsaturated ester contains also a small quantity of *δ-hydroxy-βδ-diphenylcrotolactonic acid*,  $\begin{array}{l}\mathrm{OH\cdot CPh\cdot CH\!:\!CPh}\\ \quad\mathrm{O{-\!\!-}CO{-\!\!-}CH\cdot CO_2H}\end{array}$, m. p. about 170°, which crystallises in slender needles. When this acid is heated above its m. p., it is converted into benzoylphenylvinylacetic acid and *δ-hydroxy-βδ-diphenyl-δ-crotolactone*,  $\begin{array}{l}\mathrm{OH\cdot CPh\cdot CH\!:\!CPh\cdot CH_2}\\ \quad\mathrm{O{-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-}CO}\end{array}$, m. p. 124°.

When benzoylphenylbutyrolactonic acid is heated at 170—185° until carbon dioxide ceases to be evolved, four substances are produced, namely: (1) γ-benzoyl-β-phenylvinylacetic acid; (2) an *acid*, m. p. 180°, isomeric with γ-benzoyl-β-phenylvinylacetic acid, and crystallising in large plates; (3) γ-benzoyl-β-phenyl-β-butyrolactone, and (4) a small quantity of an unsaturated *lactone*, probably  $\begin{array}{l}\mathrm{CPh\cdot CH\!:\!CPh}\\ \mathrm{CH{-}CO{-}O}\end{array}$, m. p. 172°, which forms thin, lemon-yellow plates.

γ-Benzoyl-β-phenylvinylacetic acid, $CHBz\!:\!CPh\cdot CH_2\cdot CO_2H$, m. p. 135°, forms small, colourless prisms. When a solution of this acid in methyl alcohol is saturated with hydrogen chloride, *methyl β-chloro-γ-benzoyl-β-phenylbutyrate*, $CH_2Bz\cdot CPhCl\cdot CH_2\cdot CO_2Me$, m. p. 131°, is produced, which crystallises in slender needles. The unsaturated acid combines with bromine to form two stereoisomeric *βγ-dibromo-γ-benzoyl-β-phenylbutyric acids*, $CHBzBr\cdot CPhBr\cdot CH_2\cdot CO_2H$, which decompose without melting; one form crystallises in plates and the other in slender needles. When these dibromides are added to solution of sodium hydrogen carbonate, they are converted into a *lactone*, probably  $\begin{array}{l}\mathrm{CHBz\cdot CPh\!:\!CH}\\ \mathrm{O{-\!\!-\!\!-\!\!-\!\!-}CO}\end{array}$, m. p. 131°, which forms pale yellow needles.

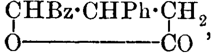
γ-Benzoyl-β-phenyl-β-butyrolactone,  $\begin{array}{l}\mathrm{CH_2Bz\cdot CPh\cdot CH_2}\\ \quad\mathrm{O{-\!\!-}CO}\end{array}$, m. p. 93°, crystallises in needles or prisms, and is very stable; it is not affected when boiled with water or sodium carbonate solution, and does not decompose when heated at 200°. When the lactone is added to alcoholic potassium hydroxide, it is converted into γ-benzoyl-β-phenylvinylacetic acid, and if treated with methyl alcohol and hydrogen chloride, it is transformed into methyl β-chloro-γ-benzoyl-β-phenylbutyrate. If a solution of the lactone in glacial acetic acid is saturated with hydrogen bromide, *β-bromo-γ-benzoyl-β-phenylbutyric acid*, $CH_2Bz\cdot CPhBr\cdot CH_2\cdot CO_2H$, is produced, which forms long needles and decomposes without melting. When an ethereal solution of γ-benzoyl-β-phenyl-β-butyrolactone is treated with magnesium ethyl bromide and the product is decomposed with water before the addition of acid, δ-*hydroxy*-$\beta\delta$-*diphenyl*-β-*heptolactone*,



$$\begin{array}{l}\mathrm{OH{\cdot}CPhEt{\cdot}CH_2{\cdot}\underset{|}{C}Ph{\cdot}\underset{|}{C}H_2}\\ \qquad\qquad\qquad\quad\mathrm{O{-\!-\!-}CO}\end{array},$$

m. p. 190°, is produced, but if the magnesium derivative is poured directly into a mixture of ice and hydrochloric acid, a *stereoisomeride*, m. p. 140°, is formed. On adding acids to solutions of the potassium salts of these lactones, a third *isomeride*, m. p. 150°, is obtained, which must be a δ-lactone.

γ-*Bromo*-γ-*benzoyl*-β-*phenylbutyric acid*, $\mathrm{CHBzBr{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H}$, was obtained in two stereoisomeric forms by the action of bromine on benzoylphenylbutyric acid, one, m. p. about 189° (decomp.), which forms flat needles or plates, and the other, m. p. 145° (decomp.), which crystallises in small prisms; the corresponding *methyl* esters have m. p. 132° and 87° respectively. When these bromo-acids are dissolved in a solution of sodium carbonate, each is converted into a mixture of two stereoisomeric γ-*benzoyl*-β-*phenyl*-γ-*butyrolactones*,

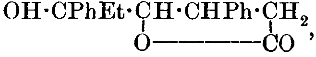


$$\begin{array}{l}\mathrm{\underset{|}{C}HBz{\cdot}CHPh{\cdot}\underset{|}{C}H_2}\\ \mathrm{O{-\!-\!-\!-\!-\!-\!-\!-\!-}CO}\end{array},$$

one, m. p. 130°, forming large tablets, and the other, m. p. 98°, lustrous needles. γ-*Hydroxy*-γ-*benzoyl*-β-*phenylbutyric acid*,

$$\mathrm{OH{\cdot}CHBz{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H},$$

m. p. 160° (decomp.), obtained when either of the lactones is dissolved in alcoholic potassium hydroxide and subsequently acidified, forms long, colourless needles. By the action of magnesium ethyl bromide on the lactone of m. p. 130°, γ-*hydroxy*-γ-*benzoyl*-β-*phenyl*-γ-*heptolactone*,

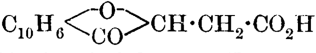


$$\begin{array}{l}\mathrm{OH{\cdot}CPhEt{\cdot}\underset{|}{C}H{\cdot}CHPh{\cdot}\underset{|}{C}H_2}\\ \qquad\quad\;\mathrm{O{-\!-\!-\!-\!-\!-\!-}CO}\end{array},$$

m. p. 103°, is produced, which crystallises in needles.

E. G.

peri-Naphthalideacetic Acid. HERMANN PAULY [with WILHELM WALTER] (*Ber.*, 1911, **44**, 2785—2786. Compare Sachs and Brigl, this vol., i, 719).—This substance,



$$\mathrm{C_{10}H_6}\!\left\langle\begin{matrix}\mathrm{-O-}\\ \mathrm{CO}\end{matrix}\right\rangle\!\mathrm{CH{\cdot}CH_2{\cdot}CO_2H},$$

was prepared by oxidation of naphthalidedimethyl ketone (Zink, Abstr., 1902, i, 159) with sodium hypobromite. It crystallises in rosettes of needles, m. p. 168·5° (bath previously heated), 158° (bath not previously heated). The *silver* salt, $\mathrm{C_{14}H_9O_4Ag}$, forms microscopic laminæ.

R. V. S.

Preparation of Acyl Derivatives of o-Salicyloxybenzoic Acids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 236196 and 237211). —When *o*-salicyloxybenzoic acid is treated with condensing agents (such as acetic anhydride), acyl derivatives of general formula

$$\mathrm{R{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H}$$

(R = an acyl group) are obtained, and the acetyl and ethylcarbonyl derivatives (Abstr., 1910, i, 386) have now been prepared by the action of acetic anhydride and ethylchlorocarbonate respectively on salicyloxybenzoic acid.

o-*Benzoyloxy*-o-*benzoyloxybenzoic acid*, leaflets, m. p. 152°, was obtained by the action of benzoyl chloride on *o*-salicyloxybenzoic acid in aqueous alkaline solution, and o-*salicyloxybenzoyl carbonate*, $C_{29}H_{18}O_{11}$, m. p. 192°, in a similar manner with carbonyl chloride.

The second patent states that the preparation of *o*-acyloxybenzoyloxybenzoic acids proceeds smoothly without the application of heat if the required *o*-acyloxybenzoic acid is left in contact with a tertiary amine during a long period. A solution of acetyloxybenzoic acid in pyridine was found after some days to contain *o*-acetyloxybenzoyloxybenzoic acid, and a dimethylaniline solution of ethylcarbonylsalicylic acid furnished *o*-ethylcarbonyloxybenzoyloxybenzoic acid. F. M. G. M.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 245—249. Compare Paolini, this vol., i, 779; Tiffeneau, Abstr., 1910, i, 379).—The author now finds that the above reaction is given also by anisylacetone and other ketones, so that he no longer maintains the opinion that the substance obtained by the dehydration of anethole glycol is an aldehyde.
R. V. S.

[Solutions of Benzaldehyde and Hydrogen Cyanide in Water.] LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1911, **249**, 510—511. Compare Abstr., 1909, i, 623).—A reply to Wirth, this vol., i, 875.
T. A. H.

Preparation of *o*-Nitrobenzaldehyde. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 237358).—When dilute aqueous solutions of salts of *o*-ω-dinitrotoluene are treated at a low temperature with potassium permanganate, they yield *o*-nitrobenzaldehyde according to the equation :

$$3NO_2\cdot C_6H_4\cdot CH:NO_2Na + 2KMnO_4 + H_2O = 3NO_2\cdot C_6H_4\cdot CHO + 3NaNO_2 + 2MnO_2 + 2KOH.$$

If the mixture is kept neutral or only slightly alkaline, a theoretical yield of pure *o*-nitrobenzaldehyde is produced. F. M. G. M.

Oxidation of *m*-Nitrobenzoylformaldehyde. WILLIAM L. EVANS and EDGAR JOHN WITZEMANN (*J. Amer. Chem. Soc.*, 1911, **33**, 1772—1779).—In an earlier paper (Abstr., 1908, i, 338) an account has been given of the behaviour of *m*-nitrobenzoylcarbinol towards oxidising agents. The work has now been extended to the preparation and oxidation of *m*-nitrobenzoylformaldehyde.

The *osazone* of *m*-nitrobenzoylformaldehyde, m. p. 223°, forms dark red needles.

When the aldehyde is treated with potassium permanganate in neutral or alkaline solution, or with potassium ferricyanide, freshly precipitated silver oxide, or freshly precipitated mercuric oxide in presence of sodium hydroxide in each case, *m*-nitrobenzoic acid is the sole product of oxidation. In the absence of alkali hydroxide, freshly precipitated silver oxide and mercuric oxide do not effect the oxidation of the compound at the ordinary temperature, but at 100° convert it into *m*-nitrobenzoic acid. When the aldehyde is treated with hot solutions of copper acetate or with alkali hydroxides, it is transformed into *m*-nitromandelic acid.

The results of these experiments and those recorded in the earlier paper (*loc. cit.*) indicate that *m*-nitrobenzoylcarbinol and *m*-nitrobenzoylformaldehyde behave similarly to the parent substances (compare Evans, Abstr., 1906, i, 269), but that they are more sensitive to reagents in the presence of alkali hydroxides. Moreover, the nitro-derivatives show a greater tendency to progress to the benzoic acid stage, yielding *m*-nitrobenzoic acid, than to give the possible intermediate compounds, namely, *m*-nitromandelic and *m*-nitrophenylglyoxylic acids. E. G.

Catalytic Conversion of 1-Methyl*cyclo*pentane-3-one into Methyl*cyclo*pentane. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2781—2782).—Skita and Ritter (this vol., i, 272) have shown that the catalytic reduction of a number of substances containing six-membered rings is attended by the production of small quantities of the corresponding saturated cyclic hydrocarbons. The author finds that catalytic reduction of 1-methyl*cyclo*pentane-3-one with nickel at 150—160° yields a mixture of water, the alcohol, the ketone, and the hydrocarbon, whilst if the temperature is raised to 250°, methyl*cyclo*pentane is obtained in good yield. The fact that at this temperature no dehydrogenisation occurs marks the difference between the five-membered and the six-membered ring. R. V. S.

Catalytic Reduction in a Vacuum. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2779—2780).—Reductions by means of hydrogen in the presence of nickel can be accomplished under reduced pressure. From 1 : 3-dimethyl-Δ^3-*cyclo*hexene-5-one at 200° and 75—80 mm., 1 : 3-dimethyl*cyclo*hexanone was obtained. From *iso*phorone at a pressure of 70—75 mm., the temperature of the nickel being 180°, dihydro*iso*phorone was produced. R. V. S.

Synthesis of New Hydroaromatic Ketones. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1911, **153**, 772—775. Compare Abstr., 1910, i, 856; 1907, i, 627).—A description of new ketones obtained by the action of an organomagnesium halides on acid chlorides at −10°. The products are purified from small quantities of tertiary alcohols through the agency of their semicarbazones.

cyclo*Hexoyl*cyclo*hexene*, $C_6H_{11}\cdot CO\cdot C_6H_9$, b. p. 136°/19 mm., forms a *semicarbazone*, m. p. 117—118°. n-*Butyryl*cyclo*hexane*,

$$C_6H_{11}\cdot CO\cdot C_3H_7,$$

b. p. 94°/13 mm., forms a *semicarbazone*, m. p. 153—154°.

The following acid chlorides were obtained by the action of thionyl chloride on the acids: cyclo*Hexeneacetyl chloride*, $C_6H_{11}\cdot CH_2\cdot COCl$, b. p. 98—100°/23 mm.; 2-*methyl*cyclo*hexeneacetyl chloride*, b. p. 104—105°/13 mm.; 3-*methyl*cyclo*hexeneacetyl chloride*, b. p. 95—96°/11 mm.; 4-*methyl*cyclo*hexeneacetyl chloride*, b. p. 109—110°/8 mm.; 4-*methyl*cyclo*hexylacetyl chloride*, b. p. 75°/7 mm.

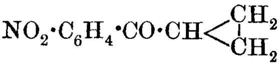
1-Methyl-4-*tert.*-butyl*cyclo*hexanone (this vol., i, 290) condenses with ethyl chloroacetate, giving *ethyl hydroxy*-1-*methyl*-4-tert.-*butyl*cyclo*hexaneacetate*, $C_4H_9\cdot C_7H_{11}(OH)\cdot CH_2\cdot CO_2Et$, b. p. 129—131°/3 mm. This has been converted into *ethyl* 1-*methyl*-4-tert.-*butyl*cyclo*hexene-acetate*, b. p. 136—139°/10 mm.; the corresponding *acid* has b. p. 174—177°/10 mm., and the *chloride*, b. p. 127—128°/8 mm. *Ethyl* 1-*methyl*-4-tert.-*butyl*cyclo*hexaneacetate* has b. p. 146—149°/14 mm.; the corresponding *acid* has b. p. 173—176°/12 mm., and the *chloride*, b. p. 134—136°/12 mm.

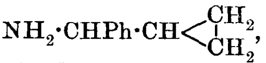
These new chlorides give rise to the following ketones when treated with magnesium methyl iodide: 1-*Acetonyl*cyclo*hexene*,

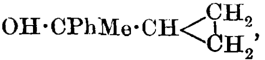
$$C_6H_9\cdot CH_2\cdot COMe,$$

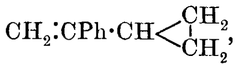
b. p. 79—80°/11 mm.; *semicarbazone*, m. p. 176°. *Acetonyl*-2-*methyl*-cyclo*hexene*, b. p. 212°; *semicarbazone*, m. p. 170°. *Acetonyl*-3-*methyl*-cyclo*hexene*, b. p. 206—207°; *semicarbazone*, m. p. 154°. 1-*Acetonyl*-4-*methyl*cyclo*hexene*, b. p. 208°; *semicarbazone*, m. p. 160—161°. *Acetonylmethylbutyl*cyclo*hexene*, b. p. 135—136°/10 mm.; *semicarbazone*, m. p. 206°. W. O. W.

Action of the Chloroanhydride of *cyclo*Propanecarboxylic Acid on Benzene in Presence of Aluminium Chloride. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1163—1173).—The author has confirmed the formation of benzoyl*cyclo*propane by the decomposition of benzoyl*cyclo*propanecarboxylic acid (Perkin), and shows that this ketone is also obtained by the interaction of the chloroanhydride of *cyclo*propanecarboxylic acid and benzene in presence of aluminium chloride at 35—60°. Benzoyl*cyclo*propane, obtained by the latter method, gives a γ-benzoylpropyl bromide, m. p. 35°, whilst this compound when prepared from the benzoyl*cyclo*propane given by Perkin's method has m. p. 30·5°; this difference is not explained The action of potassium hydroxide on γ-benzoylpropyl bromide yields benzoyl*cyclo*propane.

m-*Nitrobenzoyl*cyclo*propane*,  $NO_2\cdot C_6H_4\cdot CO\cdot CH<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, separates from methyl alcohol in rectangular plates, m. p. 77°, and on reduction with tin and hydrochloric acid yields a crystalline *base*, m. p. 97—98°, the diazo-compound of which combines with naphthols, forming scarlet azo-colouring matters.

cyclo*Propylbenzylamine*,  $NH_2\cdot CHPh\cdot CH<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, obtained by reducing the oxime of benzoyl*cyclo*propane in alcoholic solution with sodium, has b. p. 234·7—235°/749 mm., D_0^0 0·9996—1·0019, $D_0^{17\cdot5}$ 0·9884, D_0^{20} 0·9843, n_D 1·5353—1·5360. The *hydrochloride*, m. p. 220—221°, *platinichloride*, $(C_{10}H_{11}NH_2)_2,H_2PtCl_6$, m. p. 177° (decomp.), and the *thiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_{10}H_{11}$, m. p. 124°, were prepared. Oxidation of the amine by means of permanganate yields benzoyl*cyclo*propane.

*Phenyl*cyclo*propylmethylcarbinol*,  $OH\cdot CPhMe\cdot CH<\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, obtained by the interaction of benzoyl*cyclo*propane and magnesium methyl iodide, has b. p. 241—242°/761 mm., 151—152°/51 mm., D_0^{20} 1·0316, n_D 1·5350.

*α-Phenyl-α-*cyclo*propylethylene*,  $CH_2{:}CPh{\cdot}CH{<}\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}$, prepared by the action of acetic acid on the preceding compound, has b. p. 211—213°/758 mm., D_0^{19} 0·9553, n_D 1·5497, and gives a golden-yellow coloration with a drop of concentrated sulphuric acid. T. H. P.

Aromatic Amino-ketones. Franz Kunckell (*Ber. deut. pharm. Ges.*, 1911, **21**, 419—456).—Various amino-ketones, in the form of their acetyl derivatives, have been prepared by heating acetanilide and an acyl halide with aluminium chloride in carbon disulphide and decomposing the resulting aluminium double compound with very dilute hydrochloric acid at 0°; the hydrolysis of the acetyl derivative is effected by 20% hydrochloric acid. It seems essential to success in the process that the acyl halide should have a b. p. exceeding 80—90°, or should be halogenated; for instance, the method fails with acetyl chloride or *iso*butyryl chloride, but yields good results with acetyl bromide or chloroacetyl chloride.

p-*Aminopropiophenone*, $NH_2{\cdot}C_6H_4{\cdot}COEt$, m. p. 140°, yellow needles, forms an *acetyl* derivative, m. p. 161°, *hydrochloride*, m. p. 225°, *sulphate*, m. p. 225°, *oxime*, m. p. 153°, and *ethyl carbamate*, m. p. 154°. It reacts with carbonyl chloride in benzene to form *di-*p*-propionylphenylcarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}COEt)_2$, m. p. 271°, whilst its hydrochloride reacts with hot aqueous potassium cyanate to form p-*propionylphenylcarbamide*, m. p. 218°.

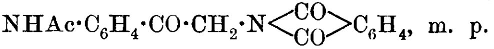
p-*Aminobutyrophenone*, m. p. 84°, colourless needles, forms an *acetyl* derivative, m. p. 142°, *hydrochloride*, m. p. 178°, *sulphate*, m. p. 216°, *ethyl carbamate*, m. p. 128°, and *benzoyl* derivative, m. p. 170°. p-*Butyrylphenylcarbamide* and *di-*p*-butyrylphenylcarbamide* have m. p. 194° and 235° respectively.

*ω-Chloro-*p*-acetylaminoacetophenone*, $NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Cl$, m. p. 212°, yields *p*-acetylaminobenzoic acid by oxidation, and forms the following derivatives in consequence of the reactivity of the chlorine atom: p-*Acetylaminophenyl phenoxymethyl ketone*,

$$NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OPh,$$

m. p. 145°; p-*acetylaminobenzoylmethyl acetate*,

$$NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OAc,$$

m. p. 162° (the hydrolysis of which yields p-*acetylamino-ω-hydroxyacetophenone*, m. p. 176°, *phenylhydrazone*, m. p. 223°); p-*acetylaminobenzoylmethylbenzoate*, m. p. 200—201°; and p-*acetylamino-ω-phthaliminoacetophenone*,  $NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}N{<}\begin{matrix}CO\\ CO\end{matrix}{>}C_6H_4$, m. p. 277°. By treatment with nitric acid, D 1·5, at 0°, ω-chloro-*p*-acetylaminoacetophenone yields *ω-chloro-*m*-nitro-*p*-acetylaminoacetophenone*, yellow crystals, m. p. 120°; *ω-chloro-*m*-nitro-*p*-aminoacetophenone*, m. p. 185°, obtained by its hydrolysis, yields *m*-nitro-*p*-aminobenzoic acid on oxidation. The bromination of ω-chloro-*p*-acetylaminoacetophenone in chloroform at 100° yields *ω-chloro-*2 : 5*-dibromo-*4*-acetylaminoacetophenone*, m. p. 137°, the oxidation of which by alkaline hydrogen peroxide yields 2 : 5-*dibromo-*4*-aminobenzoic acid*, m. p. above 350°;

this acid yields 2 : 5-dibromobenzoic acid and *p*-dibromobenzene by the successive elimination of the amino- and the carboxyl groups. *ω-Chloro-*p*-aminoacetophenone*, m. p. 146°, obtained by the hydrolysis of its acetyl derivative, forms a *hydrochloride* and *benzoyl* derivative, m. p. 177°. It reacts with potassium acetate and potassium benzoate respectively to form p-*aminobenzoylmethyl acetate*,

$NH_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_3$,

m. p. 135°, and the corresponding *benzoate*, m. p. 188°; the hydrolysis of the former yields p-*amino-ω-hydroxyacetophenone*,

$NH_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot OH$,

m. p. 165° (*phenylhydrazone*, m. p. 199°).

By bromination in glacial acetic acid at 70°, ω-chloro-*p*-acetylaminoacetophenone yields *ω-chloro-ω-bromo-*p*-acetylaminoacetophenone*,

$NHAc\cdot C_6H_4\cdot CO\cdot CHClBr$,

m. p. 162°, which is converted into *p*-acetylaminobenzoic acid by oxidation and into *ω-chloro-ω-bromo-*p*-aminoacetophenone*, m. p. 80·5° (*hydrochloride*, m. p. 182°), by hydrolysis. By diazotisation and treatment with cuprous cyanide, ω-chloro-*p*-aminoacetophenone yields p-*chloroacetylbenzonitrile*, $CN\cdot C_6H_4\cdot CO\cdot CH_2Cl$, m. p. 98—100°, which is converted into the corresponding *acid*, m. p. 210°, by hydrolysis.

Chloroacetyl chloride, *m*-chloroacetanilide, and aluminium chloride react in carbon disulphide to form ω-m-*dichloro*-p-*acetylaminoacetophenone*, $NHAc\cdot C_6H_3Cl\cdot CO\cdot CH_2Cl$, m. p. 146—147°, which has been converted successively into 2-chloro-4-aminobenzoic acid and 2-chloro-4-hydroxybenzoic acid, and yields by hydrolysis ω-m-*dichloro*-p-*aminoacetophenone*, m. p. 96—97° (*hydrochloride*, m. p. 178°). In a similar manner, chloroacetyl chloride and *m*-bromoacetanilide yield ω-*chloro*-m-*bromo*-p-*acetylaminoacetophenone*, m. p. 113°, which is converted into the *amino*-compound, m. p. 97—98° (*hydrochloride*, m. p. 180°), by hydrolysis and into 2-bromo-4-aminobenzoic acid by oxidation. Chloroacetyl chloride and *o*-acetotoluidide yield ω-*chloro*-3-*acetylamino*-4-*methylacetophenone*, $NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2Cl$, m. p. 160°, which is converted by oxidation, hydrolysis, and diazotisation successively into o-*acetylamino*-p-*toluic acid*, m. p. 267—270° (decomp.), *o*-amino-*p*-toluic acid, and *p*-toluic acid; it yields ω-*chloro*-ω-*bromo*-3-*acetylamino*-4-*methylacetophenone*, m. p. 110°, by bromination in acetic acid, and reacts with potassium acetate or benzoate to form an *acetate*,

$NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_3$,

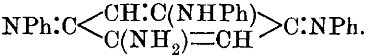
m. p. 90°, or *benzoate*, m. p. 130°. The nitration of ω-chloro-3-acetylamino-4-methylacetophenone yields a *nitro*-compound, m. p. 204°, the constitution of which is proved by its conversion ultimately into *o*-nitro-*p*-toluic acid.

ω-*Chloro*-5-*acetylamino*-3-*methylacetophenone*, m. p. 145°, yields m-*chloroacetyl*-m-*toluidine*, m. p. 132°, by hydrolysis. C. S.

α-Amino*iso*butyrophenone, $NH_2\cdot CMe_2\cdot COPh$. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 3091—3092).—When kept for three weeks, α-amino*iso*butyrophenone (this vol., i, 212) is converted into a crystalline *substance*, $C_{30}H_{37}O_2N_3$, which separates from light petroleum in lustrous, glassy, flat, obliquely-cut needles or rhombohedral crystals,

m. p. 105—106°. An aqueous solution of the compound becomes strongly alkaline when boiled with water, owing to reconversion into the original amino-ketone. It dissolves in warm hydrochloric acid, yielding α-amino*iso*butyrophenone hydrochloride, which forms a *platinichloride*, $(C_{10}H_{13}ON)_2H_2PtCl_6$, m. p. 205—206°, with previous sintering at 195°. F. B.

Oxidation of Aniline. III. RIKŌ MAJIMA and YOSHIHIKO AOKI (*Ber.*, 1911, **44**, 3080—3084. Compare this vol., i, 216).—By the oxidation of aniline with lead peroxide, Börnstein (Abstr., 1901, i, 375) obtained a compound, which he considered to be 2-amino-*p*-benzoquinonedianil. The compound is readily prepared by oxidising aniline in aqueous acetic acid solution at 0° with lead peroxide. Determinations of the molecular weight and analysis of its hydrochlorides show that it has the composition $C_{24}H_{20}N_4$, and not $C_{18}H_{15}N_3$. From its solubility in organic solvents, and the fact that it yields azophenine when heated with aniline in glacial acetic acid solution, the authors conclude that it has the constitution :



$$\mathrm{NPh{:}C}<\begin{matrix}\mathrm{CH{:}C(NHPh)}\\ \mathrm{C(NH_2){=}CH}\end{matrix}>\mathrm{C{:}NPh}.$$

2-Amino-5-anilino-*p*-benzoquinonedianil forms a *monohydrochloride*, $C_{24}H_{20}N_4,HCl$, and a *dihydrochloride*, $C_{24}H_{20}N_4,2HCl,3H_2O$; the *acetyl* derivative, $C_{26}H_{22}ON_4$, crystallises in long, bluish-red prisms, m. p. 212°. F. B.

Binary Systems of which One Component is an Organic Compound and the Other an Inorganic Salt. BORIS N. MENSCHUTKIN (*J. Chim. Phys.*, 1911, **9**, 538—558. Compare this vol., i, 65).—A résumé of the author's work since 1903 on the additive organic compounds of magnesium, aluminium, and calcium haloids. R. J. C.

Photochemical Reactions of the Nitrophenylindones. I. MARUSSIA BAKUNIN and E. LANIS (*Gazzetta*, 1911, **41**, ii, 155—184).—4-Nitro-2-phenylindone, when kept in sunlight, yields a substance, m. p. 320—325° (decomp.), which has the same percentage composition and is very indifferent to chemical reagents. Solutions of 4-nitro-2-phenylindone in various solvents, when exposed to light, deposited crystalline substances (apparently mixtures) of different and inconstant melting points. From the ethereal solution three substances are produced, which cannot be separated by recrystallisation, but on melting the mixture of all three the substance of m. p. 218° is converted into 4-nitro-2-phenylindone, which can be removed. From the remainder, two substances can be obtained, one having m. p. 280°, and the other m. p. about 320° ; the latter is identical with the substance obtained from 4-nitro-2-phenylindone without a solvent. The products obtained in the case of other solvents were similar to the three just described.

6-Nitro-2-phenylindone remains unchanged in sunlight, but when its solutions are exposed to light, mixtures of crystalline substances are produced. In the case of the benzene solution the product was separated into three substances, m. p. 227—229°, about 280°, and above 300° respectively.

In the formation of 4-nitro-2-phenylindone from 4-nitro-α-phenylcinnamic acid and phosphoric oxide in chloroform, a small quantity of a yellow, crystalline substance, m. p. 286°, is obtained.

R. V. S

Chloroiminoquinones. LEMUEL CHARLES RAIFORD (*Amer. Chem. J.*, 1911, **46**, 417—456).—Stieglitz and Earle (Abstr., 1904, i, 39) have described stereoisomeric chloroimino-acid ethers, and Stieglitz and Peterson (Abstr., 1910, i, 323; this vol., i, 879) have prepared stereoisomeric chloroimino-ketones. In the present paper, an account is given of experiments undertaken with the object of determining whether stereoisomerism could be observed in the chloroiminoquinones. Six chloroiminoquinones of a structure which should admit of the formation of stereoisomerides have been studied, but in no case was stereoisomerism discovered.

2-*Bromo*-4-*aminophenol*, m. p. 165°, crystallises in pale brown needles; its *hydrochloride* darkens at 225°, but does not melt.

2-*Bromo*-4-*chloroiminoquinone*, $O{:}C_6H_3Br{:}NCl$, prepared by the action of hypochlorous acid on 2-bromo-4-aminophenol, forms yellow crystals, and decomposes at about 60°.

2-*Chloro*-6-*bromo*-4-*aminophenol*, m. p. 181°, obtained by reducing the corresponding nitrophenol with stannous chloride, crystallises in thin plates, and is probably identical with the compound obtained by Clark (Abstr., 1893, i, 321). 2-*Chloro*-6-*bromo*-4-*chloroiminoquinone*, m. p. 87—88°, forms yellow crystals.

2 : 4 : 6-*Trichloro*-m-*cresol*, m. p. 47°, prepared by the action of sodium hypochlorite on *m*-cresol, crystallises in colourless plates, and on oxidation is converted into 2 : 6-dichlorotoluquinone; the *acetate*, b. p. 273—274°, was obtained as a colourless, viscous liquid.

When a solution of 2 : 4 : 6-tribromo-*m*-cresol in glacial acetic acid is treated with sodium nitrite, 2 : 4-dibromo-6-nitro-*m*-cresol, m. p. 134° (decomp.), and 2 : 6-dibromo-4-nitro-*m*-cresol, m. p. 87°, are obtained in yields of 35% and 40% respectively. 2 : 4-Dibromo-6-amino-*m*-cresol has m. p. 176°; the corresponding *benzoylamino*-compound, m. p. 198°, forms colourless crystals. 2 : 4-*Dibromo*-3-*hydroxy*-o-*tolyl*-6-*urethane*, $OH{\cdot}C_6HMeBr_2{\cdot}NH{\cdot}CO_2Et$, m. p. 155°, obtained by the action of ethyl chlorocarbonate on 2 : 4-dibromo-6-amino-*m*-cresol in presence of sodium hydroxide, is a brown solid. 2 : 6-*Dibromo*-4-*chloroiminotoluquinone*, $O{:}C_6HMeBr_2{:}NCl$, m. p. 86°, forms yellow, hexagonal plates. 2 : 6-*Dibromo*-4-*amino*-m-*cresol*, m. p. 116—117°, crystallises in brown scales; its *hydrochloride* is described. 2 : 6-*Dibromo*-4-*benzoylamino*-m-*tolyl benzoate*, m. p. 188°, forms colourless crystals. 2 : 6-*Dibromo*-3-*hydroxy*-p-*tolyl*-4-*urethane* has m. p. 169°. 2 : 6-*Dibromo*-4-*acetylamino*-m-*tolyl acetate*, m. p. 216°, crystallises in long, silky needles. When 2 : 6-*dibromo*-4-*nitro*-m-*tolyl ethyl carbonate*, $NO_2{\cdot}C_6HMeBr_2{\cdot}O{\cdot}CO_2Et$, m. p. 43—45°, obtained by the action of ethyl chlorocarbonate on 2 : 6-dibromo-4-nitro-*m*-cresol in presence of sodium hydroxide, is reduced with tin and hydrochloric acid, it is converted into 2 : 6-dibromo-3-hydroxy-*m*-tolylurethane.

Kehrmann and Tichvinsky (Abstr., 1899, i, 129) have shown that 4-chlorotoluquinoneoxime exists in two modifications, which, on reduction, give a chloroaminocresol, m. p. 204—205°, identical with that obtained by the reduction of the substance produced by chlorinating 6-nitro-*m*-cresol in glacial acetic acid solution. Attempts have been made to prepare stereoisomeric chloroiminoquinones corresponding with these oximes. A chloroaminocresol prepared from 6-nitro-*m*-cresol had m. p. 166—167°, and on oxidation gave a chloroiminoquinone, m. p. 87°, whilst that similarly obtained from Kehrmann's chloroaminocresol had m. p. 91°. It is shown that these compounds are 2-*chloro*- and 4-*chloro*-6-*chloroiminotoluquinone* respectively.

4-*Chloro*-6-*benzoylamino*-m-*tolyl benzoate*, m. p. 220°, prepared from Kehrmann's chloroaminocresol, forms nearly colourless crystals. 4-*Chloro*-6-*chloroiminotoluquinone*, $O{:}C_6H_2MeCl{:}NCl$, m. p. 91°, obtained by the action of hypochlorous acid on Kehrmann's chloroaminocresol, crystallises in radiating needles.

4-*Chloro*-3-*chloroiminotoluquinone*, m. p. 65°, prepared in a similar manner from the chloroaminocresol obtained by the electrolytic reduction of 3-nitro-4-chlorotoluene, forms brown nodules.

When 2-*chloro*-6-*nitro*-m-*cresol*, $OH{\cdot}C_6H_2ClMe{\cdot}NO_2$, m. p. 133°, obtained by the chlorination of 6-nitro-*m*-cresol, is reduced with stannous chloride, it is converted into 2-*chloro*-6-*amino*-m-*cresol*, m. p. 166—167°, which forms colourless crystals; its *hydrochloride* darkens above 225°. The *acetate* of the corresponding *acetylamino*-compound has m. p. 178°. On oxidation, 2-chloro-6-amino-*m*-cresol yields o-*chlorotoluquinone*, m. p. 55°, which is readily reduced to o-*chlorotoluquinol*, m. p. 173°, crystallising in colourless leaflets. By the action of hypochlorous acid on 2-chloro-6-amino-*m*-cresol, 2-chloro-6-chloroiminotoluquinone, m. p. 87°, is obtained.

By the chlorination of *o*-nitrotoluene, a mixture of 2-chloro- and 4-chloro-6-nitrotoluene is produced. These compounds on electrolytic reduction are converted into 2-chloro- and 4-chloro-6-amino-*m*-cresol, which, on oxidation, yield *p*-chlorotoluquinone, m. p. 105°, and *o*-chlorotoluquinone, m. p. 55°. E. G.

[Preparation of Condensation Products from *p*-Benzoquinone or α-Naphthaquinone.] RUDOLF LESSER (D.R.-P. 236074).—When the condensation products of quinones (or other diketo-derivatives) are reduced in alkaline solution with sodium hyposulphite, valuable dyes are produced. The *products* from dianilino-*p*-benzoquinone, $C_6H_2O_2(NHPh)_2$, chlorodianilino-*p*-benzoquinone, and chloranilanilide (from aniline and chloranil) are mentioned. The *compound*, $C_6Cl_2O_2(NH{\cdot}C_6H_4{\cdot}OMe)_2$, obtained from chloranil and *p*-anisidine, forms red needles with metallic lustre, and the *product*,

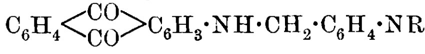
$$C_{10}H_5O_2{\cdot}NH{\cdot}C_6H_4{\cdot}OEt,$$

from *p*-phenetidine and α-naphthaquinone, glistening, metallic, reddish-brown needles. F. M. G. M.

The Partial or Total Replacement of Halogens by Hydrogen in Polyhalogenated Aminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 236604).—When polyhalogenated aminoanthraquinones or their derivatives are treated with reducing agents (such as iron and acetic acid) in the presence of pyridine, one or more of the halogen atoms are displaced by hydrogen.

Under these conditions, 2 : 4-dibromo-1-aminoanthraquinone yields 2-bromo-1-aminoanthraquinone ; 2 : 4-dibromo-1-methylaminoanthraquinone furnishes 2-bromo-1-methylaminoanthraquinone, and 1 : 3-dibromo-2-aminoanthraquinone gives 3-*bromo*-2-*aminoanthraquinone* in brownish-yellow, glistening leaflets. F. M. G. M.

Preparation of *p*-Dialkylaminobenzyl-1-aminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 236769).—When a mixture of 1-aminoanthraquinone and a tertiary aromatic amine is treated with formaldehyde, it yields a *p*-dialkylaminobenzyl-1-aminoanthraquinone of the general formula



$$C_6H_4{<}\substack{CO\\CO}{>}C_6H_3\cdot NH\cdot CH_2\cdot C_6H_4\cdot NR_2.$$

p-*Dimethylaminobenzyl*-1-*aminoanthraquinone*, $C_{23}H_{20}O_2N_2$, obtained when dimethylaniline is employed, has m. p. 211°, and forms orange-red crystals, whilst p-*diethylaminobenzyl*-1-*aminoanthraquinone*, m. p. 196°, crystallises from xylene in red prisms. F. M. G. M.

Preparation of Mixed Arylanthraquinonylcarbamides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 236979 and 236981).—Arylanthraquinonylcarbamides have previously been prepared ; it is now found that the reaction takes place when arylcarbamyl chlorides react with aminoanthraquinones. The *product* obtained by boiling a nitrobenzene solution of 2-aminoanthraquinone with diphenylcarbamyl chloride in the presence of sodium acetate forms yellow crystals, which does not fuse below 300° ; this reaction is capable of wide extension. The second patent states that when β-aminoanthraquinone is heated with phenylurethane, a yellow powder separates from the cooled mixture, which has the properties of *phenyl-β-anthraquinonylcarbamide.* F. M. G. M.

Conversion of 1 : 2-Benzanthraquinone (Naphthanthraquinone) into Anthraquinone-1 : 2-dicarboxylic Acid. ROLAND SCHOLL and EMIL SCHWINGER (*Ber.*, 1911, **44**, 2992—2998).—*Anthraquinone*-1 : 2-*dicarboxylic acid*, $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2(CO_2H)_2$, required for the synthesis of 1 : 2-phthaloylanthraquinone, has been obtained by the oxidation of 1 : 2-benzanthraquinone. By oxidation by potassium permanganate in neutral solution, diphthalylic acid and anthraquinone-1 : 2-dicarboxylic acid are both formed, but only in small amount (compare Graebe and Peter, Abstr., 1905, i, 704). However, when a 5% solution of 1 : 2-benzanthraquinone in concentrated sulphuric acid is added to twice the weight of hot water and the nearly boiling mixture is oxidised by solid potassium permanganate, anthraquinone-

1 : 2-dicarboxylic acid is formed in 75·5% yield. The same acid is obtained in about 22% yield when the oxidation is effected by nitric acid, D 1·15, at 190—195°.

Anthraquinone-1 : 2-dicarboxylic acid crystallises in pale yellow needles containing H_2O, yields anthraquinone by distillation with calcium oxide and a little water, and changes at its m. p., 267—268°, into the *anhydride*, $C_{16}H_6O_5$, m. p. 319—321°, yellow prisms and leaflets, which is converted by ammonia at 225—235° into the *imide*, m. p. 293°, yellow needles. C. S.

Relation between Bisnitroso-compounds and Arylnitroso-hydroxylamines. EUGEN BAMBERGER (*Ber.*, 1911, **44**, 3066—3072).—According to Piloty (Abstr., 1902, i, 734) the colourless, bimolecular *C*-nitroso-compounds and the coloured, unimolecular nitroso-compounds are to be considered as belonging to the same class.

This view is supported by the author, who finds that chloroform, benzene, and glacial acetic acid solutions of certain typical bimolecular nitroso-compounds (bisnitrosylbenzyl, *d*-bisnitrosocarone, *iso*safrol-ψ-nitrosite, and anethole-ψ-nitrosite) acquire a blue or bluish-green colour when heated, and accordingly must contain the nitroso-compound in the unimolecular form.

An explanation is also given of the transformation of bisnitroso-carone, by the action of hydrochloric acid, into chlorocarone and caronebisnitrosylic acid (caronenitrosohydroxylamine) observed by Baeyer (Abstr., 1895, i, 379).

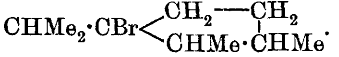
The first stage in the action consists in the dissociation of bisnitroso-carone into the unimolecular form, which under the influence of hydrogen chloride is converted into chlorocarone and nitroxyl: $C_{10}H_{15}O\cdot NO + HCl = C_{10}H_{15}OCl + NOH$. The latter compound then unites with a second molecule of the nitroso-compound to form caronebisnitrosylic acid, $C_{10}H_{15}O\cdot N(OH)\cdot NO$.

The evanescent blue coloration observed on acidifying an alkaline solution of nitroethane is considered by the author to be due to the formation of either nitrosoethyl alcohol, $NO\cdot CHMe\cdot OH$, or the ψ-nitrile, $NO_2\cdot CHMe\cdot NO$. F. B.

Transformations of Thujane. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1157—1163).—In the preparation of thujane by the oxidation of thujylhydrazine (this vol., i, 71), the purification of the latter by means of its hydrochloride may lead to the partial inversion of the thujylhydrazine, and hence of the thujane, if any excess of acid is present with the hydrochloride; thus, it was found that the thujane from the pure thujylhydrazine had $[\alpha]_D$ +53·41°, whilst two preparations from the crude hydrazine had $[\alpha]_D$ +69·29° and +73·07° respectively.

When boiled with dilute sulphuric acid (1 : 6), thujane remains unchanged, whilst in a sealed tube the rotation is slightly lowered.

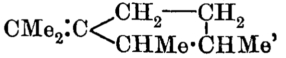
The action of hydrobromic acid on thujane for a short time yields an unstable bromo-derivative, but prolonged action gives a more stable, inactive *bromo*-compound, $C_{10}H_{19}Br$, b. p. 111—112°/19 mm., D_0^{20} 1·1812, n_D 1·4897, which is not decomposed when boiled with aqueous-alcoholic potassium hydroxide. Reduction of this compound in 80% alcohol by means of a copper-zinc couple yields a *hydrocarbon*, $C_{10}H_{20}$, b. p. 157°/746 mm., D_0^{20} 0·7923, n_D 1·4377. The formation of this hydrocarbon, which is isomeric with menthane, indicates that the action of hydrobromic acid on thujane leads to the rupture of the trimethylene ring with formation of a *cyclo*pentane derivative, probably of the structure:



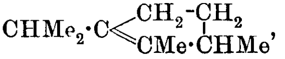
$CHMe_2\cdot CBr\lt\begin{array}{l}CH_2-CH_2\\CHMe\cdot CHMe\end{array}$.

As the stable and the unstable bromo-derivatives give one and the same unsaturated hydrocarbon on decomposition, it is to be assumed that they are structurally identical, and that the difference in stability depends on stereoisomerism of the cis- and trans-type.

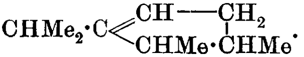
The bromo-compound stable to alcoholic potassium hydroxide is decomposed by distillation with quinoline, giving the unsaturated, inactive *hydrocarbon*, $C_{10}H_{18}$, b. p. 162—164°/755 mm., D_0^{20} 0·8108, n_D 1·4527. The similar *hydrocarbon*, $C_{10}H_{18}$, obtained by the action of potassium hydroxide on the unstable bromo-derivative, has b. p. 163—164°/755 mm., $D_4^{18\cdot5}$ 0·8131, n_D 1·4540, $[\alpha]_D$ +2·88°, whilst the isomeric hydrocarbon prepared by the action of potassium hydroxide on the iodo-compound has b. p. 162·5—163·5°/751 mm., D_0^{20} 0·8111, n_D 1·4527, $[\alpha]_D$ +0·2°. Each of these three hydrocarbons gives a raspberry-red coloration with acetic acid. These hydrocarbons are probably of identical structure, which should be one of the three following:



$CMe_2{:}C\lt\begin{array}{l}CH_2-CH_2\\CHMe\cdot CHMe\end{array}$,



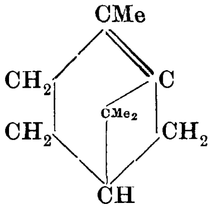
$CHMe_2\cdot C\lt\begin{array}{l}CH_2-CH_2\\CMe\cdot CHMe\end{array}$, and



$CHMe_2\cdot C\lt\begin{array}{l}CH-CH_2\\CHMe\cdot CHMe\end{array}$.

Another isomeric *hydrocarbon*, $C_{10}H_{18}$, obtained by converting thujane into the dibromo-compound, $C_{10}H_{18}Br_2$, and decomposing the latter with aqueous-alcoholic potassium hydroxide, has b. p. 162—164°/760 mm., D_0^{20} 0·8163, n_D 1·4520, $[\alpha]_D$ +23·62°. T. H. P.

Catalytic Isomerisation of α-Pinene. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2782—2784. Compare Zelinsky and Glinka, this vol., i, 870).—α-Pinene (obtained by fractionation of French turpentine) yields an isomeride when treated with hydrogen in presence of palladium black from palladium chloride. This *iso*pinene has b. p. 158·5—159·5°, D_4^{20} 0·8573, n_{20} 1·4641, $[\alpha]_D$ −38·09°. It does not absorb hydrogen chloride, and a nitrosochloride could not be prepared from it. The author supposes the substance to be produced by dehydrogenisation of the hydropinene first formed, and assigns to it the annexed formula. The same α-pinene, however, when treated with hydrogen for four weeks under the pressure of the head of acid in a Kipp's apparatus and in the presence of palladium black from palladium ammonium chloride, yields pinene of b. p. 167·5—168°/748 mm. Hydrogenisation of lævorotatory pinene by Sabatier's method gave



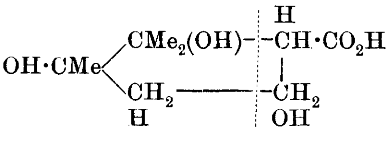
a hydropinene of b. p. 168—168·5° (corr.), D_4^{20} 0·8542, n_{20} 1·4601, $[\alpha]_D$ $-13·3°$, and another *hydrocarbon*, $C_{10}H_{18}$, b. p. 163·5—165°/750 mm., D_4^{20} 0·8512, n_{20} 1·4580, $[\alpha]_D$ $-9·58°$. R. V. S.

isoLaurolene. IWAN L. KONDAKOFF and I. SCHINDELMEISER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 992—1000).—Damsky (Abstr., 1888, 293) obtained *iso*laurolene by distilling the ammonium salt of sulphocamphylic acid in presence of ammonium chloride, but did not indicate the proportions of the two salts used. The authors have investigated this reaction, which they carried out in a current of carbon dioxide, and as molecular proportions of the two salts gave but little hydrocarbon, 2 mols. of ammonium chloride were taken per mol. of sulphocamphylate. The latter should be crystallised from 10% ammonia solution to prevent hydrolysis.

Sulphocamphylic acid, obtained by the action of sulphuric acid on camphoric anhydride, gave m. p. 162—164°, the value 160—165° having been given by earlier workers.

The products obtained by distilling the mixture of ammonium chloride and sulphocamphylate were: *iso*laurolene; di*iso*propenyl; a ketone giving an oxime, m. p. 116—118°, and a bromide, softening at 76°, m. p. 79°; β-hydroxyhexahydro-xylic acid (compare Lees and Perkin, Trans., 1907, **79**, 332), and possibly other cyclic hydrocarbons.

The reactions probably proceed as follows: The sulphocamphylic acid combines with the hydrogen chloride yielded by dissociation of the ammonium chloride, giving two compounds, which lose hydrogen chloride, with formation of α- and β-campholytic acids. The former of these readily undergoes isomeric change into the latter, which loses carbon dioxide and gives *iso*laurolene. These two acids may also be transformed, by way of their hydrochlorides, into campholactones, including ψ-campholactone; this then gives (1) the lactone of *cis*hydroxyhexahydroxylic acid, and from it the corresponding acid, and (2) xylic acid. The hydroxy-acids corresponding with the campholactones, and, to some extent, the acid corresponding with ψ-campholactone, in consequence of hydration, dehydration, and loss of carbon dioxide and other groups, give a pinacone (annexed scheme), this pinacone then undergoing dehydration to di*iso*propenyl. These hydroxy-acids also probably give an isomeride of camphorone or the latter itself.



The various products obtained are being investigated. T. H. P.

Santene and its Hydrohalides. IWAN L. KONDAKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1107—1116).—The author has previously (Abstr., 1910, i, 327) drawn the conclusion that, on loss of hydrogen chloride, true bornyl chloride and also fenchyl chloride do not yield methylenecamphene and methylenefenchene immediately, but that they give, firstly, a mixture of bornylene and cyclene, and fenchobornylene and fenchocyclene respectively, these then undergoing isomeric change into (1) methylenecamphene, *iso*-

cyclene, and *iso*camphene, and (2) fenchene, fenchocyclene, and *iso*fenchene. May (*Diss.*, Berlin, 1910) arrived at a similar conclusion. The present paper records certain observations made in the attempt to confirm the above statement experimentally.

Two natural santenes were employed: that from sandalwood oil (compare Müller, Abstr., 1900, i, 677), and that from the essential oil of the fir (compare Aschan, Abstr., 1908, i, 94), these two being regarded as identical and pure. It is found that, in the latter case, santene cannot be obtained pure by fractionation, since the lower fractions of the oil contain a hydrocarbon with a lower boiling point than santene, whilst the neighbouring fractions with higher boiling points contain camphene and pinene. The hydrocarbon of low b. p. distils at 105—110°, does not change in the air, and is not oxidised by permanganate solution; its nature is under investigation. A hydrocarbon, C_7H_{10} (?), with this b. p. was obtained by Müller (*loc. cit.*) by the dry distillation of calcium teresantalate, either alone or mixed with calcium acetate.

When treated with concentrated hydrochloric acid, the various fractions of fir-santene exhibit the following behaviour: (1) the fraction, b. p. 105—125°, is turned brown, and yields principally a black, caoutchouc-like mass, and hence very little chloro-derivative; (2) that with b. p. 125—142° is coloured yellow, owing to the admixture with that of lower b. p., and gives a chloro-compound liquid at the ordinary temperature, and (3) that boiling at 142—147° remains colourless, and yields a mixture of liquid and solid chloro-derivatives. The santene hydrochloride obtained is identical with norbornyl chloride, and consists of two isomerides, melting at 14° and 81° respectively, assuming the m. p. 81°, given by Müller and by Aschan, to be that of the pure isomeride. Using conditions for its preparation different from those of these authors, it is found that santene hydrochloride from santalol has a lower melting point than 81°. This hydrochloride, when pure, remains unchanged for a long time, but is converted into the isomeride with the lower melting point under the influence of hydrochloric acid.

Contrary to Semmler's statement, the hydrochloride with high melting point is very stable to concentrated alcoholic potassium hydroxide at the ordinary temperature. On the water-bath it undergoes only partial decomposition in five hours, whilst in a sealed tube at 170° it yields in the same space of time the two products: (1) an optically inactive *hydrocarbon*, C_9H_{14}, b. p. 138·5—142·5°, D^{18} 0·8714, n_D 1·46761, and (2) an ether, b. p. about 195°.

The action of concentrated hydrobromic acid on santalol-santene yields a solid hydrobromide, melting in some cases at 25° and in others at 18°, and gradually undergoing change into an inactive liquid *isomeride*, $C_9H_{15}Br$, b. p. 79—81°/8 mm., D^{18} 1·273, n_D 1·50573, which either corresponds with the hydrochloride of lower melting point or represents a mixture of the two isomerides.

When treated with concentrated alcoholic potassium hydroxide, both the liquid and solid hydrobromides yield a mixture of santene and the ether, b. p. 195°. The formation of this ether, in this and also in the preceding case, is regarded as due to condensation.

Oxidation of the santene from the hydrohalides by means of permanganate gives a hydrocarbon, b. p. 137·5—142·5°, santene glycol, and a small quantity of a fragrant-smelling substance. Oxidation of santene from santalol gives the glycol in larger proportion and more rapidly.

The acetyl derivative, $C_9H_{15}\cdot OAc$, of the santenol synthesised from sandalol santene at the ordinary temperature has b. p. 85—89°/8 mm., D^{20} 0·9859, n_D 1·45929, and is optically inactive. T. H. P.

Action of Nitrosyl Chloride on the Essential Oil of Bupleurum fructicosum. Nitrosochlorides. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 190—196).—The previous attempts to prepare a nitrosochloride from the essential oil of *Bupleurum fructicosum* (Francesconi and Sanna, this vol., i, 896) by the method used by Wallach (Abstr., 1889, 1069) for carvene having been unsuccessful, the oil was separated into seventeen fractions by distillation in a vacuum, but the method yielded no better results when employed on the separate fractions. By modifying the procedure, however, by omitting the water and acetic acid, a nitrosochloride has been prepared from all the fractions. A well-cooled mixture of an alcoholic solution of the oil with amyl nitrite or ethyl nitrite is well stirred and treated with a saturated alcoholic solution of hydrogen chloride in drops. The crude *nitrosochloride*, $C_{10}H_{16}ONCl$, obtained is an unstable substance, and, although its m. p. and rotatory power are fairly constant, it is a mixture of at least two nitrosochlorides, termed α and β, which have very different solubilities in chloroform. The more soluble α-nitrosochloride has m. p. 101—102°, $[\alpha]_D$ – 175°; the β-nitrosochloride has m. p. 100—101°, $[\alpha]_D$ – 285°. R. V. S.

Essential Oil of Bupleurum fructicosum, Linn. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 230—233. Compare this vol., ii, 1025; Francesconi and Sanna, this vol., i, 658, 896).—In the present paper an account is given of the fractional distillation of 10 litres of the essential oil. Seventeen fractions were collected, and the results are given of their examination in respect to refractive index, rotatory power, density, percentage composition, acidity, saponification number, etc. R. V. S.

$\Delta^{1,5}$-Dihydrocuminaldehyde [and] β-Phellandrene in the Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 325—331. Compare preceding abstract).—It is shown that the dihydrocuminaldehyde previously obtained from the nitrosochloride from this essential oil is $\Delta^{1,5}$-dihydrocuminaldehyde. The terpene of the oil is β-phellandrene, although it has a greater rotatory power than this substance as obtained from other sources. It gives a nitrosochloride, which (like its nitrosite) has a rotatory power of opposite sign to its own, and decomposes with production of $\Delta^{1,5}$-dihydrocuminaldehyde. R. V. S.

Champaca Oil. BENJAMIN T. BROOKS (*J. Amer. Chem. Soc.*, 1911, 33, 1763—1772).—The flowers of *Michelia champaca* yield 0·37% of an essential oil, two specimens of which gave the following constants: D_{30}^{30} 0·9040 and 0·9107; n_D^{30} 1·4640 and 1·4688; ester number, 124 and 146; the ester number of the latter sample after acetylation was 199. The oil contains phenylethyl alcohol, cineole, *iso*eugenol, benzyl alcohol, benzoic and acetic acids, and a crystalline ketone, $C_{16}H_{20}O_5$, first described by Bacon (this vol., i, 73). This ketone has $[\alpha]_D^{30}$ $-82·5°$; the phenylhydrazone has m. p. 161°. By a study of the action of alcoholic potassium hydroxide on the ketone, it is shown that it is probably a succinic ester of ethyl alcohol and a ketonic alcohol, $C_{10}H_{12}O_2$, containing the group $-CH{:}CH{\cdot}CO-$, and may therefore be represented by the formula $CO_2Et{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2{\cdot}C_{10}H_{11}O$.

The essential oil of *Michelia longifolia* differs considerably from that of *M. champaca*, and gives the following constants: D_{30}^{30} 0·897, n_D 1·4470, and ester number 180; its most characteristic constituent is methyl or ethyl α-methylbutyrate.

The flowers of both species of *Michelia* contain an oxydase, and it is suggested that to such enzymes the formation of aldehydes and ketones in essential oils is largely due. E. G.

Essential Oil of Santolina chamæcyparissus, L. I. LUIGI FRANCESCONI and P. SCARAFÌA (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 255—260).—The quantity of essential oil contained in the stem of the plant is small, but it is found in considerable quantity in the leaves. The extraction was effected by distillation in steam, and the yield varied from 0·2% to 1·15% of the material taken, the maximum being obtained just before flowering. The densities and the rotatory powers of the various products were not markedly different. The oil begins to distil at 176° at the ordinary pressure. At 15—20 mm., distillation was carried out from 94° to 111°, six fractions being collected. The earlier fractions contained a terpene, whilst in the later ones there are probably hydroaromatic oxygenated compounds. The saponification numbers showed the presence of an ester, and indications of the presence of ketones were obtained. The oil does not contain acids, alcohols, or phenols. R. V. S.

Essential Oil of Santolina chamæcyparissus, L. II. Action of Hydroxylamine. LUIGI FRANCESCONI and P. SCARAFÌA (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 318—324. Compare preceding abstract).—By the action of hydroxylamine hydrochloride on the essential oil in aqueous-alcoholic solution in the presence of sodium hydrogen carbonate, the following substances are produced: (1) the hydroxylamine-oxime of a ketone, $C_{10}H_{16}O$; (2) an oxime of the same ketone; (3) an oxime of another ketone; (4) a hydroxylamine; (5) terpenes and other unaltered substances.

The terpene, after fractionation, has b. p. 165—170°, and appears to contain one double linking.

When the product of the reaction is distilled with steam, the distillate contains the two oximes and the hydroxylamine. The oximes can be removed by acidifying and redistilling. The *hydroxylamine* crystallises in hexagonal laminæ, m. p. 62—64°. When oxidised with mercuric oxide it yields a *nitroso*-compound, which is a colourless, crystalline substance, m. p. 60—62°: fused or in solution it is blue.

The *oximes* are liquids which reduce Fehling's solution after they have been boiled with hydrochloric acid, and at the same time this hydrolysis leads to the production of one or more carbonyl compounds.

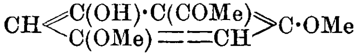
The *hydroxylamineoxime*, $\mathrm{OH{\cdot}NH{\cdot}C_{10}H_{17}{:}N{\cdot}OH}$, obtained by crystallisation from the original reaction product, forms large prisms or thin laminæ, which on heating soften at 180—185° and melt at 190°; the liquid evolves gas and resolidifies, melting again at 260°. If the heating is slow, the conversion into the substance of m. p. 260° occurs directly, no previous fusion being observed. The hydroxylamineoxime does not reduce Fehling's solution, unless it has been boiled previously with hydrochloric acid. It does not react with aldehydes. By the action of nitrous acid, a *dioxime*, $\mathrm{C_{10}H_{16}(N{\cdot}OH)_2}$, is obtained; it forms small, lustrous prisms, m. p. 268° (decomp.). The *dibenzoyl-dioxime* has m. p. 150—155°. When the hydroxylamineoxime is kept at 190—200° for an hour or more, the above dioxime is obtained, and in addition the *amino-oxime*, $\mathrm{NH_2{\cdot}C_{10}H_{17}{:}N{\cdot}OH}$, which crystallises in colourless prisms, m. p. 150°. R. V. S.

Components of Essential Oils. Composition of the Essential Oils of Xanthoxylum aubertia (Evodia aubertia), and Xanthoxylum alatum.

FRIEDRICH W. SEMMLER and E. SCHOSSBERGER (*Ber.*, 1911, **44**, 2885—2890).—The oil of *Xanthoxylum aubertia* was divided into three fractions. Fraction 1, b. p. 70—80°/16 mm., comprised 2—3%, and has D^{20} 0·8248, n_D 1·4977, α_D +30°. It is probaby an aliphatic terpene. Fraction 2, b. p. 115—130°/16 mm., comprised 80—90%. On purification it had the following properties: b. p. 119—123°/9 mm., D^{20} 0·8781, n_D 1·499, $[\alpha]_D$ −58°. It consists in part of a sesquiterpene, *evodene*, of the same type as limene; eugenol methyl ether is also present, and constitutes 40—60% of the crude oil. The third fraction is a solid, m. p. 85° (about 10% of the oil); it is phloroacetophenone dimethyl ether, $\mathrm{C_{10}H_{12}O_4}$.

Xanthoxylum alatum.—The first fraction, b. p. 50—60°/9 mm., comprised 80% of the crude oil, and is possibly l-*sabinene*, but is provisionally termed *xanthoxylene*; it has D^{20} 0·84, n_D 1·47457, α_D −26°, and forms a *hydrochloride*, b. p. 83—87°/10 mm., D^{20} 0·959, n_D 1·4824, α_D −11°. The *hydrocarbon*, $\mathrm{C_{10}H_{18}}$, obtained from this on reduction showed b. p. 52—58°/9 mm., D^{20} 0·8275, n_D 1·4582, α_D −17°. The ozonide on decomposition yielded an acid, b. p. 174—180°/10 mm. The corresponding *sabinene ketone* has b. p. 102—106°/14 mm., D^{20} 0·9612, n_D 1·47064, α_D +14°.

The second fraction, which only amounted to 5—10% of the crude oil, yields two semicarbazones, m. p. 210—211° and 221°. The former corresponds with cuminaldehyde.

The third fraction consisted of phloroacetophenone dimethyl ether,  $\mathrm{CH}\left\langle\begin{matrix}\mathrm{C(OH){\cdot}C(COMe)}\\ \mathrm{C(OMe){=\!=}CH}\end{matrix}\right\rangle\mathrm{C{\cdot}OMe}$; it forms a monobromo-derivative, m. p. 187°, an acetyl derivative, m. p. 107°, and a methyl derivative, m. p. 103° (Schimmel & Co., *Report*, 1909; Abstr., 1909, i, 313).

E. F. A.

Apparently Reversible Character of the Vulcanisation Reaction of Caoutchouc by Sulphur.

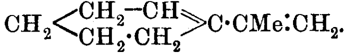
Paul Bary and L. Weydert (*Compt. rend.*, 1911, **153**, 676—678).—The free and combined sulphur in a sample of vulcanised caoutchouc was estimated, and the former removed by extraction with acetone, or else separated by removing the gum with xylene. After heating the product at 145° for eight hours, the caoutchouc was again analysed in the same way. The results show that ordinary vulcanised caoutchouc is an equilibrium mixture, and that combined sulphur is set free on diminishing the osmotic pressure of the free sulphur. The reaction of vulcanisation is represented as $C_{10}H_{16} + S_2 \rightleftharpoons C_{10}H_{16}S_2$, but the numerical data obtained are not in agreement with the ordinary law of mass action, whatever hypothesis may be adopted as to the degree of polymerisation of the hydrocarbon. The conclusion drawn is that the hydrocarbon molecules having polymerised by union at the double linkings, on vulcanisation sulphur first becomes attached only to the terminal double linkings of a chain; further vulcanisation, therefore, can only occur after depolymerisation. W. O. W.

Preparation of Substances Resembling Caoutchouc.

Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 235686).—When compounds of the general type $\colon C{:}C{\cdot}C{:}C\colon$, where the free valencies are saturated partly with hydrogen and partly with alkyl groups, are heated either in the presence or absence of condensing agents, they polymerise into substances like caoutchouc.

Piperylene, $CHMe{:}CH{\cdot}CH{:}CH_2$, when heated at 150° during twenty-four hours or at 90—100° during eight days, yielded a colourless, elastic *substance*, isomeric with natural caoutchouc.

Plastic masses of similar nature were obtained by heating δ-methyl-$\Delta^{\alpha\gamma}$-pentadiene, $CMe_2{:}CH{\cdot}CH{:}CH_2$, at 200° during twenty-four hours, also from tetramethylerythrene, $CMe_2{:}CH{\cdot}CH{:}CMe_2$, and from the substance



$$CH_2<\begin{matrix}CH_2-CH\\CH_2{\cdot}CH_2\end{matrix}\gg C{\cdot}CMe{:}CH_2.$$

F. M. G. M.

Clavicepsin, a New Glucoside from Secale cornutum.

Francesco Marino-Zuco and V. Pasquero (*Gazzetta*, 1911, **41**, ii, 368—374).—When *Secale cornutum* is extracted with hot alcohol for several days, the alcoholic solution contains a syrup partly soluble in water. From the aqueous solution, the new glucoside, $C_{18}H_{34}O_{16},2H_2O$, can be isolated in the form of acicular crystals, m. p. 91°, or, when anhydrous, 198°. It has $[\alpha]_D^{20}$ +142·27°. It is not hydrolysed by emulsin, but with acids it yields 2 mols. of dextrose (identified as phenylhydrazone) and 1 mol. of mannitol (identified by isolation and analysis) according to the equation: $C_{18}H_{34}O_{16} + 2H_2O = 2C_6H_{12}O_6 + C_6H_{14}O_6$. R. V. S.

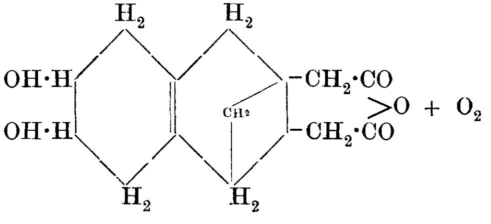
Picrotoxin.

Francesco Angelico (*Gazzetta*, 1911, **41**, ii, 337—349. Compare Abstr., 1910, i, 404, 577).—The action of hydriodic acid and phosphorus on either picrotin or picrotoxinin yields an acid, $C_{15}H_{18}O_4$, and a ketone, $C_{14}H_{16}O_3$, previously described. The reaction is accompanied by the evolution of carbon dioxide and a little carbon monoxide.

The action of alkaline permanganate on the acid $C_{15}H_{18}O_4$ gives (in addition to the acids $C_{15}H_{16}O_6$, $C_{13}H_{12}O_6$, and $C_{12}H_{12}O_7$) a small quantity of an *acid*, $C_{14}H_{16}O_6$, which forms small needles, m. p. 180°.

The acid $C_{13}H_{12}O_7$, m. p. 175°, is not a malonic derivative. When it is oxidised with chromic acid in the presence of 25% sulphuric acid, it yields a dibasic *acid*, $C_{12}H_{12}O_7$, which crystallises in needles, m. p. 289—290° (decomp.), and gives a *silver* salt, $C_{12}H_{10}O_7Ag_2$.

The series of acids which has now been obtained from picrotin and from picrotoxinin is therefore: $C_{15}H_{18}O_4$, $C_{15}H_{16}O_6$, $C_{14}H_{16}O_6$, $C_{13}H_{12}O_6$, $C_{13}H_{12}O_7$, and $C_{12}H_{12}O_7$. The author suggests the annexed formula for picrotin. Picrotoxinin would then be the unsaturated (hexahydronaphthalene) derivative containing no hydroxyl groups, but having also the two oxygen atoms of unknown function.



With a view to determining the function of these oxygen atoms, experiments have been made on various products with phosphorus pentachloride. The monocarboxylic acid, $C_{15}H_{18}O_4$, remains unaltered. The halogenated ketone yields an oily, chlorinated product, which gives a phenylhydrazone, and the halogenated ketone also yields a small quantity of a *substance*, m. p. 168—169°. The ketone, $C_{14}H_{16}O_3$, gives the same results, but in this case the substance of m. p. 168—169° was analysed, and corresponds with the union of 2 mols. of ketone less $1H_2O$, or $C_{28}H_{26}O_3Cl_2$. The ketone, $C_{14}H_{16}O_3$, when distilled with zinc dust gives traces of a substance, probably a *hydrocarbon*, of which the *picrate* has m. p. 205—206°.

The nitro-acid, $C_{13}H_{15}O_5N$ (compare Abstr., 1910, i, 578), is accompanied by a small quantity of a *substance*, m. p. 86—87°. When reduced with ammonium sulphide in the warm, the nitro-acid gives the corresponding *amino*-acid, $C_{13}H_{17}O_3N,H_2O$, m. p. 175—176°. The amino-acid is oxidised by permanganate at the ordinary temperature, giving a *tribasic acid*, $C_7H_{10}O_6$, which crystallises in small needles, m. p. 95°, and gives a *silver* salt, $C_7H_7O_6Ag_3$. R. V. S.

Composition of Tannin. WILHELM STEINKOPF and JOHANN SARGARIAN (*Ber.*, 1911, **44**, 2904—2906).—Iljin (Abstr., 1909, i, 503) has stated that tannin derived from the commercial product by repeated purification has the composition 54·13% C and 3·22% H, values which are not in agreement with those usually obtained or with Nierenstein's formula. A careful repetition of Iljin's experiments indicates values 52·69% C and 3·77% H, in full agreement with those of previous observers. E. F. A.

Bile Pigments. II. Urobilinogen of Urine and the Nature of Ehrlich's Aldehyde Reaction. HANS FISCHER and FRIEDRICH MEYER-BETZ (*Zeitsch. physiol. Chem.*, 1911, **75**, 232—261. Compare this vol., i, 803).—Urobilinogen has been prepared from pathological urine in a crystalline form, and identified with hemibilirubin by the crystallographic characters. A number of unstable pyrrole derivatives, including all the crystalline blood pigments and the bile pigments at present known, are converted into urobilin on decomposition, both in experiments in test-tubes and in the organism. All these unstable pyrrole compounds contain a hydrogen atom attached to one of the carbon atoms in the chain, and they all give the Ehrlich reaction with *p*-dimethylaminobenzaldehyde.

The urobilinogen and urobilin tests are not decisive when they are given after unnatural substances have been administered to the animal; urobilinogen, moreover, may be present in urine in considerable quantity without giving the aldehyde reaction.

Ehrlich has shown that certain pathological urines give an intense red coloration with dimethylaminobenzaldehyde in acid solution. The dye in question is now shown to be a dipyrrylphenylmethane dye formed by a secondary reaction from the corresponding leuco-base.

Ethyl 2:5-dimethylpyrrole-3-carboxylate condenses with anisaldehyde to form a colourless, crystalline substance, $C_{26}H_{32}O_5N_2$, m. p. 199—200 (corr.).

The pyrrole derivative also condenses with *p*-dimethylaminobenz aldehyde in acid alcoholic solution to a colourless, crystalline leuco-base, $C_{27}H_{35}O_4N_3$, m. p. 239°. On oxidation with ferric chloride, the dye is obtained; it forms a hard, dark red, lustrous mass, with a green reflex. The colour is stable towards acids, but altered by sodium hydroxide, although restored again on making the solution acid. It has the properties of a triphenylmethane dye.

The corresponding dye from hemibilirubin and *p*-dimethylamino-benzaldehyde is reddish-violet and very sensitive to alkali; dilute sodium carbonate changes the violet colour into brownish-yellow.

E. F. A.

Bile Pigments. III. Hemibilirubin and its Oxidation Products. Hans Fischer and Paul Meyer (*Zeitsch. physiol. Chem.*, 1911, **75**, 339—349. Compare Abstr., 1911, i, 803).—Hemibilirubin has been found to exist in two forms, an acidic and a non-acidic. The latter is the pure hemibilirubin. The former, which dissolves in solutions of hydrogen carbonates with the evolution of carbon dioxide, has not yet been obtained pure.

By the reduction of bilirubin in alkaline solution by means of sodium amalgam, three products have been obtained, namely: (I) hemibilirubin, (II) the acidic form of hemibilirubin, and (III) a substance which has not yet been identified. On oxidation all three substances yield the imide of hæmatic acid, together with methylethylmaleinimide. Hæmatic acid only was found among the products of the oxidation of bilirubin.

From determinations of molecular weight, the authors draw the conclusion that the formulæ previously ascribed to hemibilirubin are incorrect, and propose either $(C_{16}H_{22}O_3N_2)_2$ or $C_{33}H_{44}O_6N_4$.

H. W.

Melanin Pigments of Animal Origin. MAURICE PIETTRE (*Compt. rend.*, 1911, **153**, 782—785).—The material employed in this investigation was prepared by macerating sarcomatous tumours from horses, removing the cellular débris after cooling in ice, and separating the melanin pigment by centrifugation. When submitted to alkali hydrolysis the melanin yielded alanine, together with other crystalline amino-acids, the amount of which was insufficient for identification. The residual pigment had the composition C 61·72, H 4·39, N 9·4, S 1·6, Fe_2O_3 0·178%. Acid hydrolysis resulted in the separation of tyrosine (0·11%), leucine (2·95%), amorphous amino-acids (9·32%), and a pigment containing iron and sulphur, and having C 55·69, H 3·49, N 9·72%. The original melanin, therefore, appears to contain a protein group in union with a pigment.

W. O. W.

Action of Sulphurous Acid and of Sulphites on Various Dyes. HUGO WEIL, KARL DÜRRSCHNABEL and PAUL LANDAUER (*Ber.*, 1911, **44**, 3172—3179. Compare Dürrschnabel and Weil, Abstr., 1905, i, 947).—Methylene-blue is at first unchanged by sulphurous acid, but, after a time, a *substance* separates in small quantity in well-formed yellow crystals of both basic and acid character having the composition $C_{32}H_{36}O_8N_6S_5,5H_2O$ or $4\frac{1}{2}H_2O$, corresponding with the entry of three sulpho-groups into two methylene-blue residues. Characteristic derivatives could not be obtained; oxidation with dichromate gives a blue dye; with acetic anhydride a green, hygroscopic powder is obtained.

Sodium sulphite forms leucomethylene-blue, a lustrous, bronze-coloured, crystalline intermediate product being also formed, which probably represents methylene-blue sulphite.

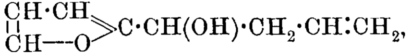
With sodium hydrogen sulphite the first product is a dull blue precipitate, which, after remaining three or four days or on warming, is converted into the yellow, crystalline precipitate of leucomethylene-blue-sulphonic acid, $C_{16}H_{19}O_3N_3S_2,2H_2O$. If the original mother liquors are allowed to evaporate at a low temperature, very soluble, lustrous, silver platelets are obtained, which instantly become blue on exposure to the air; this is regarded as a sulphaminic acid.

Sulphurous acid and nitromethylene-blue interact to form a *nitro-leucomethylene-blue-sulphonic acid*, $C_{16}H_{18}O_5N_4S_2$; this has pronounced acid properties, and forms a green dye on oxidation. The mother liquors contain basic substances, which are oxidised to blue compounds. When the *nitro-leuco-acid* is reduced with zinc and hydrochloric acid, the *zinc* salt of an *aminoleuco-acid*, $ZnC_{32}H_{38}O_6N_8S_4$, is formed; this gives a blue oxidation product.

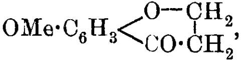
With Meldola's-blue, sulphurous acid yields a brown, crystalline compound, $C_{18}H_{16}O_4N_2S$.

Phenylindamine and sodium hydrogen sulphite form lustrous, colourless plates of a *substance*, $C_{12}H_{13}O_6N_3S_2$; tolylindamine and phenyltolylindamine behave similarly, the product in each case being a *leucodisulphonic acid*. Phenyltetramethylindamine reacts with sodium hydrogen sulphite or sulphurous acid to form lustrous, colourless crystals of a *monosulphonic acid*.

Safranines are not decolorised by sulphurous acid; coloured salts separate after a time, which appear to be a mixture of sulphite and sulphate. E. F. A.

Action of a Mixture of Allyl Bromide and Furfuraldehyde on Magnesium: Synthesis of Furylallylcarbinol. A. SEMENTSOFF and P. KONJUKOFF-DOBRYNIA (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 990—992. Compare Javorsky, Abstr., 1908, i, 753).—*Furylallylcarbinol*,  $\begin{matrix}\text{CH·CH}\\ \text{CH—O}\end{matrix}\!>\!\text{C·CH(OH)·CH}_2\text{·CH:CH}_2$, prepared by the interaction of magnesium, allyl bromide, and furfuraldehyde, is a colourless liquid, b. p. 96—97°/21 mm., $D_4^{20\cdot5}$ 1·0424, $n_D^{20\cdot5}$ 1·49192, which rapidly turns yellow. T. H. P.

7-Methoxy-3 : 4-dihydro-1 : 4-benzopyrone. ALEXEI E. TSCHITSCHIBABIN and I. V. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1185—1189).—7-Methoxy-3 : 4-dihydro-1 : 4-benzopyrone,



$$\text{OMe·C}_6\text{H}_3<\begin{matrix}\text{O—CH}_2\\ \text{CO·CH}_2\end{matrix},$$

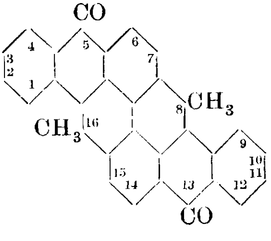
may be expected to lead to the formation of substances of the two structural formulæ which are at present regarded as the most probable for brazilin (compare Werner and Pfeiffer, *Chem. Zeitsch.*, 1904, **3**, 421; Perkin and Robinson, Trans., 1908, i, 489; von Kostanecki and Lampe, Abstr., 1902, i, 481).

The synthesis of this compound is effected in two stages: (1) the action of the sodium derivative of *m*-methoxyphenol on sodium β-iodopropionate gives sodium β-*m*-methoxyphenoxypropionate, which (2) is converted into 7-methoxydihydrobenzopyrone by the action of phosphoric oxide. The condensation of the pyrone with veratraldehyde, which should give a compound having a structure closely related to the Pfeiffer-Perkin formula for trimethylbrazilin, is being investigated.

β-m-*Methoxyphenoxypropionic acid*, $\text{OMe·C}_6\text{H}_4\text{·O·CH}_2\text{·CH}_2\text{·CO}_2\text{H}$, separates from light petroleum in flat, shining needles, m. p. 82·5°; its *silver* salt was analysed.

3-*Methoxydihydrobenzopyrone*, $\text{C}_{10}\text{H}_{10}\text{O}_3$, crystallises from water in slender, colourless needles, m. p. 55°. T. H. P.

Synthetical Experiments in the Pyranthrone Series. ROLAND SCHOLL, JULIUS POTSCHIWAUSCHEG, and JOSEF LENKO (*Monatsh.*, 1911, **32**, 687—710).—Pyranthrone homologues have been prepared in which the alkyl groups are attached to the benzene nuclei between the two anthraquinone complexes. 2 : 2′-Diethyl-1 : 1′-dianthraquinonyl condenses in a similar manner to the dimethyl compound (Scholl, Abstr., 1910, i, 271), although at a higher temperature, forming 8 : 16-dimethylpyranthrone (annexed formula), isomeric with 6 : 14-dimethylpyranthrone (Scholl, *loc. cit.*; this vol., i, 656, 676). 2 : 2′-Di-*n*-propyl-1 : 1′-dianthraquinonyl behaves similarly, but the isomeric di-*iso*propyldianthraquinonyl did not undergo condensation. The last can only react to give an aldol-like condensation product, and



the fact that none such is formed precludes the formation of aldol compounds as intermediate stages in the other condensations.

To prepare the 2-alkylanthraquinones, alkylbenzenes were condensed with phthalic anhydride in presence of aluminium chloride to 4-alkylbenzophenone-2′-carboxylic acids, these reduced to benzylbenzoic acids, condensed to alkylated anthrones, and oxidised to the corresponding anthraquinones.

In addition, *n*-propylbenzoylbenzoic acid was prepared by the Grignard reaction from *p*-iodo-*n*-propylbenzene, phthalic anhydride, and magnesium; it proved to be identical with the compound obtained by means of aluminium chloride, which in this instance does not cause isomerisation of the propyl group.

2-*n*-Propylanthraquinone could not be condensed to a homologue of the anthraflavone obtained from 2-methylanthraquinone (Bohn, Abstr., 1910, i, 405).

4-*Ethylbenzophenone*-2′-*carboxylic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4Et$, separates in needles, m. p. 122°; it dissolves in concentrated sulphuric acid with a yellow coloration, changing to a reddish-brown on heating.

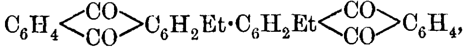
4-*Ethyldiphenylmethane*-2′-*carboxylic acid*, $CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4Et$, crystallises in colourless needles, m. p. 86°. Concentrated sulphuric acid rapidly converts it at the ordinary temperature into a mixture of 2-*ethylanthrone*-9 and 2-*ethylanthranol*-9. The desmotropic mixture consists of irregular, yellow crystals and yellow needles, m. p. 67—75°. When brominated in acetic acid and boiled with water, 2-*ethylanthraquinone* is obtained in yellow needles, m. p. 108°. It dissolves in sulphuric acid with a reddish-yellow coloration, becoming greenish-yellow when heated.

1-*Nitro*-2-*ethylanthraquinone* forms yellowish-brown needles or plates, m. p. 226°.

1-*Amino*-2-*ethylanthraquinone* is obtained on reduction in red needles, m. p. 153—154°.

1-*Iodo*-2-*ethylanthraquinone* crystallises in lustrous, small, yellowish-brown leaflets, m. p. 149°.

2 : 2′-*Diethyl*-1 : 1′-*dianthraquinonyl*,



$$C_6H_4{<}{\begin{smallmatrix}CO\\CO\end{smallmatrix}}{>}C_6H_2Et{\cdot}C_6H_2Et{<}{\begin{smallmatrix}CO\\CO\end{smallmatrix}}{>}C_6H_4,$$

prepared by heating the above iodo-compound with copper powder, crystallises in yellowish-brown prisms, m. p. 315°; in concentrated sulphuric acid it forms a yellow solution, which becomes violet-red on heating.

8 : 16′-*Dimethylpyranthrone* was obtained amorphous, m. p. much above 300°. It gives yellow solutions with a green fluorescence; the sulphuric acid solution is violet. It gives a deep violet, alkaline vat, which dyes cotton brownish-yellow.

4-n-*Propylbenzophenone*-2′-*carboxylic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CO{\cdot}C_6H_4{\cdot}C_3H_7,$$

crystallises in colourless needles, m. p. 125—126°.

4-n-*Propyldiphenylmethane*-2′-*carboxylic acid*,

$$CO_2H{\cdot}C_6H_4{\cdot}CH_2{\cdot}C_6H_4{\cdot}C_3H_7,$$

forms slender needles, m. p. 80—81°.

The mixture of 2-n-*propylanthrone*-9 and 2-n-*propylanthranol*-9 is obtained in slender, yellow, microscopic needles, m. p. 60—61°, only partly soluble in dilute sodium hydroxide.

2-n-*Propylanthraquinone* forms yellow, slender needles, m. p. 98—99°, and dissolves in concentrated sulphuric acid with a reddish-yellow coloration.

1-*Nitro*-2-n-*propylanthraquinone* crystallises in yellow plates, m. p. 180°. 1-*Amino*-2-n-*propylanthraquinone* forms red, lancet-shaped crystals of metallic lustre, m. p. 172—173°.

1-*Iodo*-n-*propylanthraquinone* separates in lancet-shaped, lustrous, golden needles, m. p. 148—149°.

2 : 2′-*Di*-n-*propyl*-1 : 1′-*dianthraquinonyl* has m. p. 214—215°; the solution in concentrated sulphuric acid is brown, becoming dark green at about 80° and violet-red at about 220°.

8 : 16-*Diethylpyranthrone* is a yellowish-brown powder more soluble than the dimethyl homologue. The coloration with concentrated sulphuric acid is blue. It gives a deep reddish-violet alkaline vat, and dyes lighter shades than pyranthrone.

[With E. Böcker.]—4-iso*Propylbenzophenone*-2′-*carboxylic acid* forms lustrous, silky needles, m. p. 133—134°.

4-iso*Propyldiphenylmethane*-2′-*carboxylic acid* crystallises in platelets, m. p. 111°

The condensation product, 2-iso*propylanthrone*-9, was not isolated, but converted into 2-iso*propylanthraquinone*, which sublimes in concentrically grouped, yellow needles, m. p. 44—45°.

1-*Nitro*-2-iso*propylanthraquinone* forms yellow plates, m. p. 210—211°. 1-*Amino*-2-iso*propylanthraquinone* separates in red platelets or in needles with a green surface reflex, m. p. 146°.

1-*Iodo*-2-iso*propylanthraquinone* crystallises in well-formed bunches of yellow needles, m. p. 133—134°.

2 : 2′-*Di*-iso*propyl*-1 : 1′-*dianthraquinonyl* forms rhombohedric crystals, m. p. 326°. E. F. A.

Oxy-2-methylthiophens. Maurice Lanfry (*Compt. rend.*, 1911, **153**, 821—823).—The action of hydrogen peroxide on 2-methylthiophen is similar to that on thiophen (this vol., i, 740), and the products closely resemble those previously obtained, the oxygen being united to sulphur. *Dioxy-2-methylthiophen*, $C_5H_6O_2S$, has b. p. 168—170°/760 mm., D^{13} 1·25. *Tetraoxy-2-methylthiophen*, $C_5H_6O_4S$, has b. p. 187—189°/760 mm., D^{13} 1·37 ; on treatment with excess of bromine it forms *tribromotetraoxy-2-methylthiophen tetrabromide*, $C_5H_3O_4Br_3S,Br_4$, a yellow substance, m. p. −8°, decomposing on distillation. Fuming nitric acid converts the oxymethylthiophens into an ill-defined, yellow *polynitro*-derivative.

Excess of hydrogen peroxide converts 2-methylthiophen into a brown, amorphous substance. W. O. W.

Preparation of Amino- and Alkylamino substituted (in the Aryl Group) Derivatives of 3-Oxy-(1)-thionaphthen-2-carboxylic Acids and of 3-Oxy-(1)-thionaphthen. Kalle & Co. (D.R.-P. 237395).—When the *N*-substitution products of arylthioglycol-*o*-carboxylic acids (such as amino, acylamino-, or alkylamino-acids) are fused with alkali hydroxides at about 170°, the fusion treated with water, and oxidised with potassium ferricyanide (or air), they furnish derivatives of "thioindigo."

3-*Acetylamino*-6-*carboxyphenylthiolacetic acid*,

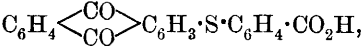
$$NHAc\cdot C_6H_3(CO_2H)\cdot S\cdot CH_2\cdot CO_2H,$$

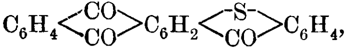
a yellow powder, is prepared from monoacetyl-2 : 4-diaminobenzoic acid by successive diazotisation, xanthogenation, and treatment with chloroacetic acid; on fusion with sodium hydroxide it yields 6-*amino*-3-*keto*-(1)-*thionaphthen*-2-*carboxylic acid*, a grey, crystalline powder, which on boiling with hydrochloric acid furnishes 6-*amino*-3-*keto*-(1)-*thionaphthen*, a crystalline powder, and this by oxidation is finally converted into an "aminothioindigo" derivative.

4-*Acetylamino*-6-*carboxyphenylthiolacetic acid*, prepared in a similar manner from monoacetyl-2 : 5-diaminobenzoic acid, successively yielded 5-*amino*-3-*keto*-(1)-*thionaphthen*-2-*carboxylic acid*, 5-*amino*-3-*keto*-(1)-*thionaphthen*, yellow needles, and, finally, "*pp*-diaminothioindigo" in black flakes. F. M. G. M.

Anthraquinone-thioxanthone. FRITZ ULLMANN and ERNST KNECHT (*Ber.*, 1911, **44**, 3125—3132. Compare Abstr., 1910, i, 270).—The colour change produced by the substitution of –S– for –NH– in the anthraquinoneacridones has been studied. Generally the result is the shifting of the colour into the yellow; thus the red anthraquinone-2 : 1-acridone corresponds with an orange anthraquinone-2 : 1-thioxanthone, and the isomeric orange 1 : 2-acridone compound corresponds with the yellow thioxanthone derivative.

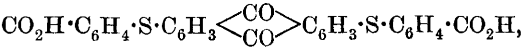
Anthraquinone-*o*-thiolbenzoic acids were prepared by interaction of the appropriate chloro-derivatives with *o*-thiolbenzoic acid, and the former condensed by means of the *p*-toluenesulphonyl chloride or phosphorus pentachloride into anthraquinone-thioxanthones.

Anthraquinone-1-o-*thiolbenzoic acid*,  $C_6H_4{<}\substack{CO\\CO}{>}C_6H_3\cdot S\cdot C_6H_4\cdot CO_2H$, crystallises in orange-yellow plates, m. p. 261° (corr.).

Anthraquinone-2 : 1-*thioxanthone*,  $C_6H_4{<}\substack{CO\\CO}{>}C_6H_2{<}\substack{S\\CO}{>}C_6H_4$, forms lustrous, orange-red platelets, m. p. 346° (corr.). The solution in concentrated sulphuric acid is red.

Anthraquinone-2-*o*-thiolbenzoic acid has m. p. 278° (corr.), and not 271° as previously stated (*loc. cit.*). Anthraquinone-1 : 2-thioxanthone forms small, yellow needles, m. p. 278° (corr.); the azine crystallises in yellow, lustrous platelets.

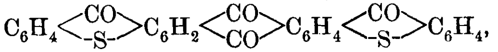
1 : 5-*Dichloroanthraquinone* forms citron-yellow needles, m. p. 251° (corr.). It condenses very readily with *o*-thiolbenzoic acid to *anthraquinone*-1 : 5-*bis*-o-*thiolbenzoic acid*,



$$CO_2H\cdot C_6H_4\cdot S\cdot C_6H_3{<}\substack{CO\\CO}{>}C_6H_3\cdot S\cdot C_6H_4\cdot CO_2H,$$

which crystallises in sealing-wax-red needles, m. p. 349° (corr.). It dissolves in alkali with an orange-red, and in concentrated sulphuric acid with a Bordeaux-red, coloration.

Anthraquinone-2 : 1′ : 6 : 5-*bisthioxanthone*,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{S}{>}C_6H_4,$$

forms red, lustrous platelets, which are not melted at 360°; they dissolve in concentrated sulphuric acid with a wine-red coloration.

1 : 8-*Dichloroanthraquinone* separates in yellow needles, m. p. 202°.

Anthraquinone-1 : 8-*bis-o-thiolbenzoic acid* forms orange-red crystals, m. p. 279° (corr.).

Anthraquinone-2 : 1 : 7 : 8-*bisthioxanthone* crystallises in Bordeaux-red, lustrous needles, giving a violet-red solution in concentrated sulphuric acid.

E. F. A.

Preparation of Diglycollic Esters of Quinine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 237450).—*Quinine diglycollate*,

$$O(CH_2{\cdot}CO_2{\cdot}C_{20}H_{23}ON_2)_2,$$

is prepared by treating a chloroform solution of quinine (11 parts) with diglycollic acid (3 parts) and allowing the mixture to remain during several days. It is a voluminous, tasteless, colourless powder, m. p. 70° (about), sparingly soluble in water, readily so in organic solvents.

Quinine diglycollyl sulphate, $C_4H_4O_3(C_{20}H_{23}O_2N_2)_2,H_2SO_4,3H_2O$, is obtained in crystalline form by treating a dichloroethylene solution of quinine with diglycollyl chloride in the same solvent and subsequently adding dilute sulphuric acid; the ester separates on the addition of sodium acetate.

The Grignard reaction with magnesium ethyl bromide, quinine, and diglycollic acid can also be employed for this preparation.

F. M. G. M.

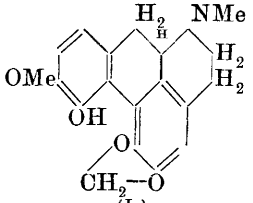
Rearrangement of Quinine by Sulphuric Acid. BRUNO BÖTTCHER and STEFANIE HOROWITZ (*Monatsh.*, 1911, **32**, 793—796).—When quinine is heated at 100° with sulphuric acid, D 1·61, two bases, *A* and *B*, are formed; the former yields a soluble oxalate and sparingly soluble tartrate; the latter yields a sparingly soluble oxalate and a soluble tartrate.

Base *A* crystallises in needles, m. p. 193·5° (corr.), $[\alpha]_D$ −237·89°; the solution in sulphuric acid fluoresces blue. The *sulphate* crystallises in bunches of needles, $[\alpha]_D$ −234·5°.

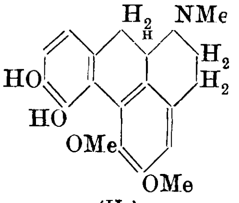
Base *B* forms colourless needles, m. p. 189° (corr.), $[\alpha]_D$ −181·67°; it is probably identical with Lippmann's *iso*quinine (Abstr., 1892, 82)

E. F. A.

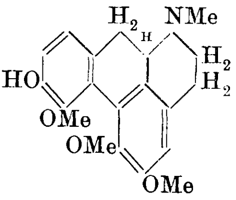
Corydalis Alkaloids. IX. Corytuberine Sub-group. JOHANNES GADAMER (*Arch. Pharm.*, 1911, **249**, 503—510. Compare Abstr., 1902, i, 391; this vol., i, 483, and following abstract).—The author has undertaken with FRITZ KUNTZE a revision of the chemistry of the alkaloids forming this sub-group. The experimental results of this work, which will be published later, are discussed, and the following constitutional formulæ for bulbocapnine (I), corytuberine (II), and corydine (III) are based on them:



(I.)



(II.)



(III.)

*iso*Corydine differs from corydine (III) only in the interchange of positions between –OMe and –OH in positions 3 and 4 in the phenanthrene nucleus. These formulæ are mainly based on the fact that in certain reactions these alkaloids show great similarity to *apo*morphine. Glaucine is the dimethyl ether of corytuberine (II). The two –OH groups in corytuberine are regarded as occupying positions 3 and 4, because (1) this alkaloid is readily oxidised by air in alkaline solutions, forming a dark green liquid. (2) The two hydroxyl groups in *apo*morphine occupy positions 3 and 4 in the phenanthrene nucleus, and the physiological action of corytuberine is very similar to that of *apo*morphine, whilst the characteristic emetic action disappears on methylation of these groups, as in bulbocapnine and corydine. (3) Bulbocapnine and *iso*corydine, like *apo*morphine, give Pellagri's reaction, so that they must contain a hydroxyl group in a position analogous to one of those in *apo*morphine, and as *iso*corydine is produced by methylation of corytuberine, the latter must also contain an –OH group similarly situated. Corytuberine itself does not give Pellagri's reaction, probably because it forms a betaine, in which the –OH group, which should function in Pellagri's reaction, is not available. T. A. H.

Corydalis Alkaloids. X. Bulbocapnine. JOHANNES GADAMER and FRITZ KUNTZE (*Arch. Pharm.*, 1911, **249**, 598—637. Compare Freund and Josephi, Abstr., 1894, i, 100; Herzig and Meyer, Abstr., 1898, i, 53, 389; Ziegenbein, Abstr., 1897, i, 175; Gadamer, Ziegenbein, and Wagner, Abstr., 1902, i, 391).—A historical résumé of work on bulbocapnine is first given, followed by a summary of the results, and analogies on which the new formula for bulbocapnine is based (preceding abstract).

In the mother liquors from the preparation of bulbocapnine, dehydrocorydaline was obtained (compare Schmidt, Abstr., 1909, ii, 85). On methylation with methyl sulphate or diazomethane, bulbocapnine yields a monomethyl ether, $C_{20}H_{21}O_4N$, m. p. 130—131°, $[\alpha]_D^{20} + 247{\cdot}2°$ in chloroform, forming hemihedral, tetragonal crystals $[a : c = 1 : 1{\cdot}0554]$, which gives a crystalline *sulphate*, $B_2,H_2SO_4,7H_2O$. On oxidation with iodine in alcohol this gives *dehydrobulbocapnine methyl ether hydriodide*, $C_{20}H_{18}O_4NI$, m. p. 228°, which with gold chloride gives the *aurichloride*, $C_{20}H_{17}O_4N,HAuCl_4$, crystallising in slender, cinnamon-brown needles, and on reduction with zinc dust in dilute sulphuric acid gives dl-*bulbocapnine methyl ether*, m. p. 136°, forming rhombic crystals [$a:b:c = 0·87288:1:0·61037$]. The latter on fractional crystallisation of the *d*-acid tartrate is separated into the optically isomeric methyl ethers.

On treatment with hot acetic anhydride, bulbocapnine yields a weakly basic diacetyl derivative, $C_{19}H_{17}O_4NAc_2$, which crystallises with $\frac{1}{2}$ mol. $C_2H_5·OH$, a fact which explains Ziegenbein's assumption that this product is a triacetyl derivative (*loc. cit.*). On warming with potassium hydroxide in alcohol, this yields the *potassium* derivative of N-*acetylbulbocapnine* as a yellow, crystalline precipitate, which rapidly becomes brown in the air, and with alcohol and dilute sulphuric acid gives N-*acetylbulbocapnine*, m. p. 163—165°, crystallising in slender, red needles. With benzoyl chloride, by the Schotten-Baumann method, bulbocapnine gives a weakly basic *monobenzoyl* derivative, m. p. 202—203°, $[\alpha]_D^{20}$ + 92·7°, rhombic crystals [$a:b:c = 0·89437:1:0·63116$], which forms a *methiodide*, m. p. 228—230° (decomp.), $[\alpha]_D^{20}$ + 28·1°, crystallising in rosettes of needles or silky leaflets, and on oxidation with iodine in alcohol gives *benzoyldehydrobulbocapnine hydriodide*, m. p. 219° (decomp.), $[\alpha]_D = 0°$. The latter on reduction with zinc dust and sulphuric acid gives dl-*monobenzoylbulbocapnine*, m. p. 201—202°, and this on hydrolysis yields dl-*bulbocapnine*, m. p. 209—210°, which can be separated into its optical isomerides by crystallisation of the *d*-acid tartrate. With hot benzoyl chloride, bulbocapnine gives a *dibenzoyl* derivative, m. p. 156—157°, $[\alpha]_D = 0°$, which on treatment with sodium hydroxide in methyl alcohol yields N-*benzoylbulbocapnine*, m. p. 160°. Oxidation of dibenzoylbulbocapnine with chromic acid did not give a crystalline quinonoid derivative such as is obtained with tribenzoyl*apo*morphine, although the red substance produced is probably a quinone.

With methyl iodide, bulbocapnine gives a methiodide (Freund and Josephi and Ziegenbein, *loc. cit.*), $[\alpha]_D^{20}$ +173·8° in alcohol, and the methyl ether on treatment with methyl iodide yields *bulbocapnine methyl ether methiodide*, $C_{20}H_{21}O_4N·MeI$, m. p. 245—247°, $[\alpha]_D^{20}$ +163·7°.

Dimethylbulbocapnimethine, $C_{17}H_{13}O_4·CH_2·CH_2·NMe_2$, best obtained by the method described by Pschorr for the analogous *apo*morphine compound (Abstr., 1906, i, 878), is a viscid, yellow liquid and is optically inactive; it furnishes an unstable *methiodide*,

$$C_{17}H_{13}O_4·CH_2·CH_2·NMe_3I.$$

and a *methosulphate*, crystallising in thick, yellow needles. Either of these on warming with sodium hydroxide in methyl alcohol furnishes 3:4-*dimethoxy*-5:6-*methylenedioxy*-8-*vinylphenanthrene*, m. p. 101°, crystallising from ether in small, yellow needles. This on distillation with zinc dust gives ethylphenanthrene, which could not be obtained pure, but furnished a picrate, m. p. 138—140° (compare Pschorr, Abstr., 1906, i, 178), and on oxidation with permanganate in acetone yields the corresponding 3:4-*dimethoxy*-5:6-*methylenedioxyphenanthrene*-8-*carboxylic acid*, m. p. 228°, which crystallises in slightly red needles. The latter on further oxidation with permanganate in water gives (1) a soft mass, and (2) a *substance*, m. p. 247°, crystallising in red needles, which is probably dimethoxymethylenedioxyphenanthraquinonecarboxylic acid; it dissolved in alkalis, forming eventually a colourless solution, from which acids liberate a colourless *substance*, m. p. 256—257°, which gradually becomes yellow on exposure to light. The soft mass referred to above, on solution in alcohol, deposits after a time a crystalline *substance*, m. p. 209°.

T. A. H.

Alkaloids of Ipecacuanha Root. OSKAR KELLER (*Arch. Pharm.*, 1911, **249**, 512—524. Compare Paul and Cownley, Abstr., 1896, i, 192; Frerichs and Tapis, Abstr., 1902, ii, 711).—The bark of the root was extracted with ether, then moistened with ammonia solution, and re-extracted with ether and finally with chloroform. The first operation gave no alkaloid. The second furnished cephaëline and emetine, and the third psychotrine. Cephaëline crystallised from the second ethereal extract on concentration, and emetine was recovered from the mother liquors. Carthagena root yielded more cephaëline than Rio root. The colour reactions of both alkaloids are given (compare Allen and Scott-Smith, Abstr., 1903, ii, 117), and the dilutions at which they cease to be precipitated by the usual reagents.

Cephaëline softens at 93°, melts at 104—105°, and is readily soluble in alcohol or chloroform, less so in ether or light petroleum.

Emetine, $C_{30}H_{44}O_4N_2$, was obtained as a snow-white, amorphous powder; the *hydrochloride*, $B,2HCl,3H_2O$, crystallised in groups of needles and melted indefinitely, the *hydrobromide*, $B,2HBr$, in minute needles, and the *hydriodide*, $B,2HI,2H_2O$, m. p. 228—230°, in small masses of needles; the platinichloride, m. p. 248—249°, is amorphous. Emetine furnishes a *dibenzoyl* derivative, m. p. 96—106°, in which one benzoyl group is probably attached to a second nitrogen atom. It contains two methoxyl groups, and on heating with methyl iodide and sodium hydroxide forms a *methyl dimethiodide*, so that it appears to contain both a secondary and a tertiary nitrogen atom.

T. A. H.

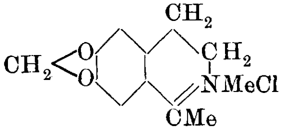
Methyl Ether of Codeine and its Behaviour on Exhaustive Methylation. Morphine. XII. LUDWIG KNORR and PAUL ROTH (*Ber.*, 1911, **44**, 2754—2758).—When α-chlorocodeide is heated in an autoclave for two days at 100—110° with sodium methoxide in methyl-alcoholic solution, codeine methyl ether is formed, and can be isolated as *hydrochloride*, $C_{19}H_{23}O_3N,HCl$, which crystallises (with ½ mol. of alcohol) in needles, m. p. about 285° (previously sintering); $[\alpha]_D^{20} - 66°$ (in water). The *hydriodide*, $C_{19}H_{23}O_3N,HI$, crystallises in rosettes of needles, m. p. about 238—240° (decomp.). The *sulphate* (m. p. 241°), and the *nitrate* (which decomposes at 219°) also crystallise well. *Codeine methyl ether*, obtained from its salts, is a well crystalline substance, m. p. 137°, $[\alpha]_D^{15} - 80°$ (in alcohol, $c = 1·965$). The *methiodide*, $C_{19}H_{23}O_3N,MeI$, crystallises in compact prisms, m. p. 270° (decomp.).

The methiodide, when boiled with sodium hydroxide, yields quantitatively a *methine base*, which is not crystalline; it suffers no rearrangement when heated with alcoholic potassium hydroxide (compare Knorr, Hörlein, and Grimme, Abstr., 1907, i, 956). The *hydriodide* (methylmorphimethine methyl ether hydriodide), $C_{20}H_{25}O_3N\cdot HI$, crystallises in needles or plates, m. p. about 204—208° (sintering from 200°), $[\alpha]_D^{15}$ $-85\cdot5°$ ($c=1\cdot4035$) or $-87\cdot3°$ ($c=1\cdot4950$). The *methiodide*, $C_{20}H_{25}O_3N\cdot MeI$, forms feathery crystals, m. p. 275°.

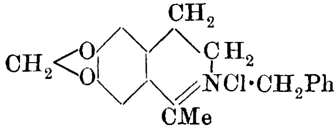
Methylmorphimethine methyl ether methiodide was deprived of iodine by means of silver oxide, and the resulting quaternary base was heated at 150° in a stream of hydrogen. Complete decomposition took place, and the following products were isolated and identified: ethylene, methylmorphenol, methyl alcohol, trimethylamine. R. V. S.

Preparation of 1-Aryl, Alkyl, or Alkylaryl Substituted Hydrastinines.

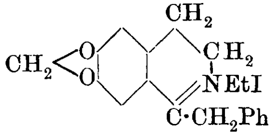
FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235358. Compare Abstr., 1908, i, 901; this vol., i, 906).—When *N*-acyl derivatives of homopiperonylamines are submitted to the action of condensing agents, they furnish hydrastinine derivatives. When *acetylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot NHAc$, colourless leaflets, m. p. 101°, is boiled with phosphoric oxide in toluene solution, it yields 6 : 7-*methylenedioxy*-1-*methyl*-3 : 4-*dihydro*iso*quinoline*; its *picrate*, a yellow, crystalline powder, has m. p. 232°; and the *methiodide*, yellow leaflets, m. p. 257°; when shaken during several hours with freshly precipitated silver chloride, it furnishes 1-*methylhydrastinine hydrochloride* (formula I), feathery needles, m. p. 232°.


(I.)

When the foregoing *iso*quinoline derivative is treated with benzyl chloride it yields 2-*chloro*-6 : 7-*methylenedioxy*-2-*benzyl*-1-*methyl*-3 : 4-*dihydro*iso*quinoline* (formula II), yellowish-brown needles, m. p. 248°.


(II.)

Phenacetylhomopiperonylamine, $CH_2{:}O_2{:}C_6H_3\cdot[CH_2]_2\cdot NH\cdot CO\cdot CH_2Ph$, yellow needles, m. p. 96°, under similar treatment yields 6 : 7-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline*, a yellow, oily liquid, b. p. 240°/16 mm.; its *picrate*, yellow crystals, has m. p. 189—190°, and the *methiodide*, yellow needles, m. p. 252°, on treatment with silver chloride furnishes 1-*benzylhydrastinine hydrochloride* (or *methochloride*), an uncrystallisable resin, readily soluble in water.


(III.)

6 : 7 - *Methylenedioxy* - 1 - *benzyl*-3 : 4-*dihydro*iso*quinoline ethiodide* (formula III) forms yellow crystals, m. p. 214°.

Benzoylhomopiperonylamine, m. p. 122°, yields 6 : 7-*methylenedioxy*-1-*phenyl*-3 : 4-*dihydro*iso*quinoline*, colourless crystals, m. p. 142—143°; its *methiodide*, yellow needles, has m. p. 241°. F. M. G. M.

Strychnine and Brucine. [III.] ROBERTO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 201—206. Compare Abstr., 1910, i, 583; this vol., i, 155).—By the action of bromine on strychnine, under the conditions employed by Löbisch and Schoop (Abstr., 1886, 267), the authors obtained a monobromostrychnine, m. p. 222—223°, identical with that formerly described by them; they consider, therefore, that the β-monobromostrychnine of Löbisch and Schoop does not exist.

When treated with bromine in glacial acetic acid, brucine yields a *perbromide*, $C_{23}H_{26}O_4N_2Br_3,H_2O$, crystallising in yellowish-white needles, which do not melt at 270°. From it a *monobromostrychnine platinichloride*, $(C_{23}H_{25}O_4N_2Br)_2,H_2PtCl_6,H_2O$, can be obtained.

On treating strychnine with potassium chlorate and hydrochloric acid in the cold, the tetrachlorostrychnine of Minunni and Ortoleva (Abstr., 1900, i, 309) is produced, together with an amorphous, isomeric *tetrachlorostrychnine*, $C_{21}H_{18}O_2N_2Cl_4,HCl,2H_2O$. When the cooling is omitted in the above reaction, an *octachlorostrychnine* is obtained as a yellowish-white, crystalline powder, which on analysis gives numbers corresponding approximately with the formula

$$C_{24}H_{14}O_2N_2Cl_8,3H_2O.$$

It yields a p-*nitrophenylhydrazone*, to which the formula

$$C_{24}H_{14}ON_2Cl_8{:}N_2H{\cdot}C_6H_4{\cdot}NO_2,3H_2O,$$

is ascribed.

The physiological action of the derivatives now and previously described has also been studied. The two dibromides, m. p. 122° and 260°, bromostrychnine, and the corresponding dibromide are as toxic as strychnine itself, whilst the octachlorostrychnine (like Minunni's tetrachlorostrychnine) and the acid, $C_{19}H_{22}O_6N_2$, are not toxic. R. V. S.

Iodine Derivatives of Strychnine, Brucine, and Some Other Alkaloids. L. KRAUZE (*Bull. Acad. Sci. Cracow*, 1911, [*A*], 6, 355—368).—True periodides of strychnine bases have been obtained by Buraczewski and Kozniewski (Abstr., 1908, i, 1007) and Kozniewski (Abstr., 1909, i, 826).

When more iodine is used, under otherwise similar experimental conditions, two modifications of a *strychnine heptaiodide*,

$$C_{21}H_{22}O_2N_2,HI,I_6,$$

are formed. One of these is obtained from solutions containing 10% excess of iodine in brownish-needles with a golden lustre, m. p. 151°; it soon decomposes when kept. The other is formed when considerably more iodine is used; it separates in hard, black prisms of a steel-like lustre, m. p. 176—177°, which are stable when kept. Both forms when warmed with alcohol or acetone are converted into Jörgensen's tri-iodide (*J. pr. Chem.*, 1870, [ii], 2, 1334).

By the action of an alcoholic iodine solution on di-iodostrychnine, a brown product is obtained containing more than three iodine atoms, which is a mixture, and could not be obtained crystalline. On warming with acetone, it becomes yellow, forming a new insoluble di-iodostrychnine. Strychnine evidently tends to form several periodides, a property entirely lacking in brucine.

Buraczewski and Dziurzyński (Abstr., 1910, i, 873) have shown that complicated reactions take place on boiling di-iodostrychnine in acetone; two non-poisonous, crystalline products were obtained. These have now been studied more fully. The one forms small, silky needles, m. p. 281°, $C_{24}H_{27}O_3N_2I,1\frac{1}{2}H_2O$, the other yields hard prisms, m. p. 271°, $C_{24}H_{29}O_4N_2I,1H_2O$.

The former, *iodo-acetonylstrychnine*, $C_{21}H_{22}O_2NI\cdot CH_2\cdot COMe$, does not interact with acids or alkalis; with moist silver oxide a soluble, easily decomposed base is obtained; it reduces Fehling's solution and forms a *phenylhydrazone*, which is not well characterised. The *picrate* forms lustrous, yellow, silky needles; the *dichromate* is yellow and flocculent. It is optically inactive and does not react with methyl iodide.

The second substance, *iodoacetonylstrychnic acid*,

$$NH:C_{20}H_{22}O(CO_2H):NI\cdot CH_2\cdot COMe,$$

when dried in a vacuum loses half a molecule of water, forming an *anhydro-acid*, $(C_{24}H_{28}O_3N_2I)_2O$. It forms salts with salts of the heavy metals; with potassium dichromate a yellow, flocculent precipitate, $(C_{24}H_{29}O_4N_2)Cr_2O_7$, is obtained. The *picrate*, $C_{30}H_{31}O_{11}N_5$, is yellow. It reduces Fehling's solution, and forms a *phenylhydrazone*, m. p. 124°. With sodium nitrite in acid solution a crystalline precipitate of the nitrosoamine sulphate is formed.

With alkaline methyl-alcoholic methyl iodide, *iodoacetonyl*-N-*methylstrychnic acid*, $C_{25}H_{31}O_4N_2I$, is obtained; it crystallises in needles, m. p. 248°.

Analogous compounds could not be obtained from other alkaloids. Di-iodobrucine and acetone interact to give a *periodide*,

$$C_{23}H_{26}O_4N_2,HI,I_2,$$

crystallising in short, hard, brownish-red columns, m. p. 260°.

From di-iodocinchonine or di-iodoquinidine and acetone, the hydriodides of the bases were obtained. E. F. A.

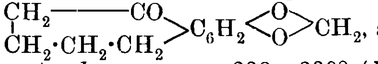
Reduction Catalysts. V. Hydrogenation of Alkaloids. ALADAR SKITA and H. H. FRANCK (*Ber.*, 1911, **44**, 2862—2867).—Strychnine in dilute acetic acid containing a little 1% palladium chloride and 1% gum arabic is reduced in hydrogen under a pressure of 2 atmospheres at the ordinary temperature to *dihydrostrychnine*, $C_{21}H_{24}O_2N_2$, m. p. 209—210°, whilst brucine is converted into *dihydrobrucine*, $C_{23}H_{28}O_4N_2$, m. p. 115°, under similar conditions; under a pressure of 3 atmospheres at 70°, dihydrostrychnine is reduced further to Tafel's tetrahydrostrychnine.

In hydrochloric acid solution containing a little palladium chloride (or platinic chloride), morphine, codeine, quinine, and cinchonine are reduced by hydrogen to dihydromorphine (Oldenberg, this vol., i, 668), *dihydrocodeine*, $C_{18}H_{23}O_3N$, m. p. 65°, dihydroquinine, and dihydrocinchonine respectively, whilst piperine is converted into *tetrahydropiperine*, b. p. 261°/14 mm. These last reductions are not effected by the colloidal metal. C. S.

Strychnine Alkaloids. XII. Derivatives of Bis*apo*methylbrucine. HERMANN LEUCHS and RUDOLPH ANDERSON (*Ber.*, 1911, **44**, 3040—3049. Compare this vol., i, 746).—The *nitrate*, $C_{21}H_{22}O_4N_2,HNO_3,1\frac{1}{2}H_2O$, *hydrobromide*, $C_{21}H_{22}O_4N_2,HBr,2H_2O$, *zincichloride*, $C_{21}H_{22}O_4N_2,H_2ZnCl_4,H_2O$, *diacetyl* derivative, $C_{25}H_{26}O_6N_2$, m. p. 232—233°, and the *methiodide*, m. p. 280° (decomp.), of bis*apo*methylbrucine are described. The action of concentrated nitric acid at −5° on bis*apo*methylbrucine yields *nitrobis*apo*methyldehydrobrucine nitrate*, $C_{21}H_{19}O_6N_3,HNO_3,3H_2O$, orange needles, which is converted by warm 10% nitric acid into cacotheline. The latter is obtained directly by warming bis*apo*methylbrucine hydrochloride with 10% nitric acid.

An attempt to regenerate brucine from bis*apo*methylbrucine by means of methyl iodide failed. However, with a large excess of methyl sulphate, bis*apo*methylbrucine hydrochloride in alkaline solution yields *brucine methosulphate*, $C_{23}H_{26}O_4N_2,Me_2SO_4,2\frac{1}{2}H_2O$, m. p. 268° (decomp.), which crystallises in three forms, has a very bitter taste, and responds to the red brucine reaction. This substance, which is identical with that obtained from methyl sulphate and brucine itself, is converted by warm aqueous sodium hydroxide into methylbrucine, the *acetyl* derivative of which has m. p. 157—158°, after strongly sintering at about 120° and resolidifying. When boiled with 10% nitric acid, methylbrucine yields *cacotheline methonitrate*, $C_{21}H_{21}O_7N_3,MeNO_3,2H_2O$, orange plates, which carbonises at about 280°. C. S.

Strychnine Alkaloids. XIII. Isolation of a Fourth Brucinesulphonic Acid. HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1911, **44**, 3049—3051).—When brucine is sulphonated by manganese dioxide and sulphurous acid in the manner described previously (Abstr., 1908, i, 563; 1909, i, 120, 253, 602, 671), and the resulting sulphonic acids are extracted with water, a very small amount (3%) of a very sparingly soluble *brucinesulphonic acid*, $C_{23}H_{26}O_7N_2S,4H_2O$, is left undissolved. This acid crystallises in large, truncated prisms, has $[\alpha]_D^{20}$ −122·2° in *N*/10-alkali, and is soluble in 170 parts of boiling water. C. S.

Tetrahydropiperine and Tetrahydropiperic Acid. WALTHER BORSCHE (*Ber.*, 1911, **44**, 2942—2945. Compare this vol., i, 880).—β-Styrylacrylic acid is readily reduced by palladium and hydrogen to δ-phenylvaleric acid, and the same method applied to piperine furnishes a quantitative yield of tetrahydropiperine, which on hydrolysis gives piperidine and tetrahydropiperic acid. The latter crystallises from dilute alcohol in colourless leaflets, m. p. 100—101° (compare Buri, Abstr., 1883, 485). The *methyl* ester, b. p. 193—195°, is a colourless, odourless oil. The *acid chloride* is a mobile oil, and on distillation decomposes, giving (1) a brown, resinous residue, which evolves hydrogen chloride, and (2) a viscid, colourless liquid, which deposits crystals. The *amide*, m. p. 110°, prepared from the chloride, crystallises in glancing leaflets. The chloride on treatment with aluminium chloride in carbon disulphide gives *methylenedioxybenzosuberenone*,  $\begin{matrix}CH_2\text{———}CO\\ CH_2\cdot CH_2\cdot CH_2\end{matrix}\!\!>\!C_6H_2\!<\!\begin{matrix}O\\ O\end{matrix}\!>\!CH_2$, as a nearly colourless oil, yielding a *semicarbazone*, m. p. 238—239° (decomp.), crystallising in small, colourless needles. T. A. H.

Synthesis of 2:4-Dimethyl-3-ethylpyrrole, a Contribution to the Question of the Constitution of Hæmopyrrole.

Ludwig Knorr and Kurt Hess (*Ber.*, 1911, **44**, 2758—2767).—According to Piloty (this vol., i, 92), hæmopyrrole is 2 : 4-dimethyl-3-ethylpyrrole, whilst phonopyrrole is 2 : 3-dimethyl-4-ethylpyrrole, but the synthesis of these substances has not yet been accomplished, The present authors have prepared 2 : 4-dimethyl-3-ethylpyrrole from 3-acetyl-2 : 4-dimethylpyrrole, obtained from the ethyl carboxylate produced by combination of nitrosoacetoacetic ester with acetylacetone. The synthetic product is similar to, but not identical with, hæmopyrrole, which must be 2 : 3-dimethyl-4-ethylpyrrole, therefore, in view of Piloty's work. The identity of 2 : 4-dimethyl-3-ethylpyrrole with phonopyrrole remains to be established, owing to the lack of crystalline derivatives of the latter substance. 2 : 3 : 5-Trimethylpyrrole (compare Ciamician and Dennstedt, *Ber.*, 1881, **14**, 1340), 2 : 5-dimethyl-3-ethylpyrrole, and 2 : 5-dimethyl-3-propylpyrrole are also described.

The preparation of the pyrrole derivatives from the oximinoketones and acetoacetic ester was effected by the method formerly described (Knorr, Abstr., 1887, 275). The saponification of the carboxylic esters was carried out with 10% alcoholic sodium hydroxide containing a little water. On heating, the carboxylic acids lose carbon dioxide, the reaction being conducted in an atmosphere of nitrogen or hydrogen.

Ethyl 2 : 3 : 5-*trimethylpyrrole*-4-*carboxylate*, $C_{10}H_{15}O_2N$ (by reduction of methyl oximinoethyl ketone and acetoacetic ester), crystallises in small needles, m. p. 104—105°. The *acid*, $C_8H_{11}O_2N$, decomposes at 198°. 2 : 3 : 5-*Trimethylpyrrole*, $C_7H_{11}N$, has b. p. 180—181°/754 mm. (corr.).

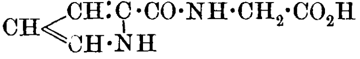
Ethyl 2 : 5-*dimethyl*-3-*ethylpyrrole*-4-*carboxylate*, $C_{11}H_{17}O_2N$ (from methyl oximinopropyl ketone and acetoacetic ester), crystallises in small needles, m. p. 106—107°. The *acid*, $C_9H_{13}O_2N$, decomposes at about 200°. 2 : 5-*Dimethyl*-3-*ethylpyrrole*, $C_8H_{13}N$, has b. p. 187—188°/759 mm. (corr.), 93—94°/21 mm. It shows the pine splinter reaction, and gives a white precipitate with mercuric chloride, but differs from its isomerides in having an odour reminiscent of chloroform, and in being much less sensitive to oxygen.

Ethyl 2 : 5-*dimethyl*-3-*propylpyrrole*-4-*carboxylate*, $C_{12}H_{19}O_2N$ (from iso*nitrosobutyl methyl ketone*, which has m. p. 60°, and acetoacetic ester), forms prismatic crystals, m. p. 110°. The *acid*, $C_{10}H_{15}O_2N$, has m. p. about 210° (decomp.). 2 : 5-*Dimethyl*-3-*propylpyrrole*, $C_9H_{15}N$, has b. p. 206—207°/760 mm.

For the preparation of 2 : 4-dimethyl-3-ethylpyrrole another method had to be devised, advantage being taken of the fact (L. Wolff, unpublished) that hydrazones can be reduced to hydrocarbons with sodium ethoxide. 3-*Acetyl*-2 : 4-*dimethylpyrrolehydrazone* (compare Knorr and Lange, Abstr., 1902, i, 821), $C_8H_{13}N_3$, forms rhombic crystals, m. p. 178—179°. When this substance is heated with an alcoholic solution of sodium ethoxide for fourteen hours at 150—160° in a sealed tube filled with nitrogen, 2 : 4-*dimethyl*-3-*ethylpyrrole* is produced, and is isolated by distillation in steam, saturation of the distillate with ammonium sulphate, and extraction with ether, care being taken to conduct all the operations in an atmosphere of hydrogen. The distillation of the substance is carried out as indicated by Piloty (*loc. cit.*) for hæmopyrrole. 2 : 4-Dimethyl-3-ethylpyrrole, $C_8H_{13}N$, has b. p. 96°/16 mm., 107°/27 mm., 118°/37 mm. It behaves like hæmopyrrole towards nitrous acid, yielding methylethylmaleinimideoxime, but is not fluorescent, and yields a *picrate* which forms compact crystals, m. p. 131—132° (hæmopyrrole picrate has m. p. 108·5°).

R. V. S.

Products from Pyrrole-2-carboxylic Acid. EMIL FISCHER and DONALD D. VAN SLYKE (*Ber.*, 1911, **44**, 3166—3171).—Pyrrole-2-carboxylic acid, in spite of the sensitiveness of the pyrrole ring to acids, is relatively easily converted into the chloride by phosphorus pentachloride. The chloride affords a convenient material for the preparation of the ester, amide, and anilide of the acid; it has also been coupled with glycine to form 2-pyrroylglycine,



$$\mathrm{CH}\Big<\begin{matrix}\mathrm{CH{:}C\cdot CO\cdot NH\cdot CH_2\cdot CO_2H}\\ \mathrm{CH\cdot NH}\end{matrix}$$

Pyrrole-2-carboxylic acid shows a very marked red coloration in aqueous or alcoholic solution with ferric chloride, and resembles in this respect the phenolcarboxylic acids.

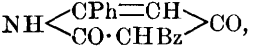
a-Pyrrolecarboxyl chloride, $C_4H_4N\cdot COCl$, crystallises in long, yellow needles, aggregated in bunches, m. p. about 90°. When carefully purified, it forms very long, colourless crystals, which sinter at 110°, and subsequently blacken without melting.

Pyrrole-2-carbanilide, prepared by interaction of pyrrolecarboxyl chloride and aniline in ethereal solution, forms colourless, long, and much intergrown prisms, m. p. 153—154° (corr.) after previous sintering.

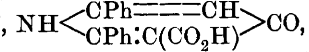
a-Pyrroylglycine ethyl ester crystallises in six-sided platelets, m. p. 118° (corr.). *a-Pyrroylglycine* forms small, spindle-shaped crystals, m. p. 167° (corr.). It gives no coloration with ferric chloride.

E. F. A.

Action of Ammonia on Benzoyldehydracetic Acid. PAVEL IW. PETRENKO-KRITSCHENKO and JOH. SCHÖTTLE (*Ber.*, 1911, **44**, 2826—2830).—Feist's so-called 2 : 6-diphenyl-4-pyridone, obtained from benzoyldehydracetic acid and ammonia (Abstr., 1891, 458), is not identical with the author's compound of the same name (Abstr., 1909, i, 605), and is proved to be probably the *lactam*,



$$\mathrm{NH}\Big<\begin{matrix}\mathrm{CPh{=}CH}\\ \mathrm{CO\cdot CHBz}\end{matrix}\Big>\mathrm{CO},$$

of benzoyldehydracetic acid by analysis, and by the fact that it is converted by alcoholic potassium hydroxide into 2 : 6-*diphenyl-4-pyridone-3-carboxylic acid*,  $NH<\begin{matrix}CPh{=}{=}{=}CH\\ CPh{:}C(CO_2H)\end{matrix}>CO$, which yields 2 : 6-diphenyl-4-pyridone (m. p. 176—178°) at its m. p., 243—245°.

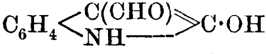
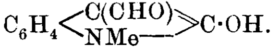
Feist's compound, which can also be converted into 2 : 6-diphenyl-4-pyridone hydrochloride by concentrated hydrochloric acid at 180°, is obtained from benzoyldehydracetic acid and alcoholic ammonia even at the ordinary temperature in two to three days (compare Feist, *loc. cit.*). C. S.

Toluoyl- and Xyloyl-picolinic Acids. OTTOKAR HALLA (*Monatsh.*, 1911, **32**, 747—751).—Just (Abstr., 1898, i, 42) has obtained 3-*p*-toluoylpicolinic acid by the condensation of quinolinic anhydride with toluene in presence of aluminium chloride. Quinolinic acid affords an exception to Kirpal's rule that two isomeric ketonic acids are formed in this reaction, as he only obtained 3-benzoylpicolinic acid on condensing it with benzene.

It is now found that when condensed with toluene, 3-*p*-toluoylpicolinic acid, m. p. 169°, is the main product, but that traces of a compound, m. p. 150°, are also formed; this has not been investigated.

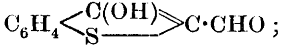
The 3-*p*-tolyl pyridyl ketone obtained by Just on heating 3-*p*-toluoylpicolinic acid at its melting point, has been synthesised from nicotinyl chloride and toluene; this establishes the formula of the 3-*p*-toluoylpicolinic acid, which has also been synthesised from quinolinic acid methyl ester chloride and toluene.

3-(m : 4)-*Xyloylpicolinic acid*, prepared in a similar manner from *m*-xylene, has m. p. 142°. On heating, *β*-m : 4-*xylyl pyridyl ketone* is obtained, identical with that prepared from nicotinyl chloride and xylene; it is a faintly yellow-coloured oil, b. p. 240°, and forms a *picrate*, crystallising in yellow plates, m. p. 134°. E. F. A.

Aldehydes of Oxindole, Indoxyl, and Hydroxythionaphthen. PAUL FRIEDLÄNDER and ST. KIELBASINSKI (*Ber.*, 1911, **44**, 3098—3108).—Friedländer and Schwenk (Abstr., 1910, i, 592) have shown that indigotin is decomposed by potassium hydroxide at 150° into anthranilic acid and indoxylaldehyde. In a similar manner the isomeric oxindolealdehyde,  $C_6H_4<\begin{matrix}C(CHO)\\ NH\end{matrix}>C{\cdot}OH$, is obtained from "thioindigoscarlet R," whilst the dye prepared by condensing hydroxythionaphthen with *N*-methylisatin yields a *N*-methyl derivative of oxindolealdehyde,  $C_6H_4<\begin{matrix}C(CHO)\\ NMe\end{matrix}>C{\cdot}OH$. All three compounds show the normal aldehyde reactions.

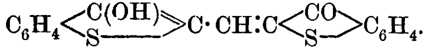
Indoxylaldehyde, however, behaves abnormally towards mineral acids, which on moderate warming convert it into an intense violet dye; this dissolves in alkalis with a bluish-green coloration.

3′-Indoxyl-2-thionaphthen-2′-one (Abstr., 1908, i, 673) is decomposed by alkali to 3-hydroxythionaphthen-2-aldehyde,



$$C_6H_4<\begin{matrix}C(OH)\\ S\end{matrix}>C{\cdot}CHO\,;$$

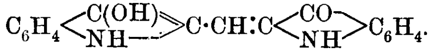
this is converted quantitatively by dilute acids into a red dye dissolving in alkali with a bluish-violet coloration. This dye is also formed from equal molecules of hydroxythionaphthen and hydroxythionaphthenaldehyde, and has the constitution



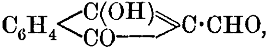
$$C_6H_4{<}\begin{matrix}C(OH)\\S\end{matrix}{>}C\cdot CH{:}C{<}\begin{matrix}CO\\S\end{matrix}{>}C_6H_4.$$

The same dye is formed from hydroxythionaphthen under a variety of conditions; for example, by the action of air on the strongly alkaline solution, particularly in presence of formaldehyde or other aliphatic aldehyde. It is also formed on heating carboxyphenylsulphoxideacetic acid, $CO_2H\cdot C_6H_4\cdot SO\cdot CH_2\cdot CO_2H$, in anhydrous potassium sodium acetate at 160—170°.

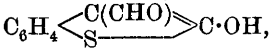
It is probable that the dye formation from indoxylaldehyde is similar in character, and that it may be formulated as



$$C_6H_4{<}\begin{matrix}C(OH)\\NH\end{matrix}{>}C\cdot CH{:}C{<}\begin{matrix}CO\\NH\end{matrix}{>}C_6H_4.$$

Other analogous hydroxyaldehydes, for example, indandionealdehyde,  $C_6H_4{<}\begin{matrix}C(OH)\\CO\end{matrix}{>}C\cdot CHO$, behave similarly towards acids.

The 3-aldehydes of oxindole and 2-hydroxythionaphthen are likewise sensitive towards mineral acids; the latter,



$$C_6H_4{<}\begin{matrix}C(CHO)\\S\end{matrix}{>}C\cdot OH,$$

is prepared by the action of potassium hydroxide on 2′-indoxyl-3-thionaphthen-2-one (*loc. cit.*).

Oxidole-3-*aldehyde* crystallises in faintly yellow-coloured needles, m. p. 213°; the aqueous solution is turned dark blue by ferric chloride. The *sodium* salt forms light grey crystals. The *phenylhydrazone* separates in stellar aggregates of pale yellow needles, m. p. 210°. The *aldazine* forms orange-yellow needles, m. p. 239°. The *oxime* forms corny crystals, m. p. 150°; its hydrochloride and sulphate crystallise well. The *anil* crystallises in yellow needles, m. p. 246° (decomp.). Analogous sparingly soluble anils are formed with *benzidine*, yellow needles, m. p. 300°, p-*toluidine*, greenish-yellow plates, m. p. 173°, m-*aminobenzoic acid*, yellow needles, m. p. above 290°, p-*phenylenediamine*, yellow plates, m. p. above 300°.

1-*Methyloxindole*-3-*aldehyde* crystallises in pale yellow needles, m. p. 186°; the *sodium* salt is sparingly soluble. The following derivatives are described: *phenylhydrazone*, broad, pale yellow needles, m. p. 193°; *oxime*, small, yellow, indefinitely formed needles, m. p. 111°; *aldazine*, orange-yellow needles, m. p. 211°; *anil*, pale yellow needles, m. p. 141°; *benzidine* derivative, greenish-yellow needles, m. p. 218°; p-*toluidine* derivative, well-formed, yellow needles, m. p. 150°; m-*aminobenzoic acid* derivative, yellow needles, m. p. 296°; p-*phenylenediamine* compound, orange-yellow needles, m. p. 210° (decomp.).

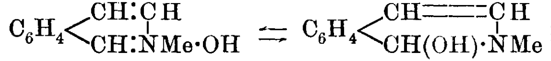
Indoxyl-2-aldehyde, m. p. 145°, forms a *phenylhydrazone*, crystallising in yellow needles, m. p. 116° (decomp.); the *aldazine* forms small, orange-red needles, decomp. above 150°; the *anil* gives orange-yellow needles, m. p. 195° (decomp.).

3-*Hydroxythionaphthen*-2-*aldehyde* crystallises in yellow needles, m. p. 107°, and gives a dark olive-green coloration with ferric chloride. The *phenylhydrazone* crystallises in broad, golden-yellow needles,

m. p. 137°. The *dye*, $C_{17}H_{10}O_2S_2$, obtained on warming with 5% sulphuric acid crystallises in large, red needles; the *sodium* salt forms lustrous, gold platelets. The corresponding *dye*, $C_{17}H_9O_2S_2Cl$, obtained on condensing hydroxythionaphthenaldehyde with 6-chlorohydroxythionaphthen, is very similar, crystallising in slender, red needles.

2-*Hydroxythionaphthen*-3-*aldehyde* crystallises in colourless needles, m. p. 126—127°; it gives a dark blue coloration with ferric chloride. The *aldazine* forms slender, yellow needles, m. p. 203°; with anthranilic acid a yellow, crystalline precipitate, m. p. 249°, of the *azomethine* is obtained. E. F. A.

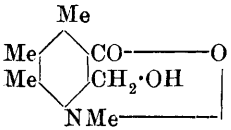
Cyclic Ammonium Bases. Herman Decker and Adolf Kaufmann (*J. pr. Chem.*, 1911, [ii], **84**, 425—448. Compare this vol., i, 807).—An aqueous solution of *iso*quinoline methiodide, when treated with potassium hydroxide and shaken with benzene, yields the corresponding carbinol base (1-hydroxy-2-methyldihydro*iso*quinoline). By shaking the benzene solution with water, the greater part of the carbinol base may be extracted in the form of the ammonium base (2-methyl*iso*quinolinium hydroxide), the amount of which may be determined by titration with hydrochloric acid. The dilute aqueous solutions thus obtained are strongly alkaline, precipitate metallic hydroxides, and show all the characteristic properties of aqueous solutions of aliphatic ammonium bases. In contrast to the carbinol base, which undergoes atmospheric oxidation very readily, the ammonium base is very stable, its aqueous solutions showing no change even on exposure to air for seventy-two hours. Dilute aqueous solutions of the ammonium base, when shaken with benzene, yield no appreciable amount of the carbinol base; on the addition of sodium hydroxide, however, considerable quantities of the carbinol base may be extracted.

From these observations the conclusion is drawn that in aqueous solution there exists an equilibrium between the ammonium and carbinol bases:  $C_6H_4\Big<\begin{matrix}CH{:}CH\\ \vert\\ CH{:}NMe\cdot OH\end{matrix} \rightleftharpoons C_6H_4\Big<\begin{matrix}CH{=}CH\\ \vert\\ CH(OH)\cdot NMe\end{matrix}$; in dilute solution the amount of the latter base is very small, but increases on the addition of an alkali hydroxide.

2-*Methyl*iso*quinolinium picrate*, $C_{16}H_{12}O_7N_4$, crystallises in long, slender, yellow needles, sintering at 183°, m. p. 187°.

Similar experiments were carried out with quinoline methiodide, but no evidence of the transformation of the carbinol base into the corresponding ammonium base was obtained.

[With Matei Sassu and Waslaw Wisloki.]—Addition of aqueous sodium hydroxide to pyridine methiodide yields a solution, which resembles in its behaviour that obtained from an aliphatic quaternary ammonium salt, and it has therefore been assumed (Hantzsch and Kalb, Abstr., 1900, i, 113) that the base is present in solution wholly in the ammonium form. The ready oxidation of such a solution to 1-methylpyridone (Decker, Abstr., 1893, i, 279) is, however, in contradiction to this view, but is readily explicable on the assumption that there exists in aqueous solution an equilibrium between the ammonium and carbinol bases, the amount of the latter being very small in comparison with that of the ammonium base. On oxidation, the carbinol base is continuously removed, and the equilibrium thereby displaced until the whole of the ammonium base is converted into 1-methylpyridone.



Reasons are given in favour of the annexed formula for the compound obtained by Wolf (Abstr., 1902, i, 677) by the action of alkalis on trimethylquinolide methiodide.

1-Alkylpyridones are readily prepared by oxidising 1-alkylpyridinium halides with potassium ferricyanide in aqueous sodium hydroxide in the presence of benzene. The preparation of 1-methylpyridinium salts is best accomplished by treating the extremely hygroscopic *additive* compound of methyl sulphate and pyridine with the acid corresponding with the salt required; the picrate, $C_{12}H_{10}O_7N_4$, is thus obtained anhydrous in needles, m. p. 113—114°, or rhombohedra, m. p. 109—110°.

1-*Propylpyridinium bromide* (*pyridine propylbromide*), prepared from pyridine and propyl bromide, yields a *cadmibromide*, $C_{16}H_{24}N_2Br_4Cd$, crystallising in white needles, m. p. 117—118°; the *chloride*, *mercurichloride*, m. p. 82°, and *platinichloride*, orange-red crystals, m. p. 196°, are also described.

1-*Propyl*-2-*pyridone*, $C_8H_{11}ON$, is a light yellow liquid, b. p. 263—264°/730 mm., having a repulsive odour of fungi.

1-iso*Butylpyridinium iodide* forms very hygroscopic, light yellow crystals; the *picrate*, leaflets, m. p. 114°; the *platinichloride*, yellow leaflets, m. p. 220° (decomp.). 1-iso*Butyl*-2-*pyridone*, $C_9H_{13}ON$, is a yellow oil, b. p. 264—265°/725 mm.

1-iso*Amylpyridinium iodide* forms hygroscopic crystals; the *picrate*, yellow needles, m. p. 145°, and the *platinichloride*, yellow leaflets, which decompose at 200°, were also prepared. 1-iso*Amyl*-2-*pyridone* has b. p. 283—284°/730 mm.

3-*Bromopyridine methiodide* crystallises in hygroscopic, yellow needles, m. p. 146°, and is oxidised by potassium ferricyanide to 3-*bromo*-1-*methyl*-2-*pyridone*, which forms a brown oil, and on treatment with bromine in glacial acetic acid solution yields 3 : 5-*dibromo*-1-*methyl*-2-*pyridone*; the latter compound, which crystallises in white needles, m. p. 176°, has also been prepared (1) by the oxidation of the *additive* compound of methyl sulphate and 3 : 5-dibromopyridine; (2) by brominating 1-methylpyridone. 3:5-*Dibromopyridine methiodide*, obtained by the action of potassium iodide on the above-mentioned additive compound, resembles *iso*quinoline methiodide in its behaviour towards alkalis.

[With S. PFEIFER, N. PROHATZKA, and A. ALBERTINI.]—The entrance of substituents into quaternary quinoline salts considerably modifies the behaviour of the latter towards alkalis; whilst 6-aminoquinoline methiodide on treatment with aqueous sodium hydroxide undergoes no change, the dinitro- and bromonitro-derivatives are converted into the corresponding carbinol bases by dilute sodium hydrogen carbonate. It thus appears that positive substituents prevent the transformation of ammonium bases into carbinol bases, whilst with negative substituents the transformation takes place with extraordinary ease.

6-*Diacetylaminoquinoline*, prepared by heating 6-aminoquinoline with acetic anhydride in benzene solution, crystallises in long, slender, white needles, m. p. 75°; the product, obtained by the interaction of the *methiodide* and silver chloride, yields either 6-*diacetylaminoquinoline methochloride* or 6-*acetylaminoquinoline methochloride*, accordingly as it is crystallised from alcohol or water.

6-Acetylamino-1-methylquinolone, prepared by oxidising 6-*acetylaminoquinoline methiodide*, crystallises in needles, m. p. 278° (compare Decker and Engler, Abstr., 1903, i, 518).

6-*Aminoquinoline methochloride*, obtained by heating the acetyl (or diacetyl) derivative with hydrochloric acid, crystallises in citron-yellow needles, m. p. 242—243°; it separates from water in efflorescent crystals containing one molecule of the solvent; the methiodide forms reddish-brown needles, m. p. 199° (compare Claus and Schnell, Abstr., 1896, i, 319). When treated with 35% aqueous sodium hydroxide, 6-aminoquinoline methiodide yields a *substance*,

$$C_{20}H_{29}O_4N_2I,$$

crystallising in microscopic, red needles, m. p. 166°, which have a vivid green, metallic lustre, and yield solutions having a yellow fluorescence.

6 : 8-*Dinitro*-2-iso*butyloxy*-1-*methyldihydroquinoline*,

$$C_{14}H_{17}O_5N_3,$$

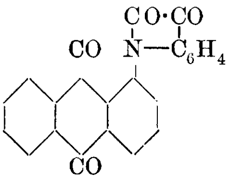
has m. p. 87°; the methyl and ethyl ethers (Kaufmann and Strübin, this vol., i, 322) are also described.

6-Bromo-8-nitroquinoline, which has m. p. 170—177° (compare Claus and Hartmann, Abstr., 1896, i, 391), on successive treatment with methyl sulphate and potassium iodide yields the *methiodide*, $C_{10}H_8O_2N_2BrI$, which crystallises in dark reddish-brown needles, decomposing at 185—186°. With dilute aqueous ammonia the methiodide yields 6-*bromo*-8-*nitro*-2-*hydroxy*-1-*methyldihydroquinoline*, which has m. p. 173—175°, and forms a *methyl ether*, m. p. 121—122°; the *ethyl ether* crystallises in prisms, m. p. 111°.

3 Bromo-8-nitro-2-hydroxy-1-methyldihydroquinoline (Decker, Abstr., 1905, i, 374) is obtained in quantitative yield by the action of very dilute aqueous ammonia on the methiodide; the *ethyl ether*, large, light brown, prismatic crystals, has m. p. 90—91°. F. B.

Preparation of Halogen-substituted Indophenol Derivatives from Carbazoles and *p*-Nitrosophenols. LEOPOLD CASSELLA & Co. (D.R.-P. 235836).—When *p*-nitrosophenol or its halogen derivatives are condensed in concentrated sulphuric acid solution with *N*-alkyl or halogenated carbazoles, indophenol derivatives of tinctorial value are produced.

The *products* from monochlorocarbazole and *p*-nitrosophenol, from carbazole and *N*-ethylcarbazole with *o*-chloronitrosophenol respectively, and from carbazole with 2 : 6-dibromonitrosophenol were prepared. They are dark blue or green substances, insoluble in water, but soluble in concentrated sulphuric acid with a blue coloration, decompose above 250° without fusion, and yield colourless leuco-compounds. F. M. G. M.

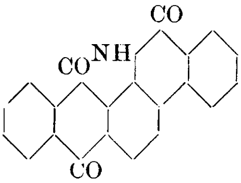


[Preparation of Anthraquinone Derivatives.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 236407).—When α-chloroanthraquinone is boiled with isatin (in nitrobenzene solution) in the presence of cuprous chloride and copper acetate and the mixture subsequently acidified, it yields the *compound* (annexed formula) as a bluish-red, crystalline powder. The *products* from 1 : 5-dichloroanthraquinone and isatin (1 mol.), a violet powder, and the same with 2 mols. of isatin were also prepared, whilst 4-bromo-1-methylaminoanthraquinone under similar conditions yielded a greenish-black powder. F. M. G. M

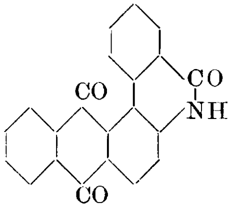
Preparation of Phenanthridone Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 236857).—When halogen-*o*-benzoylaminoanthraquinones (or their derivatives) are boiled with or without copper powder in naphthalene solution with anhydrous sodium carbonate (or acetate), condensation occurs, yielding phenanthridone derivatives.

The *compound* (I), $C_{21}H_{11}O_3N$, prepared from 2-bromo-1-benzoylaminoanthraquinone (without the addition of copper powder), crystallises from dichlorobenzene, and has m. p. 266—267°.

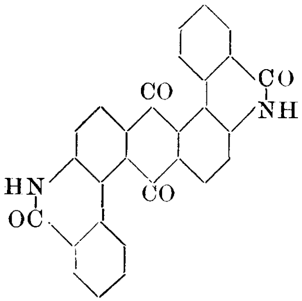
The *compound* (II), m. p. 274—275°, was obtained from 1-chloro-2-benzoylaminoanthraquinone in nitrobenzene solution without copper powder. The *products* from 2 : 3-dichloro-1 : 4-dibenzoylaminoanthra-



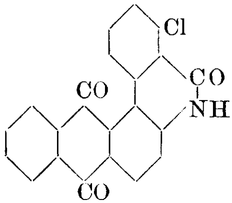
(I.)



(II.)



(III.)



(IV.)

quinone and from 3-halogen-2-benzoylaminoanthraquinone do not fuse below 325°.

The *product* (III), $C_{28}H_{14}O_4N_2$, prepared from 1 : 5-dichloro-2 : 6-dibenzoylaminoanthraquinone in the presence of copper, does not melt at 320°.

The *compound* (IV), $C_{21}H_{10}O_3NCl$, m. p. 278—280°, was obtained from 1-chloro-*o*-chlorobenzoylaminoanthraquinone (prepared from *o*-chlorobenzoyl chloride and 1-chloro-2-aminoanthraquinone).

F. M. G. M.

[Preparation of Carbamide Derivatives.] CARL JÄGER (D.R.-P. 236594).—When an aromatic *m*-diamino-sulphonic acid (1 mol.) reacts with an aminonaphtholsulphonic acid (2 mols.) and carbonyl chloride (2 mols.) in dilute aqueous sodium carbonate solution, derivatives of carbamide are obtained. The *substance*,

$$SO_3H{\cdot}C_6H_2Me[NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_5(OH){\cdot}SO_3H]_2,$$

is prepared in this manner from 2 : 6-tolylenediamine-4-sulphonic acid, 6-amino-α-naphthol-3-sulphonic acid, and carbonyl chloride. These compounds when combined with 2 mols. of a diazonium compound yield orange to bluish-red direct cotton dyes. F. M. G. M.

Catalytic Decomposition of Alkylidenehydrazines. II. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 951—962). —With a view to generalising the method of obtaining hydrocarbons previously described (this vol., i, 679), the author has studied the decomposition, in presence of potassium hydroxide, of the hydrazones of dihydrocarvone, carvenone, citronellaldehyde, and citral.

Under these conditions, dihydrocarvonehydrazone yields $\Delta^{8(9)}$-*p*-menthene (compare Perkin and Pickles, Trans., 1905, **87**, 639). The action of hydrobromic acid on this hydrocarbon gives the bromo-derivative, $C_{10}H_{19}Br$, which yields *i*-$\Delta^{4(8)}$-menthene (compare Wallach, Abstr., 1906, i, 682) when distilled with aniline.

Carvenonehydrazone, when distilled in presence of fused potassium hydroxide, yields Δ^3-menthene.

Citronellaldehydehydrazone yields the *hydrocarbon*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_3,$$

b. p. 164·5°/756 mm., D_0^{20} 0·7533, n_D 1·4304, $[\alpha]_D$ +9·28°. Oxidation of this hydrocarbon with permanganate yields acetone, active amylacetic acid (compare Welt, Abstr., 1895, i, 203), and, as an intermediate product, the *keto-alcohol*,

$$OH{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2Me,$$

b. p. 218°/755 mm., D_0^{20} 0·9069, n_D 1·4363, which reduces ammoniacal silver solution in presence of alkali, and forms a *semicarbazone*, m. p. 125—126°, $[\alpha]_D$ +1·78° to +2·20°.

The hydrocarbon, b. p. 164·5°, obtained from citronellaldehydehydrazone, gives with hydrobromic acid the *bromo*-derivative,

$$C_{10}H_{21}Br,$$

D_0^{20} 1·0772, n_D 1·4578, which gives a hydrocarbon, $C_{10}H_{20}$, with almost the same physical constants as the original one when distilled with aniline, with the exception of its specific rotation, which is $[\alpha]_D$ +4·39°.

Reduction of the hydrocarbon, b. p. 164·5°, by means of hydriodic acid in a sealed tube yields *βζ*-dimethyloctane,

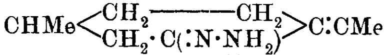
$CHMe_2·CH_2·CH_2·CH_2·CHMeEt$ (?),

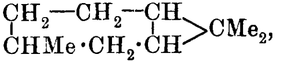
b. p. 159—159·5°/742 mm., D_4^{20} 0·7313, n_D 1·4110, $[\alpha]_D$ +1·75° (compare Markownikoff and Reformatsky, Abstr., 1893, i, 662; Skita and Ritter, *Ber.*, 1911, **44**, 668; this vol., i, 272).

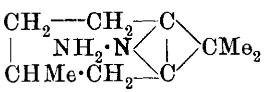
Citralhydrazone, when distilled with solid potassium hydroxide yields an inactive *hydrocarbon*, $CMe_2:CH·CH_2·CH_2·CMe:CHMe$, b. p. 164—165°/755 mm., D_0^{20} 0·7674, n_D 1·4443, which is isomeric with the dihydromyrcene, b. p. 171·5—173·5°, obtained by Semmler (Abstr., 1901, i, 732) by the reduction of myrcene. T. H. P.

Decomposition of Alkylidenehydrazines. Conversion of Pulegone [Tanacetone] into a Bicyclic Hydrocarbon, $C_{10}H_{18}$.

NICOLAI M. KIJNER and A. ZAVADOVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1132—1148. Compare this vol., i, 679).—The action of hydrazine hydrate on tanacetone would be expected to give an alkylidenehydrazine of the structure



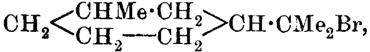
this yielding, on decomposition, $\Delta^{4(8)}$-menthene (compare Wallach, Abstr., 1908, i, 402). It is found, however, that pulegohydrazine is not hydrolysed by mineral acids, with which it forms stable salts, and that, on decomposition, it gives a dicyclic hydrocarbon, *carane*,  corresponding with carone. The action of hydrazine hydrate on pulegone is hence accompanied by isomerisation, pulegohydrazine having the annexed constitution.

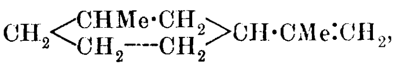


Pulegohydrazine, $C_{10}H_{18}N_2$, is an almost colourless liquid, b. p. 131—132°/23 mm., 143—144°/35 mm., D_0^{20} 0·9602, $[\alpha]_D$ − 5·55°, n_D 1·4943. The *thiosemicarbazone*,

$NHPh·CS·NH·N:C_{10}H_{16}$,

forms thin, rhombic plates, m. p. 176°, $[\alpha]_D$ − 114·33°. The hydrazine undergoes oxidation in the air, yielding pulegone, and an oily product which was not investigated.

Carane, $C_{10}H_{18}$, obtained by the slow distillation of pulegohydrazine with potassium hydroxide, has b. p. 169·5°/759 mm., D_0^{20} 0·8404—0·8411, n_D 1·4561—1·4576, exaltation of molecular refraction 0·72—0·85, $[\alpha]_D$ + 56·89° to 57·64°. Carane is quite saturated in character, and, owing to the presence of the trimethylene ring (indicated by the optical exaltation) readily combines with 1 mol. of bromine or halogen hydroacid. The *bromo*-derivative,  obtained by the action of hydrobromic acid, has b. p. 123—124°/29 mm. (slightly decomp.), D_4^{20} 1·1811, D_0^{20} 1·1691, n_D 1·4893—1·4914, $[\alpha]_D$ + 5·37° to 5·42°, and loses hydrogen bromide in two different ways: (1) with alcoholic potassium hydroxide it gives $\Delta^{3(8)}$-*m*-menthene (compare Wallach, *loc. cit.*), which yields *β*-methyladipic acid when oxidised with excess of permanganate; (2) with aniline the principal product is $\Delta^{8(9)}$-m-*menthene*,



$CH_2<\begin{matrix}CHMe\cdot CH_2\\CH_2—CH_2\end{matrix}>CH\cdot CMe{:}CH_2$, which is, however, mixed with $\Delta^{3(8)}$-*m*-menthene.

When $\Delta^{8(9)}$-*m*-menthene is treated with hydriodic acid and the iodide heated with aqueous-alcoholic potassium hydroxide, $\Delta^{3(8)}$-*m*-menthene is obtained.

Reduction of carane or $\Delta^{8(9)}$-*m*-menthene yields *m*-menthane.

Combination of carane with bromine (1 mol.) and distillation of the bromide thus obtained with quinoline gives lævorotatory menthadiene, which, after prolonged boiling with sodium, becomes inactive, and has b. p. 182—185°/749 mm., D_4^{20} 0·8544, n_D 1·4916; this hydrocarbon in acetic anhydride solution gives an intense blue coloration with sulphuric acid. Such a coloration is given by $\Delta^{2:8(9)}$-*m*-menthadiene (compare Haworth, Perkin, and Wallach, Trans., 1911, **99**, 118), but this could only be derived from carane as a result of isomerisation of the bromide previous to the removal of hydrogen bromide (see also Perkin, Trans., 1910, **97**, 2154). T. H. P.

Influence of Auxochromes on Phototropy. MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 196—200. Compare this vol., i, 693).—On comparing the phototropic substances previously obtained, it appears that the aldehydrazones which contain auxochrome groups are generally more phototropic than those which do not contain any, and this is even more noticeable in the case of the osazones of diketones. The position of the auxochrome appears to have some influence. In the present paper eight anishydrazones (*p*-methoxyphenylhydrazones) are described, which have been prepared for comparison with the corresponding phenylhydrazones.

p-Methoxyphenylhydrazine (compare Altschul, Abstr., 1892, 1080) is best obtained by diazotising *p*-anisidine and reducing the diazonium compounds with stannous chloride. It has m. p. 66° (Altschul, 65°).

Benzaldehyde-p-*methoxyphenylhydrazone*, $OMe\cdot C_6H_4\cdot NH\cdot N{:}CHPh$, crystallises in pale yellow needles, m. p. 123°, and is phototropic.

Anisaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot OMe,$$

forms lustrous, yellow scales, m. p. 126°, and is not phototropic.

Cinnamaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N{:}CH\cdot CH{:}CHPh,$$

crystallises in rosettes of short, thick needles, m. p. 126·5°, and is phototropic.

Cuminaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_4\cdot CHMe_2,$$

forms long, pale yellow needles, m. p. 99°. It is phototropic.

Piperonaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_3{:}O_2{:}CH_2,$$

crystallises in yellowish-green, lustrous needles, m. p. 134—135°, and is phototropic.

p-*Tolualdehyde*-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N{:}CH\cdot C_6H_4Me,$$

forms lustrous, yellow scales, m. p. 131°, and is not phototropic.

Vanillin-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N:CH\cdot C_6H_3(OH)\cdot OMe,$$

crystallises in minute, pale yellow prisms, m. p. 125—126°, and is phototropic.

Salicylaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N:CH\cdot C_6H_4\cdot OH,$$

forms yellowish-green needles, m. p. 132°, and is not phototropic.

R. V. S.

Phototropy of the Hydrazones of Furfuraldehyde. L. SANTI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 228—230. Compare Padoa and Graziana, Abstr., 1910, i, 509, 778).—Furfuraldehydephenylhydrazone is not phototropic.

Furfuraldehyde-α-naphthylhydrazone, $C_4H_3O\cdot CH:N\cdot NH\cdot C_{10}H_7$, forms small, canary-yellow prisms, m. p. 110·5°, and is not phototropic.

Furfuraldehyde-β-naphthylhydrazone crystallises in pale yellow needles, m. p. 137°, and is phototropic.

Furfuraldehyde-p-*tolylhydrazone*, $C_4H_3O\cdot CH:N\cdot NH\cdot C_6H_4Me$, is a pale yellow, crystalline powder, which is weakly phototropic.

R. V. S.

Action of Aldehydes on Pyrrole Derivatives. U. COLACCHI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 312—317).—Pyrrole derivatives which have only one free methine hydrogen, and have a negative substituent, react with aliphatic aldehydes when warmed with them in the presence of a little zinc chloride. The condensations with formaldehyde are best effected in the presence of hydrochloric acid.

Bis-5-acetyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Ac)_2$, forms yellow scales or needles, m. p. 272°.

Bis-3-acetyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Ac)_2$, is a yellow, crystalline powder, m. p. 268°.

Bis-5-benzoyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Bz)_2$, crystallises in small, colourless needles, m. p. 257—258°.

αα-Bis-5-acetyl-2 : 4-dimethylpyrrylethane $CHMe(C_4NHMe_2Ac)_2$, forms yellow needles, m. p. 253°.

αα-Bis-3-acetyl-2 : 4-dimethylpyrrylethane, $CHMe(C_4NHMe_2Ac)_2$, crystallises in pale, rose-coloured scales, m. p. 254°.

αα-Bis-5-benzoyl-2 : 4-dimethylpyrrylethane, $CHMe(C_4NHMe_2Bz)_2$, forms very small prisms, m. p. 244—245°.

αα-Bis-5-benzoyl-2 : 4-dimethylpyrrylbutane, $CHPr(C_4NHMe_2Bz)_2$, crystallises in small, yellow prisms, m. p. 217—218°.

*αα-Bis-5-benzoyl-2 : 4-dimethylpyrryl*iso*butane*,

$$CHMe_2\cdot CH(C_4NHMe_2Bz)_2,$$

is a yellow, flocculent substance, which on heating becomes soft at 80°, spongy at 100°, and melts at 180°.

αα-Bis-5-benzoyl-2 : 4-dimethylpyrrylheptane,

$$C_6H_{13}\cdot CH(C_4NHMe_2Bz)_2,$$

forms a yellow, crystalline powder, m. p. 178—179°. R. V. S.

Preparation of Halogenated Derivatives of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 235631. Compare this vol., i, 925).—The preparation of tetrahalogenated indigotins has previously been recorded; penta- and hexa-halogenated derivatives have now been prepared.

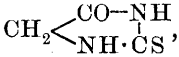
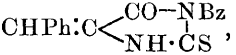
Dichlorotetrabromoindigotin is obtained when 4 : 4′-dichloroindigotin, dissolved in nitrobenzene (or acetic acid), is slowly treated with bromine and the mixture subsequently boiled until the evolution of hydrogen bromide ceases.

Pentachloroindigotin is prepared by the further chlorination of 4 : 4′-dichloroindigotin at 25—30° in acetic acid solution. The leuco-derivatives and intermediate halogenated acetylindigotins are also mentioned and their tinctorial properties described. F. M. G. M.

Hydantoins. VI. Action of Acylthioncarbamates, Acylthiocarbamates, Acyldithiocarbamates, and Acylimidodithiocarbonates on α-Amino-acids. 2-Thiolhydantoin. HENRY L. WHEELER, BEN H. NICOLET, and TREAT B. JOHNSON (*Amer. Chem. J.*, 1911, **46**, 456—474).

—This work was undertaken for the purpose of synthesising some *N*-acyl derivatives of hydantoic and thiohydantoic acids and of investigating their behaviour on hydrolysis and their reactivity towards aldehydes.

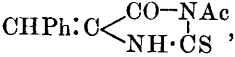
Benzoyl-ψ-ethylhydantoic acid, $NBz\colon C(OEt)\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 161°, obtained by the action of aminoacetic acid on ethyl benzoylthioncarbamate in presence of potassium hydroxide, crystallises in needles; its *ethyl* ester has m. p. 79—80°. *Ethyl benzoyl-ψ-methylhydantoate*, $NBz\colon C(OMe)\cdot NH\cdot CH_2\cdot CO_2Et$, m. p. 103°, is obtained by the interaction of ethyl aminoacetate and methyl benzoylthioncarbamate. When benzoyl-ψ-ethylhydantoic acid or ethyl benzoyl-ψ-methylhydantoate is hydrolysed with hydrochloric acid, *benzoylhydantoic acid*, $NHBz\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 253—254° (decomp.), is produced, which crystallises in plates, and is decomposed by hydrochloric acid into benzoic acid and hydantoin. An attempt to condense benzoylhydantoic acid with benzaldehyde was not successful.

Thiobenzoylhydantoic acid, $NHBz\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 202°, prepared by heating a mixture of aminoacetic acid, potassium hydroxide, and ethyl benzoyldithiocarbamate, crystallises in plates or needles; its *ethyl* ester has m. p. 128—129°. When either thiobenzoylhydantoic acid or thioacetylhydantoic acid is heated with concentrated hydrochloric acid, 2-*thiohydantoin*,  $CH_2<\begin{matrix}CO-NH\\ NH\cdot CS\end{matrix}$, m. p. 227°, is produced, which forms yellow prisms. Benzoylthiohydantoic acid condenses with benzaldehyde to form 2-*thio*-1-*benzoyl*-4-*benzylidenehydantoin*,  $CHPh\colon C<\begin{matrix}CO-NBz\\ NH\cdot CS\end{matrix}$, m. p. 181°, which crystallises in rectangular plates, and is decomposed by potassium hydroxide solution with production of 2-thio-4-benzylidenehydantoin, m. p. 258°, which can also be obtained by the condensation of thiohydantoin with benzaldehyde. Ruhemann and Stapleton (Trans., 1900, **77**, 246) have stated that this compound has m. p. 280° (decomp.) when heated slowly and m. p. 300° (decomp.) when heated rapidly, but the authors found the m. p. 258° under all conditions.

Thiobenzoyl-ψ-ethylhydantoic acid, $NBz\colon C(SEt)\cdot NH\cdot CH_2\cdot CO_2H$, m. p.

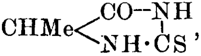
198°, prepared from aminoacetic acid and ethyl benzoyliminodithiocarbonate, forms clusters of needles; its *ethyl* ester has m. p. 77—78°.

Thioacetylhydantoic acid, $NHAc\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 205° (decomp.), from aminoacetic acid and ethyl acetyldithiocarbamate, crystallises in slender needles; its *potassium* salt has m. p. 225—227° (decomp.), and its *ethyl* ester, m. p. 104—105°. The acid condenses with benzaldehyde to form 2-*thio*-1-*acetyl*-4-*benzylidenehydantoin*,



$CHPh{:}C{<}\begin{matrix}CO-NAc\\ |\\ NH\cdot CS\end{matrix}$, m. p. 231°, which crystallises in light yellow prisms.

Thio-1-*acetyl*-4-*methylhydantoic acid*, $NHAc\cdot CS\cdot NH\cdot CHMe\cdot CO_2H$, m. p. 171°, from alanine and ethyl acetyldithiocarbamate, crystallises in prisms, and is converted by concentrated hydrochloric acid into 2-*thio*-4-*methylhydantoin*,



$CHMe{<}\begin{matrix}CO-NH\\ |\\ NH\cdot CS\end{matrix}$, m. p. 158—159°, which forms flat prisms.

E. G.

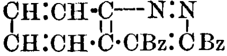
Preparation of 5 : 5-Dialkylthiobarbituric Acids. EMANUEL MERCK (D.R.-P. 235801. Compare this vol., i, 683).—The preparation of 5 : 5-dialkylthiobarbituric acids by the employment of metallic alkyloxides has previously been described; it is found that these can be replaced by the free alkali metal (or its amide), and the preparation of diethylthiobarbituric acid (m. p. 180°) from diethylmalonic ester, thiocarbamide, and sodamide (or metallic sodium) is now demonstrated.

F. M. G. M.

Constitution of the Nitro-2 : 5-dimethylbenziminazole Obtained by Nitration. DAVID MARON and D. SALZBERG (*Ber.*, 1911, **44**, 2999—3005).—The proof that the nitro-group in the nitro-compound, m. p. 200—201°, obtained by the nitration of 2 : 5-dimethylbenziminazole (Niementowsky, Abstr., 1886, 719), occupies position 6 is as follows. By reduction with iron and 50% acetic acid, the nitro-compound yields an *amine*, m. p. 85°, the *acetyl* derivative of which has m. p. 263—264°. By nitration, diacetyl-*m*-tolylenediamine yields a nitro-compound, which can be reduced to an *amine*, m. p. 252—253°, which forms an azoimide with nitrous acid (therefore the amino-group is ortho to an NHAc group), and yields the preceding acetylaminodimethylbenziminazole, m. p. 263—264°, by heating at 250°. Finally, the nitration of diacetyl-3 : 4-tolylenediamine yields a nitro-compound, the reduction of which yields an *amine*, m. p. 238°, the *acetyl* derivative of which, m. p. 273—274°, is identical with that obtained by the acetylation of the preceding amine, m. p. 252—253°. Consequently, this acetylated triamino-derivative must be triacetyl-3 : 4 : 6-triaminotoluene; the amine m. p. 238° is 6-aminodiacetyl-3 : 4-tolylenediamine, the amine m. p. 252—253° is 3-aminodiacetyl-4 : 6-tolylenediamine, and the nitrated dimethylbenziminazole is 6-nitro-2 : 5-dimethylbenziminazole.

C. S.

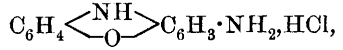
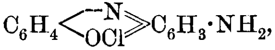
Researches on Azinetriphenylpyrrole. FRANCESCO ANGELICO (*Gazzetta*, 1911, **41**, ii, 378—381).—By the action of ammonium sulphide on the diketone,



$\begin{matrix}CH{:}CH\cdot C-N{:}N\\ |\qquad\quad \| \qquad\quad |\\ CH{:}CH\cdot C\cdot CBz{:}CBz\end{matrix}$ (compare Abstr., 1909, i, 122), the author obtained (Abstr., 1910, i, 444) the corresponding *dithioketone,* m. p. 206°, and he has now isolated from the product of the same reaction, a thiophen *compound,* $C_{22}H_{14}N_2S$, which forms large, yellow needles, m. p. 151°. When treated with nitric acid this substance regenerates the ketone of m. p. 163°.

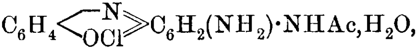
The structure of the dithioketone follows from the fact that both it and the diketone yield, when treated with hydroxylamine, the same products, namely: (1) a red pyrrole derivative; (2) a substance, probably a mixture of mono- and di-oximes; (3) a *substance,* $C_{44}H_{27}O_3N_9$, which crystallises in golden-yellow needles, m. p. 205—206°.

R. V. S.

5-Aminophenazoxonium Salts. FRIEDRICH KEHRMANN and L. LOWRY (*Ber.*, 1911, **44**, 3006—3011).—5-Aminophenazoxonium and 5-aminophenazthionium salts cannot be prepared in a similar manner to 5-aminophenylphenazonium salts (Kehrmann and Masslenikoff, this vol., i, 927). However, by the reduction of Ullmann and Kuhn's 5-nitrophenoxazine (Abstr., 1909, i, 473) by stannous chloride and concentrated hydrochloric acid, 5-*aminophenoxazine hydrochloride,*  $C_6H_4{<}\substack{NH\\O}{>}C_6H_3\cdot NH_2,HCl$, is obtained, which is oxidised by cold concentrated ferric chloride to 5-*aminophenazoxonium chloride,*  $C_6H_4{<}\substack{N\\OCl}{>}C_6H_3\cdot NH_2$, greenish-black crystals; the corresponding *bromide, iodide, nitrate,* and *platinichloride* are described.

When acetylated by sodium acetate, acetic anhydride, and a trace of zinc dust, 5-aminophenoxazine hydrochloride yields 5-*acetylaminophenoxazine,* m. p. 197° (decomp.), colourless needles, which is oxidised by ferric chloride to a mixture of two substances, m. p. about 215° (decomp.), which are probably isomeric 5-acetylaminophenazoxones.

3 : 5-Diaminophenazoxonium chloride reacts with acetic anhydride and zinc chloride to form a blackish-red, crystalline *zincichloride,* from which 3-*amino*-5-*acetylaminophenazoxonium chloride,*



$$C_6H_4{<}\substack{N\\OCl}{>}C_6H_2(NH_2)\cdot NHAc,H_2O,$$

is obtained in dark red prisms with a green lustre. The *platinichloride* is a brownish-red, crystalline powder, whilst the *base* itself, m. p. 185—190° (decomp.), crystallises in citron-yellow needles.

C. S.

Mutual Replacement of Azines and Semicarbazones. GUSTAV KNÖPFER (*Monatsh.*, 1911, **32**, 753—772).—It has been shown previously that the azine residue is readily replaced by phenylhydrazine, and this in turn by semicarbazide (Knöpfer, Abstr., 1909, i, 188; 1910, i, 432). It is now found that azines are very easily converted into semicarbazones, but that in most instances the reverse change does not take place. When aldehydes or ketones are treated with a molecular mixture of semicarbazide and hydrazine, the semicarbazone is, as a rule, the sole product.

The conversion into azine was observed in the case of the semicarbazones of salicylaldehyde, *p*-hydroxybenzaldehyde, *p*-nitrobenz aldehyde, resorcylaldehyde, protocatechualdehyde, *p*-dimethylaminobenzaldehyde, and acetone.

The *azine* of phenyl ethyl ketone forms yellow needles, m. p. 79—80°. The semicarbazone forms colourless crystals, m. p. 179—180°.

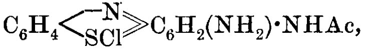
Distyryl ketone-semicarbazone forms colourless, soluble needles, m. p. 187—190°; *a-dichloroacetonesemicarbazone* has m. p. 163°, yielding a compound, m. p. 254°, which proved to be methylglyoxaldisemicarbazone.

Chloralhydrazide, $CCl_3\cdot CH(OH)\cdot NH\cdot NH_2$, forms large, colourless crystals, m. p. 85° (decomp.). The hydrazide is readily replaced by semicarbazide, forming chloral semicarbazide, m. p. 90°, but the reverse change does not take place.

The only substances to give both semicarbazone and azine on treatment with an equimolecular mixture of the two bases are *p*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde. E. F. A.

3 : 5 - Diaminophenazthionium Derivatives. FRIEDRICH KEHRMANN and J. STEINBERG (*Ber.*, 1911, **44**, 3011—3017).—The course of the reaction between picryl chloride and *o*-aminophenyl mercaptan proceeds, as stated by Kehrmann and Schild (Abstr., 1900, i, 61), not as by Mitsugi, Beyschlag, and Möhlau (Abstr., 1910, i, 337), the proof being as follows. A hot alcoholic solution of picryl chloride (2 mols.) condenses normally with *oo'*-diaminodiphenyl disulphide hydrochloride in the presence of sodium acetate, yielding oo'-*dipicryldiaminodiphenyl disulphide*, $[C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4]_2S_2$, which is reduced by alcoholic sodium sulphide to o-*picrylaminophenyl mercaptan*, $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_4\cdot SH$. The latter, in which the picryl group must be attached to the nitrogen atom, is converted by warm aqueous sodium hydroxide into the same dinitrophenthiazine as results from the condensation of *o*-aminophenyl mercaptan and picryl chloride; consequently in this condensation the amino-, not the sulphydryl, group reacts with the chlorine atom of the picryl chloride.

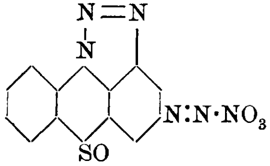
3 : 5-Diaminophenazthionium chloride, acetic anhydride, and zinc chloride react to form a violet-black, crystalline *zincichloride*, from which 3-*amino*-5-*acetylaminophenazthionium chloride*,



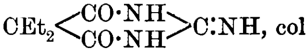
$$C_6H_4<\genfrac{}{}{0pt}{}{-N-}{SCl}>C_6H_2(NH_2)\cdot NHAc,$$

can be obtained in violet needles; the corresponding *nitrate*, *platinichloride*, and *dichromate* are described, whilst the *base* itself, $C_{14}H_{11}ON_3S$, crystallises in brick-red needles.

In the hope of eliminating an amino-group, 3 : 5-diaminophenazthionium chloride, dissolved in moderately-concentrated sulphuric acid, has been treated with 10% sodium nitrite at 0°; however, the product, isolated as the *nitrate*, brownish-yellow needles, appears to be a diazonium salt of the annexed constitution from its analysis, explosiveness, and general behaviour. When treated with boiling water containing a little sulphuric acid, nitrogen is evolved, and a brownish-red *substance*, $C_{12}H_7ON_3S$, is obtained. C. S.



Preparation of 5 : 5-Dialkyliminobarbituric Acids (2-Imino-4 : 6-diketo-5-dialkylpyrimidines). EMANUEL MERCK (D.R.-P. 235802).—Dialkylmalonic esters react with guanidine in the presence of condensing agents to yield dialkylmalonylguanidines (5 : 5-dialkyliminobarbituric acids).

2-*Imino*-5 : 5-*diethylbarbituric acid*,  $CEt_2<\substack{CO\cdot NH\\CO\cdot NH}>C:NH$, colourless needles, which on heating decompose without fusion, forms a crystalline *nitrate*, and on boiling with mineral acids furnishes diethylbarbituric acid, m. p. 191°. F. M. G. M.

1-Phenyl-5-methyl-1 : 2 : 4-triazole and Cyanophenylacetamidine. GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, ii, 93—100. Compare following abstract).—Bladin (Abstr., 1891, 472) described 1-phenyl-5-methyl-1 : 2 : 4-triazole (at first erroneously as 1-phenyl-3-methyl-1 : 2 : 4-triazole) as an uncrystallisable oil, b. p. about 250°, whilst Bamberger and Gruyter (Abstr., 1894, i, 23) recorded the same substance as a crystalline solid, m. p. 191°. The author has prepared 1-phenyl-5-methyl-1 : 2 : 4-triazole from formylphenylhydrazine and acetamide (compare following abstract), and finds that it is identical with the substance described by Bladin. The substance, m. p. 191°, of Bamberger and Gruyter is cyanophenylacetamidine,

$$NPh:CMe\cdot NH\cdot CN,$$

identical with that obtained from ethyl*iso*acetanilide and cyanamide by the method used by Comstock and Wheeler (Abstr., 1892, 747) for cyanophenylformamidine. Cyanophenylacetamidine has m. p. 193°. With warm potassium hydroxide it yields acetanilide and cyanamide. When treated with concentrated hydrochloric acid, it takes up water with formation of carbamidophenylacetamidine, $NPh:CMe\cdot NH\cdot CO\cdot NH_2$, which crystallises in lustrous plates, m. p. 180° (decomp.) if rapidly heated, or about 166° if slowly heated.

R. V. S.

Triazole and its Derivatives. GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, ii, 20—42. Compare Abstr., 1895, i, 308; Pellizzari and Massa, Abstr., 1897, i, 205; 1901, i, 488).—The author gives a summary of the triazole derivatives which have been prepared by himself and his collaborators, and describes a number of other compounds obtained in the same way. Some of these have been prepared already by other investigators by different methods.

2-Phenyl-1 : 3 : 4-triazole (compare Young, Trans., 1901, **79**, 659) can be prepared from benzoylhydrazine and formamide, or from formylhydrazine and benzamide. The *hydrochloride*, $C_8H_7N_3,HCl$, forms colourless needles, m. p. 195°. The *platinichloride*,

$$(C_8H_7N_3)_2,H_2PtCl_6,2H_2O,$$

crystallises in orange-yellow plates, decomposing at 255°. Young obtained this salt with $3H_2O$. The platinic chloride compound, $(C_8H_7N_3)_2,PtCl_4$, obtained by boiling the preceding salt with water, is a yellow, flocculent substance.

2 : 5-Dimethyl-1 : 3 : 4-triazole (compare Stollé, Abstr., 1904, i, 453) can be prepared from acetylhydrazine and acetamide.

2 : 5-Diphenyl-1 : 3 : 4-triazole (compare Pinner, Abstr., 1894, i, 386) can be obtained from benzoylhydrazine and benzanilide.

1-Phenyl-3-methyl-1 : 2 : 4-triazole (compare Andreocci, Abstr., 1892, i, 636) is obtained, mixed with 1-phenyl-1 : 2 : 4-triazole and 1-phenyl-5-methyl-1 : 2 : 4-triazole, by the action of acetylphenylhydrazine on formamide. The 1-phenyl-1 : 2 : 4-triazole is separated with the aid of the insolubility of its *nitrate*, $C_8H_7N_3,HNO_3$, which forms white needles, m. p. 141°. 1-*Phenyl*-1 : 2 : 4-*triazole picrate*, $C_8H_7N_3,C_6H_3O_7N_3$, has m. p. 159°. 1-*Phenyl*-3-*methyl*-1 : 2 : 4-*triazole picrate*,

$$C_9H_9N_3,C_6H_3O_7N_3,$$

forms long, pale yellow needles, m. p. 171°.

1-Phenyl-5-methyl-1 : 2 : 4-triazole, b. p. 275° (compare preceding abstract), can be obtained from formylphenylhydrazine and acetamide. It is mixed with 1-phenyl-1 : 2 : 4-triazole and 1-phenyl-3-methyl-1 : 2 : 4-triazole, of which the former can be removed in the form of nitrate, and the latter by distillation. 1-*Phenyl*-5-*methyl*-1 : 2 : 4-*triazole picrate*, $C_9H_9N_3,C_6H_3O_7N_3$, forms short, prismatic crystals, m. p. 146°. The *platinichloride*, $(C_9H_9N_3)_2,H_2PtCl_6,2H_2O$, crystallises in yellow plates, m. p. 129° (decomp.). The *platinic chloride* compound, $(C_9H_9N_3)_2,PtCl_4$, is obtained as a pale yellow precipitate by boiling the preceding substance with water. 1-Phenyl-5-methyl-1 : 2 : 4-triazole yields the same methyltriazole as 1-phenyl-3-methyl-1 : 2 : 4-triazole (compare Andreocci, *loc. cit.*), so that there is only one 3-methyl-1 : 2 : 4-triazole.

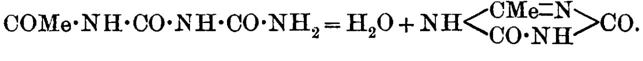
1 : 3 : 5-Triphenyl-1 : 2 : 4-triazole (compare Engelhard, Abstr., 1897, i, 127) can be obtained: (1) from benzamide and β-benzoylphenylhydrazine; (2) from benzamide and α-benzoylphenylhydrazine; (3) from dibenzoylphenylhydrazine and ammonia. Its *hydrochloride* crystallises in needles, m. p. 174°.

1-*Phenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, $C_{10}H_{11}N_3$, from acetamide and acetylphenylhydrazine, forms colourless crystals, m. p. 43°, b. p. 281°. The *platinichloride*, $(C_{10}H_{11}N_3)_2,H_2PtCl_6,2H_2O$, forms orange-coloured, acicular crystals, m. p. 185—186°; the anhydrous salt has m. p. 195°. The *picrate*, $C_{10}H_{11}N_3,C_6H_3O_7N_3$, crystallises in long, yellow needles, m. p. 156°.

1-*Phenyl*-2-*methyl*-1 : 3 : 4-*triazole*, $C_9H_9N_3$, from acetylphenylhydrazine and formanilide, forms laminar crystals (containing $1H_2O$), m. p. 68°; the anhydrous salt has m. p. 112°. The *picrate*, $C_9H_9N_3,C_6H_3O_7N_3$, has m. p. 134°. The *platinichloride*, $(C_9H_9N_3)_2,H_2PtCl_6$, crystallises in orange-coloured laminæ, m. p. 206°; when it is boiled with water the *platinic chloride* compound, $(C_9H_9N_3)_2,PtCl_4$, is obtained as a pale yellow precipitate.

R. V. S.

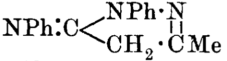
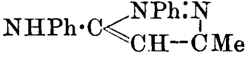
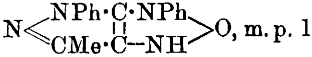
Action of Acetyl Chloride on Acetylbiuret. ADRIANO OSTROGOVICH (*Gazzetta*, 1911, 41, ii, 70—74).—Further examination of the base obtained by the action of acetyl chloride on acetylbiuret (compare Abstr., 1898, i, 336) has shown that it is diketomethyltriazine (identical with that of Nencki, *Ber.*, 1876, 9, 234), formed by a dehydration analogous to that which occurs in the case of acetylguanylcarbamide (compare Abstr., 1909, i, 461):



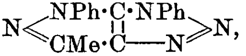
$$COMe{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 = H_2O + NH{<}{\begin{matrix}CMe{:}N\\CO{\cdot}NH\end{matrix}}{>}CO.$$

This method is the most convenient for the synthesis of the substance, since it is only necessary to heat biuret with an excess of acetyl chloride for two or three hours at 100°, and then to raise the temperature to 140—145° for about four hours. R. V. S.

5-Aminopyrazoles and Iminopyrines. II. AUGUST MICHAELIS (*Annalen*, 1911, **385**, 1—43. Compare Abstr., 1905, i, 476).—The paper contains a description of the derivatives of 5-anilo- and 5-tolyliminopyrazolones (5-anilino- and 5-toluidino-pyrazoles). A general method of preparing these substances is the heating of the primary aromatic base and antipyrine chloride or the 2-methochlorides of other 5-chloropyrazoles at 200°.

5-*Anilo*-1-*phenyl*-3-*methylpyrazolone* (5-*anilino*-1-*phenyl*-3-*methylpyrazole*),  $NPh{:}C<\begin{matrix}NPh\cdot N\\ CH_2\cdot CMe\end{matrix}$ or  $NHPh\cdot C<\begin{matrix}NPh{:}N\\ CH-CMe\end{matrix}$, m. p. 120°, b. p. 365—366°, thus prepared from aniline and antipyrine chloride forms a *hydrochloride*, $C_{16}H_{15}N_3,HCl$, m. p. 118°, *platinichloride*, m. p. 135°, *hydriodide*, $C_{16}H_{15}N_3,HI,H_2O$, m. p. 110°, *nitrate*, m. p. 150°, and *hydrogen sulphate*, m. p. 153°. [With FELIX RISSE.]—It is converted by concentrated hydrochloric acid and sodium nitrite in a freezing mixture into 4-*oximino*-5-*anilo*-1-*phenyl*-3-*methylpyrazolone* (4-*nitroso*-5-*anilino*-1-*phenyl*-3-*methylpyrazole*), m. p. 168°, deep green needles (*hydrochloride*, $C_{16}H_{14}ON_4,HCl$, yellow needles). This nitroso-compound is unstable in solution, readily changing to the isomeric 3 : 4-*diphenyl*-6-*methyldihydropyrazofurazan*,  $N<\begin{matrix}NPh\cdot C\cdot NPh\\ CMe\cdot C-NH\end{matrix}>O$, m. p. 157°, yellow needles, which is also obtained by the action of concentrated hydrochloric acid and sodium nitrite (in small excess) on 5-anilino 1-phenyl-3-methylpyrazole at a moderate temperature.

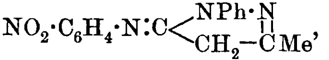
4-*Amino*-5-*anilino*-1-*phenyl* - 3 - *methylpyrazole*, $C_{16}H_{16}N_4$, m. p. 140—141°, white needles, obtained by the reduction of the nitroso-compound, forms a *hydrochloride*, m. p. 240°, *phenylcarbamide*, m. p. 220°, *phenylthiocarbamide*, m. p. 160°, and *acetyl* derivative, m. p. 130 (decomp.), and is converted by sodium nitrite and warm dilute acetic acid into 3 : 4-*diphenyl*-6-*methylaziminopyrazole*,



$$N<\begin{matrix}NPh\cdot C\cdot NPh\\ CMe\cdot C-\!\!-N\end{matrix}>N,$$

white needles, m. p. 152°.

5-p-*Nitroanilino*-1-*phenyl*-3-*methylpyrazolone*,



$$NO_2\cdot C_6H_4\cdot N{:}C<\begin{matrix}NPh\cdot N\\ CH_2-CMe\end{matrix},$$

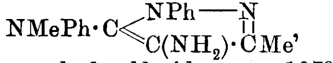
yellow needles, m. p. 153°, can be obtained in bad yield by the action of concentrated nitric acid on the anilophenylmethylpyrazolone, but is best prepared by heating 2 : 5-*p*-nitroanilopyrine hydrochloride or hydriodide (following abstract); the m-*nitro*-isomeride, m. p. 138°, has been obtained by a method similar to the latter.

[With FRITZ ISERT.]—5-*Anilo*-1-p-*bromophenyl*-3-*methylpyrazolone*, $C_{16}H_{14}N_3Br$, m. p. 106°, is obtained by distilling *p*-bromoanilopyrine (2 : 5-*endo*anilo-1-*p*-bromophenyl-2 : 3-dimethylpyrazole) hydrochloride (following abstract) under 11 mm. pressure, or by heating aniline and 5-chloro-1-*p*-bromophenyl-3-methylpyrazole-2-methochloride at 200°; the corresponding p-*chloro*-compound has m. p. 94°.

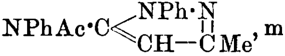
[With W. THOMAS.]—5-p-*Bromoanilo*-1-*phenyl*-3-*methylpyrazolone*, m. p. 136°, and the corresponding *chloro*-compound, m. p. 139°, are obtained by methods similar to the preceding. The action of bromine (3 mols.) in acetic acid on 5-anilo-1-phenyl-3-methylpyrazolone produces a tribrominated *substance*, m. p. 131° (4-*bromo*-5-*bromoanilo*-1-*bromophenyl*-3-*methylpyrazolone*?), which certainly contains a bromine atom in position 4, since it is unattacked by nitrous acid.

[With FELIX RISSE.]—5-*Anilo*-1-*phenyl*-4-*benzylidene*-3-*methylpyrazolone*, m. p. 164°, yellow prisms, and the corresponding *anisylidene* derivative, m. p. 205°, yellow needles, are prepared by heating the anilophenylmethylpyrazolone and benzaldehyde or anisaldehyde with zinc chloride at 125° for four to five hours.

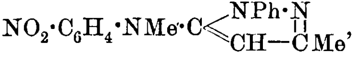
[With FELIX ABRAHAM.]—The reduction of 4-nitroso-5-methylanilino-1-phenyl-3-methylpyrazole (4-nitroso-ψ-anilopyrine) (Abstr., 1908, i, 61) yields 4-*amino*-5-*methylanilino*-1-*phenyl*-3-*methylpyrazole*,



$$\mathrm{NMePh\cdot C}\Big\langle\begin{array}{l}\mathrm{NPh{-}{-}N}\\ \mathrm{C(NH_2)\cdot CMe}\end{array},$$

m. p. 85°, which forms a *hydrochloride*, m. p. 197°, *benzylidene* derivative, m. p. 101° (by means of which the base is best purified), *salicylidene* derivative, m. p. 133°, *cinnamylidene* derivative, m. p. 114°, *benzoyl* derivative, m. p. 167°, and *carbamide*, $C_{17}H_{16}N_3\cdot NH\cdot CO\cdot NH_2$, m. p. 193°. By diazotisation, 4-amino-ψ-anilopyrine yields a stable, crystalline *diazo-ψ-anilopyrine chloride*, which couples with β-naphthol to form a red, crystalline *substance*, $C_{17}H_{16}N_3\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 173°. 4-*Amino*-5-*ethylanilino*-1-*phenyl*-3-*methylpyrazole* (4-*amino*-ψ-*ethylanilopyrine*), obtained by the reduction of 4-nitroso-ψ-ethylanilopyrine (Abstr., 1908, i, 61), crystallises in white leaflets, has m. p. 129·5°, and forms a *hydrochloride*, $C_{18}H_{20}N_4,HCl$, m. p. 220°, and *benzoyl* derivative, m. p. 208°. 5-Anilino-1-phenyl-3-methylpyrazole cannot be acetylated (or alkylated) directly, but 5-*acetylanilino*-1-*phenyl*-3-*methylpyrazole*,  $\mathrm{NPhAc\cdot C}\Big\langle\begin{array}{l}\mathrm{NPh\cdot N}\\ \mathrm{CH{-}CMe}\end{array}$, m. p. 96°, can be prepared by distilling a solution of anilopyrine in chloroform with acetyl chloride, at first under ordinary, and finally under reduced, pressure.

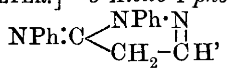
5-p-*Nitromethylanilino*-1-*phenyl*-3-*methylpyrazole*,



$$\mathrm{NO_2\cdot C_6H_4\cdot NMe\cdot C}\Big\langle\begin{array}{l}\mathrm{NPh\cdot N}\\ \mathrm{CH{-}CMe}\end{array},$$

m. p. 174°, and the meta-*isomeride*, m. p. 125°, form stout, yellow crystals, and are prepared by heating the methiodides of the corresponding 2 : 5-nitroanilopyrines. 5-p-*Chloromethylanilino*-1-*phenyl*-3-*methylpyrazole* and the corresponding *p*-bromo-*compound* have m. p. 61° and 84° respectively, whilst the isomeric 5-*anilino*-1-p-*chlorophenyl*-2 : 3-*dimethylpyrazole* and 5-*anilino*-1-p-*bromophenyl*-2 : 3-*dimethylpyrazole* have m. p. 126° and 120° respectively.

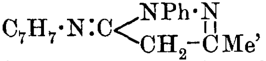
[With FRIEDRICH WALTER.]—5-*Anilo*-1-*phenylpyrazolone*,



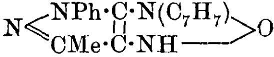
$$\mathrm{NPh{:}C}\Big\langle\begin{array}{l}\mathrm{NPh\cdot N}\\ \mathrm{CH_2{-}CH}\end{array},$$

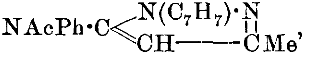
m. p. 138°, is prepared by heating 5-chloro-1-phenylpyrazole-2-methiodide (following abstract) with aniline (2 mols.) at 200°, forms a green, crystalline 4-*oximino*-(or *nitroso*-)-compound, m. p. 113°, and yields a *methiodide* (identical with 2 : 5-anilo-1-phenyl-2-methylpyrazole hydriodide [following abstract]) with methyl iodide at 110—120°, an *ethiodide*, m. p. 149°, and a *propiodide*, m. p. 165°. 5-*Methylanilino*-1-*phenylpyrazole*, m. p. 51°, prepared by heating 5-anilo-1-phenyl-2-methylpyrazole methiodide under 13 mm. pressure, forms a stable, dark green 4-*nitroso*-derivative, m. p. 99°.

[With F. Risse.]—5-p-*Tolylimino*-1-*phenyl*-3-*methylpyrazolone*,

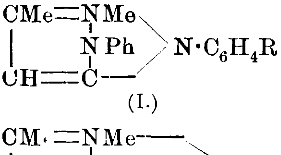


$$C_7H_7\cdot N{:}C<\begin{matrix}NPh\cdot N\\ CH_2-CMe\end{matrix},$$

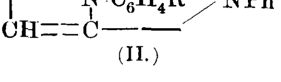
m. p. 109°, is prepared by heating 2 : 5-*p*-tolylimino-1-phenylpyrine hydriodide (following abstract) under 15—20 mm. pressure, or, better, by heating antipyrine chloride and *p*-toluidine (2 mols.) at 200°. Its 4-*oximino*-derivative, m. p. 117°, dark green leaflets, forms a reddish-yellow *hydrochloride*, $C_{17}H_{16}ON_4,HCl$, m. p. 152°, and yields by reduction 4-*amino*-5-p-*toluidino*-1-*phenyl*-3-*methylpyrazole*, m. p. 131° (*hydrochloride*, m. p. 241—242°; *acetyl* derivative, m. p. 193°; *azoimido*-compound, m. p. 111—112°). 4-*Phenyl*-3-p-*tolyl*-6-*methyldihydropyrazofurazan*,  $N<\begin{matrix}NPh\cdot C\cdot N(C_7H_7)\\ CMe\cdot C\cdot NH\end{matrix}>O$, obtained by intramolecular change from the preceding oximino-compound, forms yellow needles, m. p. 176°. 5-*p*-Tolylimino-1-phenyl-3-methylpyrazolone condenses with benzaldehyde and with anisaldehyde in the presence of zinc chloride to form the *benzylidene* and *anisylidene* derivatives, m. p. 163° and 184° respectively.

5-*Anilo*-1-p-*tolyl*-3-*methylpyrazolone*, m. p. 106°, and the corresponding o-*tolyl* compound, m. p. 131°, are obtained by heating the hydriodides of the respective tolylanilopyrines (following abstract). 5-*Methylanilino*-1-p-*tolyl*-3-*methylpyrazole*, m. p. 96°, forms a *hydrochloride*, m. p. 133·5°, and *platinichloride*, m. p. 189°. 5-*Methylanilino*-1-o-*tolyl*-3-*methylpyrazole* has m. p. 67°. 5-*Acetylanilino*-1-p-*tolyl*-3-*methylpyrazole*,  $NAcPh\cdot C<\begin{matrix}N(C_7H_7)\cdot N\\ CH\text{———}CMe\end{matrix}$, and the corresponding *benzoyl* derivative have m. p. 84° and 114° respectively. C. S.

Substituted Iminopyrines. August Michaelis (*Annalen*, 1911, **385**, 44—102. Compare preceding abstract).—The chief object of the research is an investigation of various iminopyrines and their derivatives, in order to show that the substances represented by the constitutions (I) and (II) are isomeric and not identical.

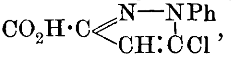


(I.)



(II.)

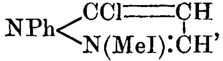
[With Friedrich Walter.]—5-*Chloro*-1-*phenylpyrazole*-3-*carboxylic acid*,

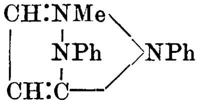
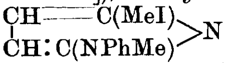


$$CO_2H\cdot C<\begin{matrix}N—NPh\\ CH{:}CCl\end{matrix},$$

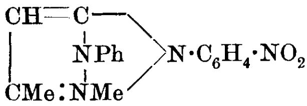
m. p. 158° (*ethyl* ester, m. p. 46°; *chloride*, m. p. 96°), is obtained by heating ethyl 1-phenyl-5-pyrazolone-3-carboxylate with phosphoryl chloride and benzene at 160—170°. The action of chlorine or bromine on its acetic acid solution yields

4 : 5-*dichloro*-1-*phenylpyrazole*-3-*carboxylic acid*, m. p. 214°, and 5-*chloro*-4-*bromo*-1-*phenylpyrazole*-3-*carboxylic acid*, m. p. 222°, respectively. When heated at 200—210°, the chlorophenylpyrazolecarboxylic acid yields 5-chloro-1-phenylpyrazole, which is also conveniently prepared by heating 1-phenyl-5-pyrazolone and phosphoryl chloride at 140—150°. The bromination of 5-chloro-1-phenylpyrazole in acetic acid yields 5-*chloro*-4-*bromo*-1-*phenylpyrazole*, m. p. 65° ; 4 : 5-*dichloro*-1-*phenylpyrazole*, m. p. 48°, which cannot be prepared in a similar manner, is obtained by heating 5-chloro-1-phenylpyrazole and phosphorus pentachloride at 150—160°. 3 : 4 : 5-*Trichloro*-1-*phenylpyrazole*, m. p. 82°, is prepared by chlorinating Michaelis and Rohmer's 3 : 5-dichloro-1-phenylpyrazole in chloroform or by heating it with phosphorus pentachloride at 150°. 3 : 5-*Dichloro*-4-*bromo*-1-*phenylpyrazole*, m. p. 85°, is prepared by brominating the dichlorophenylpyrazole. 3 : 5-*Dibromo*-1-*phenylpyrazole*, m. p. 50°, prepared by heating 3-hydroxy-1-phenyl-5-pyrazolone (Michaelis and Schenk, Abstr., 1907, i, 966) with phosphoryl bromide at 120—130°, yields 3 : 4 : 5-*tribromo*-1-*phenylpyrazole*, m. p. 122°, by bromination in boiling acetic acid.

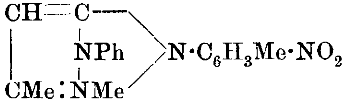
5-*Chloro*-1-*phenylpyrazole* 2-*methiodide*,  $\mathrm{NPh}{<}\begin{array}{l}\mathrm{CCl{=}CH}\\ \mathrm{N(MeI){:}CH}\end{array}$, m. p. 161° (decomp.), is obtained from its constituents and a little methyl alcohol at 100°. The corresponding *methochloride*, m. p. 147°, forms a *platinichloride*, $2C_{10}H_{10}N_2Cl,PtCl_6,H_2O$, m. p. 207°, and a *picrate*, m. p. 106°. The *ethiodide*, m. p. 209°, *ethochloride*, m. p. 181° (*platinichloride*, m. p. 217°), and *propiodide*, m. p. 156° (decomp.), are also mentioned.

2 : 5-*Anilo*-1-*phenyl*-2-*methylpyrazole*,  m. p. 128°, prepared by the general method of heating 5-chloropyrazole-2-alkyliodides and primary aromatic bases (preceding abstract), forms a *hydrochloride*, *platinichloride*, m. p. 177°, *hydriodide*, m. p. 161° (identical with 5-anilo-1-phenylpyrazolone-2-methiodide [preceding abstract]), *thiocyanate*, m. p. 137°, *picrate*, m. p. 104°, *methiodide*,  m. p. 124—125°, *ethiodide*, m. p. 146°, and *benzoyl iodide*, $C_{16}H_{15}N_3,C_6H_5{\cdot}COI$, m. p. 108°. 2 : 5-*Anilo*-1-*phenyl*-2 *ethylpyrazole*, m. p. 155°, and 2 : 5-*anilo*-1-*phenyl*-2-*propylpyrazole*, m. p. 124·5°, are prepared by the general method ; the former forms a *platinichloride*, m. p. 197°, *hydriodide*, m. p. 149°, *picrate*, m. p. 172°, and *methiodide*, m. p. 119°, whilst the *platinichloride* and *hydriodide* of the latter have m. p. 195° and 165° respectively.

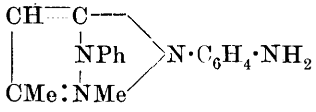
[With Erich Wurl and Felix Doepmann.]—2 : 5-m-*Nitroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (2 : 5-m-*nitroanilopyrine*) (annexed formula), m. p. 114°, garnet-red crystals, and 2 : 5-p-*nitroanilopyrine*, m. p. 129°, dark red crystals with a green shimmer, are obtained from antipyrine chloride and the nitroanilines



by the general method. The former forms a *platinichloride*, $2C_{17}H_{16}O_2N_4,H_2PtCl_6,3\frac{1}{2}H_2O$, m. p. 204° (decomp.), *hydriodide*, m. p. 164°, *methiodide*, m. p. 144°, *acetyl iodide*, m. p. 196° (decomp.), and *benzoyl iodide*, m. p. 178°, whilst 2 : 5-*p*-nitroanilopyrine forms a *platinichloride*, m. p. 217°, *hydriodide*, m. p. 198° (decomp.), and *methiodide*, m. p. 194° (decomp.) (compare this vol., i, 232, for the isomeric nitroanilopyrines and their derivatives). 2 : 5-o-*Nitro*-p-*tolylimino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (formula I), m. p. 100°, stout, red crystals, forms a *platinichloride*, m. p. 131°, and *picrate*, m. p. 145°.



(I.)



(II.)

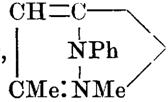
2 : 5-m-*Aminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (formula II), m. p. 45—50°, can be prepared by reducing the nitro-compound, but is far more conveniently obtained by heating antipyrine chloride and acetyl-*m*-phenylenediamine at 125—130° and hydrolysing the resulting *acetyl* derivative, m. p. 212°. It forms a *dihydrochloride*,

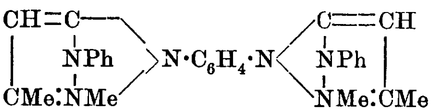
$$C_{17}H_{18}N_4,2HCl,$$

decomp. 260°, *platinichloride*, decomp. 227°, *benzoyl* derivative, m. p. 172°, and *benzoyl iodide*, m. p. 218°, the *hydrochloride*,

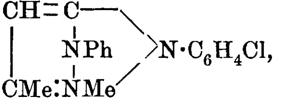
$$C_{24}H_{23}ON_4I,HCl,$$

of which has m. p. 222°. 2 : 5-p-*Aminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 112°, prepared by similar methods as the meta-isomeride, forms a *dihydrochloride*, m. p. 245°, and an *acetyl* derivative, m. p. 196°, the *hydriodide* of which has m. p. 151°.

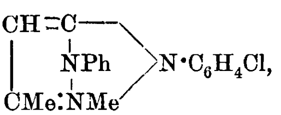
as-Dimethyl-*p*-phenylenediamine and antipyrine chloride react best at 125° to form 2 : 5-p-*dimethylaminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 120°, green plates or greenish-yellow prisms, which is a very strong base, absorbs carbon dioxide, and forms two series of salts, according as one equivalent of an acid combines with the dimethylamino-group, or as yet another equivalent breaks the bridge; the former salts are green, faintly alkaline, and contain H_2O, whilst the latter are colourless, faintly acidic, and anhydrous. The *dihydrochloride*, m. p. 224°, *dihydriodide*, m. p. 208°, *hydrochloride*, m. p. 116°, *hydriodide*, m. p. 72—73°, *dimethiodide*, m. p. 205°, and *methiodide*, m. p. 153°, are described. The action of sodium nitrite (3 mols.) on 2 : 5-*p*-dimethylaminoanilopyrine in acetic acid yields formaldehyde and the *nitrosoamine*,  m. p. 169°, orange-yellow leaflets, which is converted by reduction into 2 : 5-p-*methylaminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 143°, sulphur-yellow needles (*acetyl* derivative, m. p. 142°). The *nitrosoamine*, m. p. 164°, dark red needles (*hydriodide*, m. p. 192°), of 4-nitro-2 : 5-*p*-methylaminoanilo-1-phenyl-2:3-dimethylpyrazole is obtained by passing nitrous fumes into an alcoholic solution of the preceding nitrosoamine containing a little acetic acid.

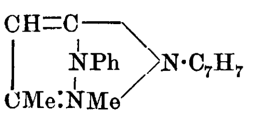


m-*Phenylenebis*-2 : 5-*imino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (annexed formula), m. p. 204°, yellowish-white crystals, is obtained by heating *m*-phenylenediamine and antipyrine chloride at 130—135°, and forms a *platinichloride*, decomp. 300°, *dihydriodide*, m. p. 203°, and *dimethiodide*, m. p. 154°.

[With WILHELM THOMAS and FRITZ ISERT.]—2 : 5-p-*Chloroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*,  m. p. 78°, yellow prisms, is obtained by heating *p*-chloroaniline (2 mols.) and antipyrine chloride or 5-chloro-1-phenyl-3-methylpyrazole-2-methiodide on the water-bath. It forms a *hydrochloride*, *platinichloride*, m. p. 89° (decomp. in its $6H_2O$ of crystallisation), *hydriodide*, m. p. 180°, *picrate*, m. p. 147°, *methiodide*, m. p. 192°, *ethiodide*, m. p. 172°, and *benzoyl iodide*, m. p. 183°. 2 : 5-m : p-*Dichloroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, a yellow oil (*picrate*, m. p. 152°; *methiodide*, m. p. 191°), 2 : 5-p-*bromoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 81° (*platinichloride*, m. p. 115°; *hydriodide*, m. p. 206°; *picrate*, m. p. 159°; *methiodide*, m. p. 193°; *ethiodide*, m. p. 176°), and 2 : 5-m-*bromoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, a yellow oil (*platinichloride*, m. p. 211°; *hydriodide*, m. p. 205°; *picrate*, m. p. 190°; *methiodide*, m. p. 133°; *ethiodide*, m. p. 118°), have also been prepared.

1-p-*Chlorophenyl*-3-*methyl*-5-*pyrazolone*, m. p. 88°, is obtained by heating equal molecular quantities of *p*-chlorophenylhydrazine and ethyl acetoacetate in 50% acetic acid at 100°. Its *methiodide*, m. p. 233° (decomp.), reacts with an excess of aniline at 110° to form 1-p-*chloroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (annexed formula), m. p. 96°, yellow needles (*hydrochloride*, m. p. 200°; *platinichloride*, m. p. 199°; *hydriodide*, m. p. 189°; *picrate*, m. p. 192°; *methiodide*, m. p. 70° [hydrated] or 159° [anhydrous]; *methochloride*, m. p. 155°). 1-p-*Bromoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 119°, forms a *hydrochloride*, m. p. 202—203°, *platinichloride*, decomp. 202°, *aurichloride*, m. p. 166°, *hydriodide*, m. p. 176°, *picrate*, m. p. 193°, *methochloride*, m. p. 157°, and *methiodide*, m. p. 101° (hydrated) and 158° (anhydrous).

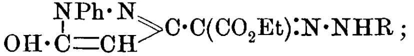




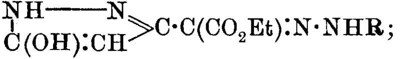
[With WALDEMAR MENTZEL.]—The 2 : 5-tolylimino-1-phenyl-2 : 3-dimethylpyrazoles have been prepared by the general method from antipyrine chloride and *o*- or *p*-toluidine (2 mols.) at 125°. 2 : 5-p-*Tolylimino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (annexed formula), m. p. 106°, white leaflets, forms a *hydrochloride*, m. p. 207°, *platinichloride*, m. p. 138°, *hydriodide*, m. p. 166°, *picrate*, m. p. 144°, *methiodide*, m. p. 187°, *acetyl iodide*, m. p. 166°, and *benzoyl iodide*, m. p. 207°. 2 : 5-o-*Tolyl*-

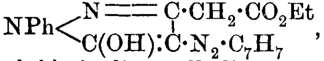
imino-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 69°, forms a *hydriodide*, m. p. 157°, and *methiodide*, m. p. 192°. The isomeric 1-*p*- and *o*-tolylanilopyrines have been prepared from aniline (2 mols.) and 1-*p*- or *o*-tolylantipyrine chloride at 125°. 2 : 5-*Anilo*-1-p-*tolyl*-2 : 3-*dimethylpyrazole*, m. p. 106°, forms a *platinichloride*, m. p. 210°, *hydriodide*, m. p. 165·5°, *picrate*, m. p. 169°, *methiodide*, m. p. 175°, *acetyl iodide*, m. p. 206°, and *benzoyl iodide*, m. p. 147°, whilst 2 : 5-*anilo*-1-o-*tolyl*-2 : 3-*dimethylpyrazole*, m. p. 129°, yields a *hydriodide*, m. p. 196°, and *methiodide*, m. p. 167°. C. S.

Ethyl Arylazoacetonedicarboxylates and their Isomeric Condensation Products with Hydrazines. CARL BÜLOW and HERMANN GÖLLER (*Ber.*, 1911, **44**, 2835—2847).—The reaction between a diazonium salt and ethyl acetonedicarboxylate in cold aqueous alcohol in the presence of sodium acetate yields *ethyl arylazoacetonedicarboxylates*, $R\cdot N_2\cdot CH(CO_2Et)\cdot CO\cdot CH_2\cdot CO_2Et$, which are yellow, crystalline substances soluble in dilute alkalis: R = Ph, m. p. 48·5°; $R = o\text{-}C_7H_7$, m. p. 80—85°, decomp. 195°; $R = p\text{-}C_7H_7$, m. p. 81—81·5°; $R = m\text{-}C_6H_3Me_2$, m. p. 71—72°; $R = o\text{-}C_6H_4\cdot CO_2H$, m. p. 145—146°. These substances react with phenylhydrazine in glacial acetic acid at the ordinary temperature to form *ethyl* 5-*hydroxy*-1-*phenylpyrazole*-3-*glyoxylate-arylhydrazones*,



$$\begin{array}{l}\text{NPh}\cdot\text{N}\\ \text{OH}\cdot\text{C}{=}\text{CH}\end{array}\!\!>\!\text{C}\cdot\text{C}(\text{CO}_2\text{Et})\text{:N}\cdot\text{NHR};$$

R = Ph, m. p. 137—138°; $R = o\text{-}C_7H_7$, m. p. 171° (decomp.); $R = p\text{-}C_7H_7$, m. p. 170—171° (decomp.); $R = m\text{-}C_6H_3Me_2$, m. p. 151°; $R = o\text{-}C_6H_4\cdot CO_2H$, m. p. 218—219° (decomp.). These compounds, which are yellow and crystalline, are given the constitution stated, because they respond to the Bülow reaction, and are soluble in dilute alkalis or aqueous piperidine. In a similar manner, the ethyl arylazoacetonedicarboxylates react with 60% hydrazine hydrate to form yellow, crystalline ethyl 5-hydroxypyrazole-3-glyoxylate-arylhydrazones,  $\begin{array}{l}\text{NH}\text{———}\text{N}\\ \text{C(OH):CH}\end{array}\!\!>\!\text{C}\cdot\text{C}(\text{CO}_2\text{Et})\text{:N}\cdot\text{NHR}$; R = Ph, m. p. 170—171° (decomp.); $R = o\text{-}C_7H_7$, m. p. 162°; $R = p\text{-}C_7H_7$, m. p. 180—181° (decomp.); $R = m\text{-}C_6H_3Me_2$, m. p. 207—208° (decomp.); $R = o\text{-}C_6H_4\cdot CO_2H$, decomp. 255°, darkening at 235°.

The two preceding groups of compounds are isomeric with the ethyl 4-arylazo-5-hydroxy-1-phenylpyrazole-3-acetates or ethyl 4-arylazo-5-hydroxypyrazole-3-acetates obtained by condensing ethyl 5-hydroxy-1-phenylpyrazole-3-acetates or ethyl 5-hydroxypyrazole-3-acetates respectively with diazonium salts in the presence of sodium acetate; thus ethyl 5-hydroxy-1-phenylpyrazole-3-acetate and *p*-toluenediazonium chloride yield *ethyl* 4-p-*tolueneazo*-5-*hydroxy*-1-*phenylpyrazole*-3-*acetate*,  $\text{NPh}\!<\!\begin{array}{l}\text{N}{=\!=}\text{C}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}\\ \text{C(OH):C}\cdot\text{N}_2\cdot\text{C}_7\text{H}_7\end{array}$, m. p. 132—134°, orange needles, which is soluble in dilute alkalis or aqueous piperidine; its constitution is proved by the fact that the *acid*, obtained by its hydrolysis by 10% alkali, loses carbon dioxide at 175—180°, yielding Lapworth's 4-*p*-tolueneazo-5-hydroxy-1-phenyl-3-methylpyrazole. The constitution of ethyl 4-*p*-nitrobenzeneazo-5-hydroxy-1-phenylpyrazole-3-acetate, prepared by the preceding or by Bülow and Höpfner's method (Abstr., 1901, i, 239), has been similarly proved by converting the substance into 4-*p*-nitrobenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole. C. S.

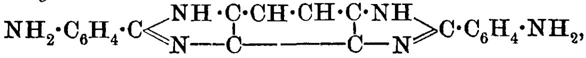
Quadriurates. WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1911, **75**, 13—18. Compare Kohler, this vol., i, 243, 690; also Ringer, Abstr., 1910, ii, 838).—It is considered that the non-existence of quadriurates has not been proved as yet. The possibility of the formation of mixed crystals of urates and uric acid is suggested. On cooling such a mixture, the solid would remain in presence of its mother liquor for a time, although not in equilibrium with it, and still less in equilibrium with water. In time, decomposition and liberation of part of the uric acid would take place. The mixed crystals formed on evaporation at a constant temperature are in equilibrium with the mother liquors; they therefore do not decompose when kept, and decompose only very slowly in presence of water at the same temperature. Such substances would correspond in composition with the quadriurates without being true chemical compounds. E. F. A.

Benziminazoles and Benzoxazoles and Azo-dyes Derived Therefrom. OTTO KYM and S. KOWARSKI (*Ber.*, 1911, **44**, 2919—2932. Compare Abstr., 1904, i, 453).—The effect on the colour and affinity for vegetable fibres of an increasing number of amino-groups in azo-dyes of this class has been investigated already, and in this paper the effect in this direction of introducing (*a*) a second iminazole group or (*b*) a second oxazole group, is shown to be the production of a red tone in the dye, with no increase in the affinity for cotton.

3-*Nitro*-1 : 4-*di*-p-*nitrobenzoyl*-p-*phenylenediamine*,

$$NO_2\cdot C_6H_3(NH\cdot CO\cdot C_6H_4\cdot NO_2)_2,$$

m. p. above 305°, prepared by the action of *p*-nitrobenzoyl chloride on either nitro-*p*-phenylenediamine or nitrodiacetyl-*p*-phenylenediamine, crystallises from pyridine on adding hot alcohol in glancing, golden-yellow leaflets. On nitration with fuming nitric acid, it gives 2 : 3-*dinitro*-1 : 4-*di*-p-*nitrobenzoyl*-p-*phenylenediamine*, m. p. 262°, which may also be obtained by the action of *p*-nitrobenzoyl chloride on dinitrodiacetyl-*p*-phenylenediamine. This crystallises from acetone on addition of water in small, yellow needles, is much more soluble in organic solvents than the mononitro-compound, and on reduction with tin and hydrochloric acid furnishes the corresponding 2 : 5-*di*-p-*aminophenyl*-o-*benzdi-iminazole*,

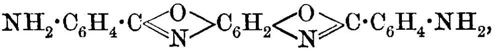


$$\mathrm{NH_2\cdot C_6H_4\cdot C}\left\langle\begin{array}{c}\mathrm{NH\cdot C\cdot CH\cdot CH\cdot C\cdot NH}\\ \mathrm{N{-}{-}C{-}{-}{-}{-}{-}{-}{-}C{-}{-}N}\end{array}\right\rangle\mathrm{C\cdot C_6H_4\cdot NH_2},$$

which sinters at 230°, losing water of crystallisation, and then melts at 255°; it crystallises from pyridine on addition of water in bright brown, glancing needles, and shows a bluish-violet fluorescence in all solutions. The *diacetyl* derivative is colourless and practically insoluble in all solvents.

4 : 6-*Dinitroresorcinyl di*-p-*nitrobenzoate*, m. p. 178°, prepared by treating dinitroresorcinol with *p*-nitrobenzoyl chloride, crystallises in

slender, yellowish-brown needles from boiling acetic acid on addition of water, and is insoluble in acetone or pyridine, but appears to undergo change in the latter solvent, since addition of water causes the separation of an intensely yellow jelly. On reduction with stannous chloride, tin, and hydrochloric acid, it furnishes a 5% yield of 1 : 5-*di*-p-*aminophenylbenzdioxazole*,



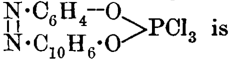
$$NH_2\cdot C_6H_4\cdot C{<}^{O}_{N}{>}C_6H_2{<}^{O}_{N}{>}C\cdot C_6H_4\cdot NH_2,$$

which sinters at 170° and remains unchanged on further heating, crystallises from hot acetone on addition of water in small, brown needles, and shows a bluish-violet fluorescence in alcohol. The same substance was obtained in larger yield in the following series of reactions.

When 4 : 6-diaminoresorcinol hydrochloride is heated with *p*-nitrobenzoyl chloride in xylene solution, *di*-p-*nitrobenzoylaminoresorcinol*, $C_6H_2(OH)_2(NH\cdot CO\cdot C_6H_4\cdot NO_2)_2$, is obtained as an orange-coloured, insoluble, sandy powder, which does not melt at 300°, but on heating at 260—270° is converted into 1 : 5-*di-p-nitrophenylbenzdioxazole*, which alone is formed if the initial reaction is carried out in nitrobenzene solution instead of xylene, This has m. p. above 300°, forms small, bright yellow needles, and is insoluble in acids or alkalis, but can be recrystallised from nitrobenzene. On reduction by heating with zinc dust and acetic acid, it gave the corresponding 1 : 5-di-*p*-aminophenylbenzdioxazole described above.

The diaminobenzdi-iminazole and diaminobenzdioxazole bases here described were diazotised and coupled with aminonaphtholdisulphonic acid, *β*-naphtholdisulphonic acid, and *α*-naphthol, and gave in each case dyes which on cotton furnished colours distinctly redder in shade than those given by the corresponding products from the monoiminazole and mono-oxazole respectively. T. A. H.

Azoxy-compounds. ANGELO ANGELI and LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 170—176. Compare this vol., i, 817).—The *p*-nitroazoxybenzene of Zinin is unaltered when treated with nitric acid (D 1·48) for four minutes at room temperature (27°), whilst under these conditions the compound of m. p. 148° (now given as 149°), previously described, yields 4 : 4′-dinitroazoxybenzene, which is only formed from Zinin's compound when the action of the nitric acid is prolonged. Both substances remain unaltered when treated with bromine in glacial acetic acid, but if they are mixed with a little iodine and added to bromine, Zinin's compound is unacted on, whilst from the other a *bromo*-derivative is produced, crystallising in yellow prisms, m. p. 199°. Azoxybenzene in similar circumstances gives a *bromo*-derivative, m. p. 75°. R. V. S.

Action of Phosphorus Pentachloride on the Azoxy-compounds. G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1911, **46**, 1009—1023).—The authors have studied the action of phosphorus pentachloride on the azoxy-compounds obtained by uniting *β*-naphthol with *o*- and *p*-methoxyphenyldiazonium chloride, and with *o*- and *p*-ethoxyphenyldiazonium chloride. They find that in the case of the compounds from *p*-anisidine and *p*-phenetidine, the hydroxyl group is substituted by chlorine. The derivatives of *o*-anisidine and *o*-phenetidine, however, behave differently; hydrogen chloride and methyl or ethyl chloride are evolved, and a compound containing phosphorus and chlorine is obtained, for which the formula  $\left.\begin{array}{l}N\cdot C_6H_4\text{—}O\\ \|\\ N\cdot C_{10}H_6\cdot O\end{array}\right\rangle PCl_3$ is suggested This substance yields *o*-hydroxybenzeneazo-β-naphthol when treated with water. In addition, all the azoxy-compounds give small quantities of infusible substances containing phosphorus.

o-*Methoxybenzeneazo-β-naphthol*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4\cdot OMe$, forms yellowish-red needles, m. p. 178°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration.

o-*Ethoxybenzeneazo-β-naphthol*, $C_{18}H_{16}O_2N_2$, crystallises in minute, orange-red leaves, m. p. 138°. It gives a reddish-violet coloration with concentrated sulphuric acid.

o-Hydroxybenzeneazo-β-naphthol crystalises in three forms: (1) green tablets (from ethyl alcohol and ethyl acetate); (2) in crusts of small, red needles (from benzene and toluene); (3) red needles with a golden lustre (from methyl alcohol). The last two forms change into the first in contact with alcohol or on heating. The *sodium* salt, $C_{16}H_{11}O_2N_2Na,3H_2O$, and the *potassium* salt, $C_{16}H_{11}O_2N_2K,1\frac{1}{2}H_2O$, which both crystallise in green scales, were prepared. The *acetyl* derivative, $C_{18}H_{14}O_3N_2$, forms ruby-red needles, m. p. 153°. The *benzoyl* derivative, $C_{23}H_{16}O_3N_2$, forms small, orange-yellow needles, m. p. 216°. The *benzyl* derivative, $C_{23}H_{18}O_2N_2$, crystallises in small, red needles, m. p. 152—153°.

p-*Methoxybenzeneazo-β-naphthol*, $C_{17}H_{14}O_2N_2$, forms red needles, m. p. 137°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration, and is reprecipitated on addition of water. When it is heated with an equimolecular quantity of phosphorus pentachloride on the water-bath, 1-p-*methoxybenzeneazo*-2-*chloronaphthalene*, $C_{10}H_6Cl\cdot N\colon N\cdot C_6H_4\cdot OMe$, is produced; it crystallises in small, orange-red prisms or lustrous, reddish-yellow scales, m. p. 87°. It gives a reddish-violet coloration with concentrated sulphuric acid. On reduction with zinc and acetic acid, it yields *p*-anisidine and 2-chloro-1-naphthylamine, of which the *monoacetyl* derivative, $C_{12}H_{10}ONCl$, crystallises in colourless needles, m. p. 191°, and the *diacetyl* derivative, $C_{14}H_{12}O_2NCl$, forms colourless prisms, m. p. 88°. With nitrous acid, 2-chloro-1-naphthylamine yields in solution 2-*chloro*-1-*naphthyldiazonium chloride*, which reacts with β-naphthylamine to form 2-*chloro*-1-*naphthaleneazo*-2′-*naphthylamine*, $C_{10}H_6Cl\cdot N\colon N\cdot C_{10}H_6\cdot NH_2$, which crystallises in red needles, m. p. 125°; this substance dissolves in concentrated sulphuric acid with production of an intense blue coloration. 2-Chloro-1-naphthyldiazonium chloride and β-naphthol yield 2-*chloro*-1-*naphthaleneazo-β-naphthol*, $C_{10}H_6Cl\cdot N\colon N\cdot C_{10}H_6\cdot OH$, which forms minute, red needles, m. p. 177°, and gives a bluish-violet coloration with concentrated sulphuric acid.

p-*Ethoxybenzeneazo-β-naphthol*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4\cdot OEt$, crystallises in red needles, m. p. 132°; it dissolves in concentrated sulphuric acid, giving a reddish-violet coloration, and is reprecipitated on addition of water. 1-p-*Ethoxybenzeneazo*-2-*chloronaphthalene*,

$C_{18}H_{15}ON_2Cl$, crystallises in orange-yellow leaflets, m. p. 94°, and gives a violet coloration with concentrated sulphuric acid. R. V. S.

Behaviour of Some Nitroazo-derivatives Towards Phenylhydrazine. C. GASTALDI (*Gazzetta*, 1911, **41**, ii, 319—324. Compare Ponzio, Abstr., 1909, i, 443).—o-*Nitrobenzoylazobenzene*,

$NO_2\cdot C_6H_4\cdot CO\cdot N:NPh$,

is obtained by the action of nitrous anhydride on an ethereal suspension of *o*-nitrobenzoylphenylhydrazine; it crystallises in red needles, m. p. 89°, and is reduced by phenylhydrazine to *o*-nitrobenzoylphenylhydrazine.

m-Nitrobenzoylphenylhydrazine, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot NHPh$, is obtained by acting on an ethereal solution of phenylhydrazine with *m*-nitrobenzoyl chloride; it forms yellow laminæ, m. p. 158° (Autenrieth gave 205°; compare Abstr., 1901, i, 186).

m-*Nitrobenzoylazobenzene*, $C_{13}H_9O_3N_3$, crystallises in dark red laminæ, m. p. 117°, and is reduced to *m*-nitrobenzoylphenylhydrazine by phenylhydrazine.

p-*Nitrobenzoylazobenzene*, $C_{13}H_9O_3N_3$, forms small, red laminæ, m. p. 136°, and is similarly reduced by phenylhydrazine.

o-*Nitrobenzoyl*-p-*bromophenylhydrazine*,

$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot NH\cdot C_6H_4Br$

(from *p*-bromophenylhydrazine and *o*-nitrobenzoyl chloride), crystallises in colourless needles tinged with yellow, and has m. p. 193°. When oxidised it gives o-*nitrobenzoylazo*-p-*bromobenzene*, m. p. 119—120°, which is, however, not pure.

m-*Nitrobenzoyl*-p-*bromophenylhydrazine*, $C_{13}H_{10}O_3N_3Br$, crystallises in pale yellow needles, m. p. 198°. m-*Nitrobenzoylazo*-p-*bromobenzene*, $C_{13}H_8O_3N_3Br$, forms bronze-coloured laminæ, m. p. 124°, and is reduced to *m*-nitrobenzoyl-*p*-bromophenylhydrazine by phenylhydrazine.

p-*Nitrobenzoyl*-p-*bromophenylhydrazine*, $C_{13}H_{10}O_3N_3Br$, crystallises in yellow needles, m. p. 194°. p-*Nitrobenzoylazo*-p-*bromobenzene*,

$C_{13}H_8O_3N_3Br$,

crystallises in bronze-coloured laminæ, m. p. 153°, and is reduced to *p*-nitrobenzoyl-*p*-bromophenylhydrazine by phenylhydrazine.

R. V. S.

Preparation of Bromonaphthalene-1-diazo-2-oxide-4-sulphonic Acid. CHEMISCHE FABRIK VORM. SANDOZ (D.R.-P. 236656).—When naphthalene-1-diazo-2-oxide-4-sulphonic acid is dissolved in concentrated sulphuric acid or chlorosulphonic acid, treated with bromine, and heated at 60—65°, bromination takes place, yielding *bromonaphthalene*-1-*diazo*-2-*oxide*-4-*sulphonic acid*, decomp. 180°; the *zinc* salt forms glistening, greenish-yellow needles.

F. M. G. M.

Nitrogen Chains: Diazohydrazides from Diazotetrazole. KARL A. HOFMANN and HEINRICH HOCK (*Ber.*, 1911, **44**, 2946—2956. Compare Abstr., 1910, i, 446, 547; this vol., i, 359).—Diazotetrazoleaminoguanidine (guanyltetrazyltetrazen),

$NH:C(NH_2)\cdot NH\cdot NH\cdot N:N\cdot CN_4H,H_2O$, prepared as already described (Abstr., 1910, i, 446), crystallises in yellow, doubly refractive needles, is stable in air at 25—35°, and decomposes with slight explosion at 142°. It is acid to litmus, but dissolves in dilute nitric acid. It does not react with mercuric oxide or benzaldehyde, but Fehling's solution furnishes copper diazotetrazole (?) as a brown powder. Sodium hydroxide decomposes it into cyanamide, ammonia, and tetrazylazoimide. When heated with dilute sulphuric or nitric acid, cyanogen and nitrogen are evolved, and the residue contains aminoguanidine and its decomposition products, as well as aminotetrazolic acid. The *periodide*, $C_2H_7N_{10}I_2$, which forms brown to black, pleochroic, cubical crystals, explodes gently when heated, but very violently in contact with nitric acid and silver nitrate.

Diazotetrazole-semicarbazide, $NH_2\cdot CO\cdot NH\cdot NH\cdot N\colon N\cdot CN_4H,H_2O$, m. p. 122°, obtained by adding diazotetrazole to semicarbazide hydrochloride in aqueous solution in presence of sodium acetate, forms colourless, doubly-refractive crystals when dilute nitric acid is added to its solution in alkali. It is acid to litmus, and is only slowly decomposed by alkali, forming tetrazylazoimide and carbamide. The same products result from heating the substance with water or dilute acids.

The decompositions of these two substances are in harmony with the constitution assigned to them (compare Curtius, Abstr., 1893, i, 463; Wohl, Abstr., 1893, i, 509; Thiele and Marais, Abstr., 1893, i, 440).

Diazotetrazolebenzylideneaminoguanidine,

$$NH\colon C(NH_2)\cdot N(C_7H_6)\cdot N\cdot N\colon N\cdot CN_4H,$$

obtained by admixture of its components in acetic acid, is an orange-red substance, decomposes at 132°, and crystallises in groups of needles from alcohol by evaporation of its solution under reduced pressure. It is decomposed by acids, yielding nitrogen, cyanogen, benzaldehyde, and hydrazine. With concentrated sodium hydroxide solution it gives a *sodium* derivative, orange-red needles. *Diazotetrazolephenylhydrazide*, $NH_2\cdot NPh\cdot N\colon N\cdot CN_4H$, obtained by interaction of phenylhydrazine with diazotetrazole in acetic acid, separates from methyl alcohol on adding ether, in orange-red crystals, gives a brownish-red *sodium* derivative, and is decomposed by acids, yielding nitrogen, cyanogen, and phenylhydrazine. The mode of decomposition of these two compounds indicates that they are α-hydrazides, their behaviour with acids and alkalis clearly distinguishing them from the β-hydrazides represented by the first two (compare Wohl and Schiff, Abstr., 1900, i, 706).

Bisdiazotetrazolehydrazide, $HN_4C\cdot N\colon N\cdot NH\cdot NH\cdot N\colon N\cdot CN_4H$, obtained by adding hydrazine hydrochloride to diazotetrazole hydrochloride, both being in strongly cooled solution, occurs in doubly refractive spangles, and can be kept for a month in a desiccator at 25°, but explodes with great violence when pressed with a glass rod or heated to 90°. It is decomposed by acids, yielding nitrogen (5 atoms), cyanogen, ammonia, and tetrazylazoimide, but no hydrazine. Concentrated sodium hydroxide solution gives a *sodium* derivative, as intensely yellow, doubly refractive plates, which in water decomposes, giving nitrogen, tetrazylazoimide, and aminotetrazole, but no ammonia. These reactions are in harmony with the constitution assigned to the substance, as are also its acid reaction and non-reactivity with benzaldehyde. With Fehling's solution gas is evolved, the solution becomes brownish-yellow, and, on warming, reddish-brown flocks are deposited, probably of a copper derivative or diazotetrazole.

Guanidine and dicyanodiamidine react with diazotetrazole to form salts of diazoaminotetrazolic acid (compare Abstr., 1910, i, 547). The *dicyanodiamidine* salt forms yellow groups of microscopic needles, and dissolves in sodium hydroxide solution, from which alcohol precipitates the *sodium* salt, $C_2N_{11}Na_3,H_2O$, doubly refractive, yellow needles. The well crystallised *barium* salt, $(C_2N_{11})_2Ba_3,8H_2O$, may be obtained from this by double decomposition. T. A. H.

A New Method of Preparing Diazoamino-compounds, and a New Reaction for Nitrous Acid. WILHELM VAUBEL (*Chem. Zeit.*, 1911, **133**, 1238).—Sodium nitrite, in aqueous solution, acts on the salts of aromatic amines with mineral acids to form diazoaminobenzene and its derivatives. Aniline hydrochloride and sodium nitrite yield diazoaminobenzene, the best yield of the latter being obtained when the proportions taken are 1 mol. of aniline hydrochloride and ½ mol. of sodium nitrite. Hydrochlorides may be replaced by nitrates. Reaction proceeds more slowly when salts of different amines are mixed before addition of the nitrite.

A similar action occurs when solid sodium nitrite is added to an alcoholic solution of the amine salt, and also when the dry salts are intimately mixed. In these cases the reaction can easily become so violent that a portion of the diazoaminobenzene is decomposed.

The reaction may also be used in testing the presence of nitrites in water. The presence of 0·00035% of nitrite could be recognised by the yellow coloration formed on addition of aniline hydrochloride.

H. W.

Losses in the Isolation of Monoamino-acids [from Proteins] by the Ester Method. I. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1911, **74**, 445—471. Compare Osborne and Breese Jones, Abstr., 1910, i, 598).—The isolation of the monoamino-acids obtained on hydrolysing proteins is not a quantitative operation. In the case of glutamic and aspartic acids, the yields obtained, starting from the pure acids, esterifying, and converting the ester into acid again, have been determined. The experiments have been carried out in a variety of ways, and the losses at each stage of the process determined by nitrogen determinations; for the details, the original should be consulted.

Starting from pure aspartic acid, about 40% is lost during the isolation by the ester method; with glutamic acid the loss is 30%. Glutamic acid is usually isolated without the help of the ester method, and the loss in this case will not be larger, but it is considered that the values for aspartic acid previously obtained can be doubled. E. F. A.

Ochrein. FRANCESCO MARINO-ZUCO and IDA FOA (*Gazzetta.*, 1911, **41**, ii, 331—336).—Ochrein is the name given by the authors to the substance containing iron which is obtained when biotoxin acts on blood or hæmoglobin (compare Marino-Zuco and Giuganino, Abstr., 1910, ii, 223). It is prepared by incubating a sterile solution of biotoxin and oxyhæmoglobin for five or six days at 41°, until the absorption spectrum of hæmoglobin is no longer present, and the liquid does not become turbid on heating. The substance is an amorphous, ochre-coloured powder, insoluble in most solvents. The percentage composition of different samples is the same, and corresponds with the formula $C_{288}H_{508}O_{70}N_{79}Fe$. When heated with extremely dilute sodium hydroxide, a very small quantity of the substance dissolves, and the solution shows the spectrum which appears when biotoxin acts on blood (compare Marino-Zuco and Giuganino, *loc. cit.*). R. V. S.

3:5-Di-iodotyrosine from Iodised Protein. III. From Iodocasein. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, 74, 290—296).—3:5-Di-iodotyrosine was prepared from iodocasein, but the yield is small, namely, about 1%. Iodocasein contains 10—14% of iodine; of this, only 4—5% is united to tyrosine; the amount obtained represents only about one-tenth of the tyrosine present. W. D. H.

Composition of Different Kinds of Silk. XIII. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, 74, 427—428).—Silk from the cocoon of *Anapha* contained tyrosine, alanine, and glycine in large quantity, and was similar in composition to other kinds of silk. Silk from *Bombyx mori* and African tussore silk was also qualitatively similar.

Silks as a class are very similar in composition, all consisting mainly of tyrosine, alanine, and glycine. They are not, however, identical, showing differences in the nature and amount of their rarer constituents. E. F. A.

The Proteoses. EDGARD ZUNZ (*Bull. Acad. roy. Belg.*, 1911, 653—734).—The hetero- and prot-albumoses prepared by the methods of Pick, Adler, and Haslam, as well as the synalbumose and thioalbumose of Pick, were prepared in quantity, and a large number of both chemical and physical constants of the preparations were ascertained. The experimental methods are given in full detail, and the analytical results and physical constants are tabulated. Further separations were also attempted by the methods of ultra-filtration (Bechhold) and precipitation by colloids (Michaelis and Rona). It was found that the method of Pick yields products of the most constant composition, and his method of classification of the proteoses appears to be preferable to that suggested by Haslam, although it can be improved in certain details in the technique of precipitation introduced by Haslam. Certain differences in the physiological action of the fractions previously observed by the author are also summarised.

S. B. S.

Plastein Formation. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1911, 75, 273—281).—The Danilewski reaction is not due to the action of any specific substance, but plastein formation occurs in the case of all proteoclastic enzymes, rennet included. W. D. H.

Nomenclature of Enzymes. HANS VON EULER (*Zeitsch. physiol. Chem.*, 1911, 74, 13—14).—Enzymes are usually named after the substances they split, for instance, for example, maltase after maltose. This rule is difficult to apply to enzymes which produce syntheses. The suggestion made is that the termination in such cases should be *ese* instead of *ase*, for instance, lipase, lipese. W. D. H.

The Mode of Action of Phosphatese. HANS VON EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, 74, 15—28).—There is no evidence that the enzyme which synthesises carbohydrate phosphoric acid esters has any splitting action. The term *phosphatese* is suggested (see preceding abstract); it is active in faintly alkaline media, but its stability is small. The ester formed from dextrose and lævulose is optically inactive, and on decomposition by acids or bases yields no optically active products. The enzyme is found in yeast and *Aspergillus*. Two enzymes are really in all probability concerned, one which changes the dextrose or lævulose into an ester-forming carbohydrate, and the second is the phosphatese which builds together the carbohydrate and phosphate ions. W. D. H.

The Electrical Transport of Pepsin. CORNELIS A. PEKELHARING and WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1911, 75, 282—289).—Using a commercial preparation of pepsin, Michaelis and Davidsohn (Abstr., 1910, i; 795) drew the conclusion that with acid of a certain strength, the pepsin travelled to both poles; on lessening the strength of acid, it went only to the cathode; with still weaker acid it again went to both poles, and finally with the weakest acid only to the anode. The preparation they used was mixed with proteoses. In the present research, the authors prepared their own pepsin from pig's stomach; they do not pretend it is absolutely pure, but at any rate it was free from any large admixture with grosser impurities. It always travelled to the anode; when, however, proteoses were added, it was carried more or less to the cathode also. No separation of pepsin from rennet occurred by this method. W. D. H.

The Influence of Hydrogen Ion Concentration on Trypsin Action. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, 36, 280—290).—The principles of the experiments and the methods of interpreting the results are precisely the same as those used by the authors in their investigations on the influence of hydrogen ion concentration on the action of invertin (next page). They draw the conclusion that trypsin is an amphoteric electrolyte existing in solution in the form of anions, cations, or unchanged molecules according to the $[H^{\cdot}]$ concentration. Only the cations act proteoclastically, and the trypsin action is directly proportional to the number of these present in solution. The acid dissociation constant is 5.10^{-7}. Above 10^{-8} the tryptic action diminishes, possibly owing to the formation of doubly charged inactive anions. The optimal action takes place therefore in solutions when $[H^{\cdot}]$ concentration $=10^{-8}$.

S. B. S.

Preparation of Pure Invertase. Reginald O. Herzog (*Zeitsch. physiol. Chem.*, 1911, **74**, 511. Compare Euler and Kullberg, this vol., i, 825).—Polemical. Euler and Kullberg have ignored the measurements of the molecular weight of invertase from the diffusion constants made by Herzog and Kasarnowski (Abstr., 1908, i, 707).

E. F. A.

The Action of Hydrogen Ions on Invertin [Invertase]. Leonor Michaelis and Heinrich Davidsohn (*Biochem. Zeitsch.*, 1911, **35**, 386—412).—The action of invertase on sucrose solutions was investigated in solutions with varying [H′] concentrations, and the zone of optimal action was found to occur between $[H'] = 0{\cdot}65 \times 10^{-5}$ and $0{\cdot}98 \times 10^{-3}$. A standard curve was obtained when x, the amount of change (estimated polarimetrically), was plotted against t, the time of action of the ferment, the curve being constructed from the various data obtained from certain closely agreeing experiments carried out under conditions of optimal ferment action. Another curve was constructed when the ratio T/t and log[H] were plotted against one another, T being the time necessary to produce a given change read from the standard curve, t being the actual time taken to produce that change in the concentration [H]. The form of the curve thus obtained is similar to that of the dissociation curve of weak acids obtained by Michaelis. The conclusions drawn from the result are, that invertase is an amphoteric electrolyte with acid dissociation constant $= 2 \times 10^{-7}$ and basic dissociation constant 10^{-12}. The inverting action on sucrose is due to the presence of undissociated electrolyte, its optimum action corresponding with its isoelectric point. As $k_a.k_b$ is greater than k_w, there is a broad isoelectric zone. Neither the cations nor the anions can act as ferments, and the action of the hydrogen ions depends, therefore, entirely on the degree of dissociation of invertase. The latter is not readily adsorbed by kaolin. Preliminary experiments on emulsin show that this is adsorbed to a greater extent than invertase.

S. B. S.

Influence of Certain Acids on the Inversion of Sucrose by Sucrase [Invertase]. Frederick Stoward (*Bio-Chem. J.*, 1911, **6**, 131—140).—Acids favour the inversion of sucrose by invertase. The action proceeds most rapidly when small amounts of sulphuric, hydrochloric, nitric, and phosphoric acid are present, and also in the presence of larger amounts of acetic acid. Increase of acid beyond a certain concentration, which differs in the case of different acids, retards, and finally arrests, the action.

W. D. H.

Diastase. Józef Buraczewski, L. Krauze, and A. Krzemecki (*Bull. Acad. Sci. Cracow*, 1911, [*A*], **6**, 369—370).—Pure commercial diastase was treated in suspension in methyl alcohol with bromine or iodine. The compounds obtained contained 6·23% Br and 9·0% I respectively. When heated with water for half an hour, a greyish-white, insoluble substance, probably a halogenated protein, remained. The soluble portion was precipitated by alcohol, and behaved as a carbohydrate, giving a blue coloration with iodine like starch. Unchanged diastase converted it first into dextrin and then into reducing sugar;

mineral acids acted similarly. The carbohydrate gave the orcinol reaction. The phenylosazone obtained from the reducing sugar had m. p. 156—157°.

Diastase which has been boiled with very dilute mineral acids gives a blue coloration with iodine. It is regarded as an unstable compound of protein and a carbohydrate of the nature of starch, which is probably a pentosan. The araban described by Wroblewski as accompanying diastase is probably a dextrin-like decomposition product of this pentosan. E. F. A.

Action of Emulsin on Gentiopicrin in Alcohol. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1911, [vii], 4, 385—390).—It has generally been assumed that the activity of emulsin is inhibited by small quantities of alcohol (compare Bougarel, *Thèse*, Paris, 1877), but the authors find that emulsin still hydrolyses gentiopicrin to a slight extent even in presence of 95° alcohol.

In alcohol at 60°, gentiopicrin is hydrolysed to the extent of 77·2% in forty days, and the action then stops. In 80° alcohol the same equilibrium is reached in seventy-five days, whilst in 85° alcohol 69·1% is hydrolysed in the same time. In 90° alcohol action ceases at the end of fifty-three days, when 48·4% of the glucoside is decomposed, and in 95° alcohol no further hydrolysis takes place after the twentieth day, when 6 to 7% of the glucoside is hydrolysed.

Even after keeping ninety days in alcohol of 80° strength, emulsin is still active towards gentiopicrin, although its activity is diminished by this treatment.

Emulsin is insoluble in alcohol over 50° in strength, but with progressive dilution of the alcohol with water it becomes more soluble, and saturated, filtered limpid solutions of the enzyme in 10° or 20° alcohol are almost as active as similar solutions in water. In alcohols of strength above 50°, emulsin appears therefore to act by simple contact. T. A. H.

The Ricinus Lipase. Y. W. JALANDER (*Biochem. Zeitsch.*, 1911, 36, 435—476).—The microscopic appearance of the mixture of fat and lipase in the presence of acetic acid and water vapour is described. The lipase imbibes water, and an emulsion is formed of the colloidal hydrated particles in oil (disperse phase). Details are given as to the methods for producing the oil–enzyme–acetic acid emulsion so as to obtain the maximum enzymatic activity. With 5 mg. enzyme (prepared by a modification of Nicloux's method) and 1 gram of triolein or cotton-seed oil, the best results are produced with about 0·6 c.c. of acetic acid. The concentration of the latter can vary between $N/500$ and $N/10$ without producing appreciable variations in the results. Much depends, however, on the mechanical treatment of the mixture, about which point full experimental details are given. The ricinus powder contains a small amount of acid which can be washed away. This washed powder in the presence of water alone is only slightly active. If it is first treated, however, with $N/10$-acid, it reaches its maximal activity in the presence of water alone. The results seem to indicate that a free acid plays the activating part in the enzyme action. By keeping the purified enzyme, however, for some time with water or acid, its activity is diminished. The purified enzyme loses its activity when kept with neutral fats alone, without the presence of either acid or water. Of the fats investigated, triolein exerts the greatest action in this respect. In experiments lasting over one hour, the Schütz law $x/\sqrt{\epsilon}=$ constant (when $x=$ amount saponified, $\epsilon=$ quantity of enzyme) was found to hold good over a comparatively large range. With more rapid hydrolysis, however, the law no longer held. The relationship between the time of action and the amount saponified was also investigated in numerous experiments. It was found that the relationship can be best expressed by the equation $x/t^m=$ constant, when m varied between 0·57 and 0·70. No perfectly satisfactory formula could, however, be found. The lipase can also produce fats synthetically from oleic acid and glycerol. The presence of a small quantity of water, sufficient to produce the swelling of the lipase, accelerates the synthetical reaction, especially if the mixture be kept in continual rotation. S. B. S.

Synthesis of Fats by the Action of Enzymes. F. L. DUNLAP and L. O. GILBERT (*J. Amer. Chem. Soc.*, 1911, **33**, 1787—1791).—Experiments are described which show that the lipase of castor oil seed is capable of effecting the synthesis of fat by its action on a mixture of glycerol and oleic acid (compare Taylor, *Univ. California Pub.*, *Path.*, 1904, 1, 33, and Welter, this vol., i, 409). E. G.

Extraction of Zymase from Fresh Brewers' Yeast by Plasmolysis. P. RINCKLEBEN (*Chem. Zeit.*, 1911, **35**, 1149—1150).—Brewers' yeast was incubated with glycerol (25 c.c. to 400 grams yeast) at 25° for fifteen to forty hours, whereby the yeast was plasmolysed and the mass became liquid. By filtering through hardened filter-paper, a liquid was obtained which, as a rule, was without fermentative activity. In a few cases, however, the liquid readily fermented sugars, whilst in others it was only active after the addition of a boiled yeast-juice. The last cases thus owed their inactivity to a disappearance of the co-enzyme of alcoholic fermentation during the plasmolysis.

An active liquid was also obtained when yeast was plasmolysed by means of disodium hydrogen phosphate in the presence of boiled yeast-juice which had previously been dried in a vacuum.

W. J. Y.

p-Aminophenylarsine Tetraiodide. ALDO PATTA and PIERO CACCIA (*Boll. Soc. Med.-Chirurg. Pavia*, 1911; Reprint, 9 pp. Compare Mameli and Patta, Abstr., 1909, i, 543; 1910, i, 531; also Bertheim, this vol., i, 593).—p-*Aminophenylarsine tetraiodide hydriodide*, $AsI_4{\cdot}C_6H_4{\cdot}NH_2,HI$, is obtained when *p*-aminophenylarsinic acid is heated with hydriodic acid (D 1·7) until iodine vapour is evolved in moderation; it forms orange-red crystals, m. p. 140°, and give a white, insoluble substance on treatment with water. The toxicity of this tetraiodide does not differ greatly from that of the atoxyl derivatives of Mameli and Patta (*loc. cit.*), but its injection produces a marked local action. R. V. S.

Preparation of Arsenophenols. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235430. Compare Abstr., 1909, i, 347; 1910, i, 452).—The reduction of hydroxyarylarsinic acids has been previously described, and the preparation of halogenated derivatives is now recorded. When sodium *p*-hydroxyphenylarsinite is treated with sodium hypochlorite (or hypobromite) in aqueous solution at the ordinary temperature, and the solution acidified after twelve hours, the dihalogenated acid (accompanied by trihalogenated phenol) separates; it crystallises from water, and does not melt below 260°.

p-*Di-iodohydroxyphenylarsinic acid* is obtained when sodium *p*-hydroxyphenylarsinite (285 parts) is treated with potassium iodate (220 parts) in dilute sulphuric acid solution, heated at 100°, and potassium iodide (220 parts) subsequently added; on cooling the product separates in crystalline form.

Tetrachloroarsenophenol, a yellow powder insoluble in water, is prepared by treating the foregoing dichloro-acid with alkaline sodium hyposulphite in the presence of magnesium chloride at 50° for some time; the corresponding *tetrabromo-* and *tetraiodo-arsenophenols* can be analogously prepared, have similar properties, and are decomposed at 200° into arsenophenol. F. M. G. M.

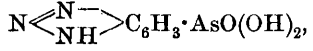
Preparation of Aminohydroxyarylarsenious Oxides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235391. Compare Abstr., 1909, i, 148).—*Aminohydroxyphenylarsenious oxide* separates as a colourless, microcrystalline powder when a very dilute sulphuric acid solution of aminophenolarsinic acid (Abstr., 1909, i, 804) is treated with potassium iodide, saturated with sulphur dioxide at the ordinary temperature, and subsequently rendered alkaline with ammonium hydroxide; it is somewhat soluble in water, readily so in mineral acids and alkali hydroxides. F. M. G. M.

Nitro- and Amino-arsanilic Acids. ALFRED BERTHEIM (*Ber.*, 1911, **44**, 3092—3098).—The toxicity of phenylarsinic acid is considerably diminished by the entrance of an amino-group into the benzene nucleus. A similar effect accompanies the introduction of a second amino-group, the toxicity of 3 : 4-diaminophenylarsinic acid being only one-twentieth that of *p*-aminophenylarsinic acid.

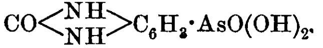
p-Oxalylaminophenylarsinic acid (D.R.-P. 231969),

$$CO_2H\cdot CO\cdot NH\cdot C_6H_4\cdot AsO(OH)_2,H_2O.$$

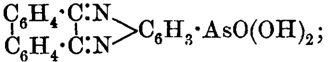
prepared by heating *p*-aminophenylarsinic acid or its sodium salt with oxalic acid, forms a white crystalline powder, consisting of short, microscopic prisms, which do not melt or decompose below 300°. On nitration, it yields 3-nitro-*p*-oxalylaminophenylarsinic acid, which forms almost colourless, short prisms, and is hydrolysed to 3-nitro-*p*-aminophenylarsinic acid, $NO_2\cdot C_6H_3(NH_2)\cdot AsO(OH)_2$. This crystallises in yellow needles, decomposing explosively above 300°; it is reduced by aqueous sodium hyposulphite to 3 : 4-*diaminophenylarsinic acid*, $C_6H_3(NH_2)_2\cdot AsO(OH)_2,\frac{1}{2}H_2O$, which forms small, colourless prisms, m. p. 158—159° (decomp.), with previous darkening at 140°.

Aziminophenylarsinic acid,  $N{<}\substack{N-\\ NH}{>}C_6H_3\cdot AsO(OH)_2$, prepared by the action of nitrous acid on diaminophenylarsinic acid, crystallises in stout, colourless prisms, decomposing explosively above 300°.

The diamino-acid reacts with carbonyl chloride, yielding o-*phenylenecarbamidearsinic* (*benziminazolonearsinic*) *acid*,



$$CO\begin{matrix}\diagup NH \diagdown \\ \diagdown NH \diagup\end{matrix}C_6H_3\cdot AsO(OH)_2,$$

which crystallises in prisms or platelets, and with phenanthraquinone in glacial acetic acid solution to form *diphenylenequinoxalinearsinic* (*phenanthraphenazinearsinic*) *acid*,  $\begin{matrix}C_6H_4\cdot C{:}N\diagdown \\ \vert \qquad \vert \\ C_6H_4\cdot C{:}N\diagup\end{matrix}C_6H_3\cdot AsO(OH)_2$; both substances remain unchanged below 300°. F. B.

Preparation of Nitrohydroxyarylarsinic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235141).

—When nitro-1-aminophenyl-4-arsinic acid (this vol., i, 594, 760) is stirred into a solution of potassium hydroxide (36 Bé) and heated at 80°, it yields the corresponding nitrophenol-4-arsinic acid, which is isolated by acidification, whilst by an analogous series of operations *o*-toluidine-4-arsinic acid furnishes nitro-*o*-cresol-4-arsinic acid. F. M. G. M.

Diphenylstibine Compounds. AUGUST MICHAELIS and ARWED GÜNTHER (*Ber.*, 1911, 44, 2316—2320).

—The substance produced by the reaction of triphenylstibine with antimony trichloride in presence of xylene is not chlorophenylstibine, as stated by Hasenbäumer (Abstr., 1899, i, 209), but chlorodiphenylstibine, $SbPh_2Cl$, and certain of the derivatives obtained from it have been described previously by Michaelis and Reese (Abstr., 1886, 885).

Chlorodiphenylstibine, m. p. 68°, crystallises from ether on addition of light petroleum, decomposes when heated in air, but melts unchanged under water, and irritates the skin when applied to it. Sodium carbonate converts it into *diphenylstibine oxide*, $O(SbPh_2)_2$, m. p. 78°, which separates on evaporation of its solutions in alcohol as an oil, which slowly solidifies into colourless needles. Both these substances have faint odours in the cold, but develop strong, unpleasant odours when heated. The oxide is transformed into *diphenylstibine sulphide*, m. p. 69°, by hydrogen sulphide in alcohol; it crystallises from hot alcohol in long, colourless needles. T. A. H.

Preparation of Nuclear Substituted Mercury Derivatives of Halogenated or Nitrated Phenols, or Halogenated Nitrophenols. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 234851).

—When halogen or nitro-derivatives of phenols are treated with mercuric oxide or mercuric salts, substitution products possessing both acidic and basic characters are formed; they can be purified by solution in alkali hydroxide and precipitation by carbon dioxide, and are decomposed by concentrated mineral acids into their generators.

p-*Chlorophenylmercuric oxide* was prepared by boiling *p*-chlorophenol with an aqueous acidified (sulphuric acid) solution of mercuric sulphate; o-*nitrophenylmercuric oxide*, a yellow powder, was prepared in an analogous manner, whilst 4-*chloro*-2-*nitrophenylmercuric oxide*, a yellow, crystalline powder, was obtained from mercuric oxide and 4-chloro-2-nitrophenol in boiling acetic acid solution. F. M. G. M.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Anisotropic Liquids. GEORGES FRIEDEL and F. GRANDJEAN (*Compt. rend.*, 1910, **151**, 988—989. Compare Abstr., 1910, ii, 809).—Polemical against Mauguin (*Compt. rend.*, 1910, **151**, 886). The authors suggest that the term "liquid crystals" should be restricted to those fluids showing discontinuous vectorial properties, and not applied to substances, such as *p*-azoxyphenetole, which are, strictly speaking, merely anisotropic liquids. W. O. W.

The Ultra-violet Absorption of Oxygen. H. VON WARTENBERG (*Physikal. Zeitsch.*, 1910, **11**, 1168—1172).—The adsorption of ultra-violet rays by oxygen, heated at temperatures varying from 1200° to 1800°, has been investigated. The oxygen was contained in an electrically heated iridium tube provided with quartz end-plates, and by means of a quartz-mercury lamp and a quartz prism, ultra-violet rays of wave-lengths $\lambda = 254$, 239, 230, 220, and 210 $\mu\mu$ were separately examined. The photo-electric measuring apparatus consisted of a platinised quartz plate, contained in a highly exhausted tube, and connected with a Dolezalek electrometer and a Bronson resistance.

The observations show that the absorption increases as the wave-length diminishes, and for a given wave-length it increases with the temperature. This absorption is not due to the formation of ozone at the high temperatures, but to an extension of the limit of the absorption region. In the case of oxygen at the ordinary temperature, the absorption limit lies at 186 $\mu\mu$, but at 1800° it extends beyond 300 $\mu\mu$.

H. M. D.

Absorption Spectra and the Constitution of Benzene Derivatives. II. NICOLAI A. WALIASCHKO (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 961—1023. Compare Abstr., 1910, ii, 1015).—Phenol, benzaldehyde, and the hydroxy-derivatives of the latter yield two types of absorption spectra. The para-compounds give the phenol spectrum, characterised by one absorption band and designated "ψ." The meta- and ortho-compounds give the aldehyde spectrum "a" with two absorption bands, a_1, a_2. These two types of spectra can occur simultaneously, when a complex spectrum is obtained. Since the molecules of benzene derivatives can often exist in two isomeric forms, such complex spectra are often obtained. Tables and curves are given for the absorption spectra of nitrobenzene, benzaldehyde, *o*-, *m*-, and *p*-tolualdehydes, -nitrotoluenes, -nitrophenols, -nitrophenyl acetates, -nitroanisoles in aqueous, alcoholic chloroform and hexane solutions at various concentration, also of *o*- and *p*-acetoxybenzaldehydes in alcohol and hexane solution, of benzoquinone in aqueous, alcoholic and hexane solution, and of a-benzaldoxime in alcohol. The results are discussed in detail, and are shown to confirm completely the author's view that the entrance of a group in the benzene ring induces a new form of internal vibration, and does not have, as Baly maintains, a merely retarding influence. Nitrobenzene has a strong selective absorption, and in hexane solution gives three absorption bands, a_1, ψ, a_2, lying very close to one another, their heads being $a_2 = 1/\lambda$ 3050/3000 mm., $\psi = 1/\lambda$ 3650/160 mm., $a_1 = 1/\lambda$ 4000/40 mm. In alcohol the whole curve lies nearer the red end of the spectrum, and only the bands a_2, a_1 are to be observed, whilst in water the curve is still nearer the red end and shows only the band a_1. The other bands now form part of the general absorption, and the selective absorption is thus masked. Benzaldehyde in the same solvents gives similar results, only the whole curve lies nearer the ultra-violet end and the bands are narrower and more stable. Nitrotoluene and tolualdehyde at greater concentrations than those studied by Baly, Tuck, and Marsden (Trans., 1910, **97**, 584) give similar absorption curves, with three bands, but, owing to the influence of the methyl group, the bands are broader and nearer the red end of the spectrum. In general, the relation between the *o*-, *m*-, and *p*-nitrophenols and their respective derivatives is almost exactly the same as that between the corresponding hydroxybenzaldehydes.

o-Nitrophenol gives the same type of curve [a_2 and $(\psi + a_1)$] in water, alcohol, chloroform, and hexane, but in the first the spectrum is nearest the red end, and in the last furthest away from that end; the bands are also not equally stable in all the solvents. The curves are complex, and similar to those of *o*-nitroanisole and *o*-nitrophenetole, but the curves of the two latter are of a more strongly marked phenolic character.

o- and *p*-Acetoxybenzaldehydes in very concentrated hexane and alcohol solution also give the three absorption bands, α_2, ψ, α_1, the difference between the ortho- and para-derivatives consisting, like that of the corresponding nitro-derivatives, in the greater stability of the band ψ in the spectrum of the para-compound.

With the formation of an alkali salt, the band α_2 in the *o*- and *m*-isomerides of nitrophenol is moved towards the red end of the spectrum, whereas in the para-isomerides it is the band ψ which is thus affected, but in each case the type of curve is not fundamentally altered.

Whilst not defending the quinonoid theory, the author finds that the spectra of hydroxybenzaldehydes and nitrophenols in alkaline and neutral solutions, and also the spectra of benzaldehyde and nitrobenzene, seem to be very closely related to the absorption spectrum of *p*-benzoquinone.

The disappearance of the yellow colour of an aqueous or alcoholic solution of *p*-nitrophenol on the addition of hydrochloric acid cannot be due to a change in structure of that compound, for the neutral and acid alcoholic solutions give exactly the same form of absorption curve, the only difference being that in the acid solution the curve is slightly nearer the ultra-violet end. Z. K.

Spectrum of Progressive Phosphorescence of Organic Compounds at Low Temperatures. JOSEPH DE KOWALSKI and J. DE DZIERZBICKI (*Compt. rend.*, 1910, **151**, 943—945. Compare Abstr., 1910, ii, 1016).—The phosphorescence spectrum of benzene derivatives in alcoholic solution at the temperature of liquid air is discontinuous, and consists of two superposed series of bands, one of which is due to instantaneous phosphorescence ceasing on removal of the exciting light, whilst the other depends on the more persistent progressive phosphorescence already described. The position of bands of the latter origin has been measured for benzene, toluene, ethylbenzene, propylbenzene, *o*-, *m*- and *p*-xylenes, ψ-cumene, *o*-, *m*- and *p*-tolyl methyl ethers. Introduction of a methyl group into the ring changes the seven doublets of the benzene spectrum into seven broad bands occupying practically the same positions, whilst little effect is produced when the substituent group is in a side-chain. A hydroxyl group in the ring diminishes the number of bands shown by the hydrocarbon, whilst in the side-chain it has little influence. Aromatic amines give a less well defined spectrum when the amino-group is in the ring than when it occurs in the side-chain. W. O. W.

The Connexion between the Colour and the Structure of Organic Compounds. A. E. PORAI-KOSCHITZ (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1237—1279).—A theoretical discussion of the structure of a large number of compounds in relation to their colour, and a generalisation of the oscillation theory of the cause of colour in compounds advanced by Baly, Hartley, Hedley, and others. The change in colour of a compound is due to the retarding, or the setting up, of a new type of oscillation within the molecule, by the entrance of a new group, by the formation of a molecular compound, or by the association of the molecules of a solute with those of its solvent. Three cases are possible: (1) The new oscillation may coincide with and increase the original oscillation; then the absorption bands will move further towards the ultra-violet end of the spectrum, and the colour will remain or become, visibly, colourless. (2) The new oscillation may be of an entirely different type from the original, in which case new bands will appear, and since the original oscillation will be retarded to some extent, there will be a change, but not a very considerable one, in the visible colour of the substance. (3) The new oscillation may combine with the original and greatly retard it, when there will be a considerable, sharp change in colour. Many examples of the three cases are discussed. Z. K.

Absolute Measurement of Magnetic Double Refraction of Nitrobenzene. A. Cotton and Henri Mouton (*Compt. rend.*, 1910, **151**, 862—864. Compare Abstr., 1909, ii, 773; 1910, ii, 368).—The recent determinations of the constant for the magnetic double refraction of nitrobenzene not being in good agreement with those of Skinner (*Physical Review*, 1910, **29**, 541), fresh determinations were made in conjunction with the latter investigator. As a result of these, the superiority of the method employed by the present authors was established. Application of corrections to Skinner's measurements of the magnetic field, however, bring both sets of results into agreement. The new determinations gave the value $2{\cdot}53 \times 10^{-12}$ for the constant of nitrobenzene at 16·3°. W. O. W.

Photochemical Studies. I. and II. Oxidation of Iodoform by Oxygen. Joh. Plotnikoff (*Zeitsch. physikal. Chem.*, 1910, **75**, 337—356, 385—404).—I. The measurements were made in a special form of apparatus, which is fully described. As solvent, benzene was most largely used, and the majority of the measurements were made at 22°. The oxygen concentration was kept constant by bubbling it through the solution; the rate of reaction was followed by titrating the liberated iodine with thiosulphate.

In the dark no oxidation occurs, but in light it proceeds fairly rapidly, and continues in the dark, but less rapidly, after illumination (after-reaction). In light, the rate of the reaction alters in a linear manner with the iodoform concentration. The temperature-coefficient of the after-reaction is 2·61, and the rate is proportional to the 1·28th power of the iodoform concentration. Light appears to have a slight retarding influence on the after-reaction. When allowance is made for the after-reaction, it is shown that the temperature-coefficient of the light action is 1·42, and that the speed tends to a limiting value with increasing concentration. The velocity is proportional to the light intensity, the blue rays being most efficient.

The mechanism of the reaction is discussed. It is possible that it proceeds in the following stages: (1) $CHI_3 + O = COI_2 + HI$; (2) $COI_2 = CO + I_2$; (3) $2HI + O = H_2O + I_2$, and that it is therefore closely connected with the rate of oxidation of hydriodic acid under the influence of light.

II. The oxidation of iodoform was investigated by the method already described in a number of other solvents. The rate of reaction is greatly influenced by the nature of the solvent, the velocity coefficient at 20° varying from 0·7 in acetone to 39·4 in carbon tetrachloride. The extinction-coefficient for blue rays (and in some instances for violet rays also) has been determined for iodoform in the same solvents by means of the König-Martens-Grünbaum spectrophotometer. Beer's law is valid, but there is no apparent relationship between reaction velocity and the magnitude of the extinction coefficients.

With increase in concentration, the reaction velocity in alcohol tends to a limiting value. The temperature-coefficient is the same as in benzene, 1·42, and the activity of the blue rays constitutes 78% of the total action, as compared with 77% in benzene solution.

Measurements of light absorption have been made for solutions of iodine in benzene, alcohol, and carbon tetrachloride for blue and also for violet rays. For some of these solutions, Beer's law does not apply, as has already been shown by Waentig (Abstr., 1910, ii, 117). It was found that in certain concentrations a solution of iodine in carbon tetrachloride is an efficient filter for blue rays. G. S.

Solution of Oxalic Acid and Uranium Salts as a Chemical Photometer. RAYMOND F. BACON (*Philippine J. Sci.*, 1910, 5, 281—303).—The suitability of a solution containing uranyl acetate and oxalic acid as a photometer has been investigated under various conditions, the quantity of oxalic acid left undecomposed being estimated. The results indicate that sunlight in the tropics is much more powerfully actinic than light in temperate zones.

It is now well established that uranyl salts in solution absorb ultraviolet rays (compare Jones and Strong, Abstr., 1910, ii, 87). Experiments with solutions of varying relative concentrations in (*a*) oxalic acid and (*b*) uranyl acetate show that: (1) each increment of 0·05 gram of uranyl acetate increases the speed of reaction by 18% to a maximum at which 92% of the oxalic acid is decomposed, and (2) the reaction is constant for varying amounts of oxalic acid. Acids and alkalis have no effect provided they do not reduce the content of the solution in uranyl salt, and ammonium oxalate behaves like oxalic acid. Uranyl nitrate has about the same effect as an accelerator as uranyl acetate. No decomposition takes place if the solution is made slightly alkaline, so that a certain proportion of hydrogen ions appears to be necessary, but these ions do not act *per se*, and probably merely serve to ensure the presence of uranium in the form of a uranyl salt. Oxalic acid solution is decomposed by sunlight alone, but the action is greatly accelerated by uranyl acetate. Alkaloids act as poisons in this catalysis. The action takes place at much the same rate over temperatures ranging from 30° to 100°. Fay (Abstr., 1896, i, 464) has stated that there is possibly no limit to the decomposition of oxalic acid by sunlight in presence of uranyl acetate, but in the present experiments it was found that 0·1 gram of uranyl acetate can in sunlight effect the decomposition at most of 1·5 grams of oxalic acid. Bach's observation that formaldehyde and hydrogen peroxide are formed by the action of carbon dioxide on water in presence of uranyl acetate (Abstr., 1893, ii, 484) could not be confirmed, but it was noted that glyoxylic acid is one of the products of the decomposition of uranyl acetate by sunlight. Observations carried out by Duclaux, utilising the decomposition of a solution of oxalic acid by sunlight, indicated that the actinic power of sunlight is greater in the temperate zone than in the tropics, but the author considers that these observations were due to stratification of the air in the district in which Duclaux's experiments were carried out, and experiments carried out by Duclaux's method in Manila indicated a higher rate of decomposition there than in temperate regions. The decomposition of oxalic acid in solutions exposed to sunlight is due to the formation of hydrogen peroxide and the increased sensitiveness of old solutions of the acid to which Duclaux calls attention is due to the large amount of hydrogen peroxide present. T. A. H.

The Volatilisation of Radium Emanation at Low Temperatures. R. W. Boyle (*Phil. Mag.*, 1910, [vi], **20**, 955—966. Compare Laborde, Abstr., 1909, ii, 634).—Almost inappreciable differences in the temperature at which small quantities of radium emanation, condensed in spiral tubes, volatilise were found for surfaces of metals and of glass. Using the emanation in equilibrium with from 2×10^{-4} to 2×10^{-3} mg. of radium bromide, a rate of rise of the spiral, immersed in a bath of pentane, of about 0·4° per minute, and gas currents of 0·12 c.c. per second (at −160°), there was a slight and increasing volatilisation until the temperature approached −160°, and then the volatilisation became very sudden, practically none being condensed above −160°. For the glass spiral the volatilisation temperature was about 4° lower than for a metal one, the error of temperature reading being about ±2°. With spirals of only 2 or 3 coils arranged with their axes horizontal instead of vertical, and the thermocouples inside the tubes, no difference in the volatilisation temperature between glass and lead spirals could be detected. F. S.

Attempts to Evaluate the Period of Ionium. Frederick Soddy (*Le Radium*, 1910, **7**, 295—300).—The paper deals with the attempts that have been made to detect a growth of radium from uranium, and a growth of α-radiation from uranium-*X* preparations (Abstr., 1910, ii, 921, 922), which agree in giving for the minimum period of ionium at least 35,000 and probably 50,000 years, on the assumption that only one long-lived product is intermediate between uranium and radium. A further attempt to estimate the period depends on the simultaneous determinations of (1) the quantity of helium, and (2) the proportion of the equilibrium amount of radium (Soddy and Pirret, Abstr., 1910, ii, 922) in Portuguese autunite. It was found, unexpectedly, that the quantity of helium did not vary in the same direction, in different specimens, as the proportion of radium. The specimen with the smallest quantity of helium, corresponding with less than would be produced in 30 years, had the highest proportion of radium, which was about 70% of the equilibrium proportion. Another specimen with helium corresponding with an age of 600 or 700 years had a radium proportion of 44%. A specimen of French autunite found by A. S. Russell (*Nature*, 1910, **84**, 238) to have a radium proportion of only 27%, the lowest yet observed, contained helium corresponding to an age of at least 3000 years. The first specimen examined, for which a radium proportion of 44% had been found previously (Pirret, *loc. cit.*), contained 77,000 years' production of helium. The suggestion is advanced that the radium in autunite is often that initially deposited with the mineral during formation, owing to the isomorphism of calcium and radium, and that this decays for the first few thousand years, owing to the initial absence of ionium, to a minimum proportion, and then rises more slowly, owing to the regeneration of ionium from the uranium. A method of deducing the period of ionium from the radium proportion and helium content of specimens more than a few thousand years old is discussed, which depends on the possibility of regarding radium as a short-lived product by comparison with its direct parent, ionium. F. S.

Chemical Investigation of Actinium-containing Residues of Radium Extraction. I. C. AUER VON WELSBACH (*Sitzungsber. K. Akad. Wiss. Wien*, 1910, **119**, [ii *a*], 1—44 *).—The chemical operations in the treatment of 1800 kilograms of "hydroxides," containing 78% of water, derived from 10 tons of Joachimsthal pitchblende, are described in detail. The material contained actinium and ionium. Two different methods were employed, the "sulphate method" for a relatively small part, and the "oxalate method" for the remainder. The ionium followed all the reactions of thorium, whereas actinium stands between lanthanum and calcium. In the first method the moist hydroxides were treated with sulphuric acid, the residue of basic bismuth sulphate, lead and rare earth sulphates filtered off, and the mother liquor concentrated to remove iron alum and precipitated with oxalic acid. In the residue, the radioactive matter (actinium) followed the reactions of lanthanum. It separated out in several cases as a manganate when the mother liquor from the oxalate precipitations was kept, a reaction which proved of great service, for actinium is, in the presence of ammonium salts, not completely precipitated either by ammonia or ammonium oxalate. From the solution of the first precipitate of rare earth' oxalates, freed from heavy metals, hydroxides were fractionally precipitated in presence of much ammonium nitrate by precipitating a portion with ammonia and stirring it into the main quantity ("hydroxide method"). The most basic part is iron, then come thorium, uranium, scandium, the ytterbium group, the yttrium group, the cerium group, whilst calcium and analogous elements remain in solution. From the rare earths the greater part were removed inactive by precipitation of the sulphates with ammonium sulphate, the radioactive matter keeping with the earths not precipitated, and with those the oxalates of which are soluble in ammonium oxalate (thorium).

In the "oxalate method" the hydroxides were dissolved in hydrochloric acid, the bismuth precipitated as basic chloride by ammonia, and the filtrate precipitated with oxalic acid and then ammonia, so long as the oxalate precipitate increased. The solution of the rare earth oxalates, freed from heavy metals, was precipitated by the

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* and *Monatsh.*, 1910, **31**, 1159—1202.

"hydroxide method," so as to give the iron, thorium, and uranium in one fraction, which contained all the radioactive matter. By various methods the actinium was obtained with the lanthanum and the ionium with the thorium. All attempts to concentrate the ionium from the thorium failed, although numerous methods were tried. Heating the preparations in an electric arc did not effect the proportion of ionium and thorium. F. S.

Units of Measurement of Radium and of Radioactivity. A. Jaboin (*J. Pharm. Chim.*, 1910, [vii], 2, 494—497).—The new proposals of the Brussels Congress of Radiology for units of measurement in radioactivity are reviewed. With regard to the γ-ray method of measuring radium, Mme. Curie will prepare a standard, to be kept in Paris, containing about 20 mg. of radium (element). With regard to the emanation method, the unit, to be called the "curie," is to be the quantity of radium emanation in equilibrium with 1 gram of radium (element), with the subdivisions "millicurie" and "microcurie." F. S.

Mesothorium. Wilhelm Marckwald (*Ber.*, 1910, **43**, 3420—3422).—An investigation of a "radium preparation" sent for examination from a factory, where it had been prepared from the residues of uranium and thorium earths, showed that only about 20% of the γ-rays was due to radium, as estimated by means of its emanation, and that the remainder was derived from mesothorium. Mesothorium is apparently completely similar in chemical nature to radium, and no reaction was found capable of separating it from barium and radium. By crystallisation of the chloride, the mesothorium is concentrated with the radium in the less soluble portion. The complete chemical similarity of radium and mesothorium is analogous to that existing between thorium, radio-thorium, ionium, and uranium-*X*. Mesothorium can therefore be separated from the residues of the thorium manufacture by copying the methods employed in separating radium from uraninite residues. The danger of intentional or unintentional adulteration of radium preparations by mesothorium must be borne in mind. The simplest test is to heat or dissolve the preparation to drive off the emanation. In three hours the γ-rays from the preparation after this treatment should have completely disappeared. If mesothorium is present, the proportion of the γ-radiation before and after this treatment gives a measure of the proportion of radium and mesothorium. F. S.

Analysis of the Radioactivity of Some Thermal Waters of the Island of Ischia. Oscarre Scarpa (*Gazzetta*, 1910, **40**, ii, 285—321).—The author has examined the waters of a number of thermal springs in the island of Ischia, and has found all to be radioactive, although the different sources differ considerably in this respect. In all cases the activity seems to be due to radium emanation, but the waters of Porto d'Ischia probably contain also a very small quantity of thorium emanation. R. V. S.

[Radioactivity of] the Hot Springs of Iceland. THORKELL THORKELSSON (*Mémoires de l'Acad. Royale des Sciences et des Lettres de Danemark, Copenhague*, 1910, [vii], 8, 182—264).—The radioactivity of numerous hot springs in Iceland, both of the evolved gases and of the mud, siliceous sinter, and other deposits, has been examined. No activity could be detected in the deposits, and it is estimated that none of them could have contained more than twenty-five times as much radium as the average common rocks. The gases were also analysed, and their content of argon and helium in some cases determined.

The results are fully discussed from the point of view of existing theories of geyser action. The presence of radium emanation in the springs and the absence of radium in the deposits is in favour of the view that the heat of the hot springs is derived from steam from lower levels, not from hot water. The data indicate that for one class of hot springs carbon dioxide, hydrogen, and hydrogen sulphide are produced simultaneously by the same process in the ratio 71 : 11·5 : 14·5, about 3% being nitrogen, probably of atmospheric origin. In other springs the gas consists entirely of nitrogen and rare gases, the percentage of argon (maximum 2·5) being, with only one exception, greater than in the atmosphere, the percentage of helium and neon in the argon varying from 0·5 to 4·8. Some of the samples showed a pure helium spectrum, whilst in others the neon spectrum was intense. Only the emanation of radium was found in the springs, other emanations being either absent or present only in small amount. The emanation measurements did not throw light on the nature of hot springs, and there is no definite proof that the heat energy is directly connected with the radioactivity, which apparently increases with the height of the spring above sea level. The general order of the radioactivity of the Icelandic springs is the same as those of Germany and Austria. The unit of emanation employed per c.c. of water is that produced by the radium in equilibrium with 1 gram of uranium per second (which multiplied by 2·11 gives Mache units). The highest result in these units is 35 ("Kerlingarfjöll, No. 3"). The majority of the springs examined possess from 3 to 7 of these units. F. S.

Radioactivity and Ferment Action. KORNÉL VON KÖROSY (*Pflüger's Archiv*, 1910, 137, 123—143).—Radium rays caused no inversion of a sucrose solution. Minute quantities of a radium-barium salt containing 0·005% of radium bromide increased the velocity of decomposition of hydrogen peroxide, on the average, nine times. Radium emanation dissolved in water acted similarly. Many experiments pointed to an after working, the velocity of decomposition in a preparation which had been exposed to the rays of radium continuing for some days after exposure to be greater than that of an unexposed preparation. A review of the literature of the action of radioactive substance on ferments is given. F. S.

The Positive Thermions Emitted by the Alkali Sulphates. OWEN W. RICHARDSON (*Phil. Mag.*, 1910, [vi], 20, 981—999. Compare Abstr., 1910, ii, 923).—The value of e/m for the positive ions emitted by the sulphates of the different alkali metals was determined by the method previously employed. Values were found for the sulphates of lithium, sodium, potassium, rubidium, and cæsium, which, on the assumption that e is the single atomic charge, give values for m in close agreement with the atomic weights of the alkali metals. The conclusion is drawn that the positive ions emitted from the alkali metal sulphates, when heated, are identical with the positive ions existing in their solutions. So far the only negative thermions detected have been electrons. F. S.

The Positive Thermions Emitted by the Salts of the Alkali Metals. OWEN W. RICHARDSON (*Phil. Mag.*, 1910, [vi], 20, 999—1000).—Sodium iodide and fluoride showed no difference in the value of e/m for the positive ions emitted, the value found being within 5% the same as that found for the electrolytic sodium ion. The nature of the positive thermion emitted depends only on the nature of the metal, not on that of the acid radicle. F. S.

Electrical and Mechanical Properties of Alloys of the Noble Metals. WILHELM GEIBEL (*Zeitsch. anorg. Chem.*, 1910, 69, 38—46).—The relations established between the constitution of alloys and their electrical properties render it possible to determine the constitution from electrical measurements in cases in which the melting points are too high for thermal analysis.

Binary alloys containing the platinum metals, gold, and silver have been examined, the electrical conductivity and thermo-electric power (against platinum) being determined with wires 0·1 mm. in diameter, and the tensile strength with wires 1 mm. in diameter. The temperature-coefficients of the conductivity are determined by means of measurements at intervals of temperature during cooling from 180°.

In the alloys of palladium and gold, the curves are of the expected form, but the minima do not coincide. The minimum conductivity occurs at 35 atomic % of gold, the minimum temperature-coefficient and thermo-electric power at 45, and the maximum tensile strength at 56 atomic % of gold. The addition of gold greatly increases the thermo-electric power of palladium measured against platinum. Thus the alloy with 60% Au has against platinum four times, and against gold six times, as great an *E.M.F.* as the platinum platinum–rhodium couple. C. H. D.

Conductivity, Dissociation, and Temperature-coefficients of Conductivity at 35°, 50°, and 65° of Aqueous Solutions of a Number of Salts. XIV. A. P. WEST and HARRY C. JONES (*Amer. Chem. J.*, 1910, 44, 508—544).—This work is a continuation of that of Clover and Jones (Abstr., 1910, ii, 256), in which the conductivities of aqueous solutions of various compounds, both inorganic and organic, were determined at temperatures between 35° and 80°. In the present case, however, the measurements have not been made at temperatures above 65° on account of the solubility of glass in water at the higher temperatures.

The results obtained at various dilutions are recorded for ammonium bromide, ammonium hydrogen sulphate, sodium iodide, carbonate and acetate, potassium hydrogen sulphate, potassium iodide, carbonate, dichromate and ferrocyanide, lithium bromide, nitrate and sulphate, calcium bromide, nitrate and formate, strontium bromide, nitrate and acetate, barium nitrate, formate and acetate, magnesium bromide, formate and acetate, cadmium chloride, bromide and iodide, zinc sulphate, manganese chloride, cobalt chloride, bromide, nitrate and acetate, nickel chloride, aluminium nitrate and sulphate, chromium nitrate and acetate, and uranyl chloride, nitrate, sulphate and acetate. These data show that the same relations exist between conductivity and temperature in the case of these salts as in that of the substances previously studied (Jones, Abstr., 1906, ii, 327; Jones and Jacobson, Abstr., 1908, ii, 1011; Clover and Jones, *loc. cit.*). The various factors which contribute to the increase of conductivity of solutions of electrolytes with rise of temperature are again discussed. E. G.

Electrical Conductivity of Potassium Bromide and Potassium Silver Cyanide in Mixtures of Glycerol and Alcohols.

LEO PISSARJEWSKY and A. SHAPOVALENKO (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 905—938. Compare Pissarjewsky and Trachoniotowsky, Abstr., 1910, ii, 402).—The purpose of the research was to elucidate the relation between the equilibrium constant (of a certain reaction in different solvents) and the change in the degree of dissociation of the reacting substances.

Potassium silver cyanide is the salt of a monobasic acid, $HAg(CN)_2$. At 25° the electrical conductivity of potassium bromide and potassium silver cyanide respectively are practically identical in corresponding solvents and dilutions—the only exception being a 25% methyl alcohol and 75% glycerol solution, when the values for potassium bromide are higher than for potassium silver cyanide. At 45°, however, the corresponding values for the two salts are not identical. The addition of glycerol to both methyl and ethyl alcohol considerably decreases the electrical conductivity of the dissolved salts, and for both salts the relation μ_∞ in mixtures of glycerol and methyl alcohol / μ_∞ in mixtures of glycerol and ethyl alcohol, is constant and equals 2·08.

In glycerol itself, the electrical conductivity of the salts is very slight. The product $\mu_\infty . \eta_\infty$ is constant for pure (unmixed) solvents of similar chemical properties, and belonging to the same homologous series; thus it is constant for both salts in methyl and ethyl alcohol respectively, whatever the temperature, also for one and the same salt in any one given solvent at varying temperatures, but not, in general, for mixtures of glycerol with either alcohol. Consequently, the law deduced by Walden for tetraethylammonium iodide, NEt_4I, in various organic solvents, that $\mu_\infty . \eta_\infty$ does not depend on the nature of the solvent and on the temperature, is not generally applicable.

The relation between the degree of dissociation of potassium silver cyanide (a) and that of potassium bromide, a_1, that is, a/a_1, is constant for mixtures of glycerol with methyl and ethyl alcohols, and also for both the latter with water.

The alteration in the equilibrium constant of the reaction: $2AgCN + KBr \rightleftarrows KAg(CN)_2 + AgBr$ is not due to the unequal alteration in the degree of dissociation of the reacting substances when passing from one solvent to another. Z. K.

Influence of the Solvent on the Equilibrium Constant. LEO PISSARJEWSKY and I. LITVIN (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1062—1068. Compare preceding abstract).—The reaction $2AgCN+KBr \rightleftarrows KAg(CN)_2+AgBr$ in pure water has an equilibrium constant $K=8\cdot5$. As the non-electrolytes acetone, methyl and ethyl alcohols are added respectively, K diminishes until they constitute 25% of the solvent, at which it is a minimum in each case. Further addition now raises K; at 50% ethyl alcohol, $K=8\cdot8$, whilst at 75% methyl alcohol, $K=21\cdot8$.

There is no definite relation between μ (specific conductivity) and A (diminution of the free energy of the reaction).

For the reaction $AgCNS+KBr \rightleftarrows KCNS+AgBr$ in aqueous solutions, $K=0\cdot531$, which is not appreciably diminished by the addition of mannitol. The experiments, in general, confirm the conclusion arrived at by the author and Trachoniotowsky (Abstr., 1910, ii, 402). Z. K.

Influence of Pressure on the Electrolytic Conductivity of Solutions in Different Solvents. E. W. SCHMIDT (*Zeitsch. physikal. Chem.*, 1910, **75**, 305—336).—The effect of varying the pressure from 1 to 3000 kilog./cm.^{2} on the electrical conductivity of highly dissociated electrolytes (tetraethylammonium iodide, and, in a few instances, sodium and potassium iodides) in eleven typical organic solvents at intervals of temperatures from 0° to 60°, and of a weak electrolyte (malonic acid) in some of these solvents, has been investigated by the method used by Bogojawlensky and Tammann (compare Abstr., 1899, ii, 137). As solvents, methyl, ethyl, and *iso*amyl alcohols, glycerol, furfuraldehyde, benzaldehyde, anisaldehyde, acetic anhydride, phenylacetonitrile, nitrobenzene, and acetone were used. The effect of pressure on the conductivity is due to three factors: (*a*) change of volume, (*b*) alteration of viscosity, (*c*) change in degree of dissociation, and the experimental results are discussed in terms of the relative importance of these factors.

For solutions of highly dissociated electrolytes in organic solvents, the resistance increases considerably with the pressure, the magnitude of the effect being much greater than in aqueous solution. For weak electrolytes the effect is less. In the case of $N/10$-malonic acid in ethyl alcohol, the resistance above 8° diminishes, below 8° increases, with increase of pressure. For the same solute in equal concentration in *iso*amyl alcohol, there is a minimum in the resistance at 40° and 60°. The influence of pressure on the ionic viscosity diminishes as the temperature is raised; the temperature-coefficient of the pressure influence is smaller the higher the temperature. The influence of pressure on the resistance also diminishes with increasing concentration.

As regards the solutions of tetraethylammonium iodide, the logarithm of the resistance increases approximately, in some cases quite accurately, in proportion to the increase of pressure. For non-associated solvents the influence of pressure on the resistance at 20° increases in a linear manner with the viscosity of the solvent referred to the same temperature and 1 kilog./cm.^{2} pressure. Solutions in associated solvents do not follow the above rule, the influence of pressure being much smaller. G. S.

Dependence of Contact Electrification on the Capacity of Ionic Dissociation and on Superficial Density. NICOLAUS A. HESEHUS (*J. Russ. Phys. Chem. Soc.* (Phys.), 1910, **42**, 368—374. Compare *ibid.*, 1901, **33**, 19).—The dependence of contact electrification on the capacity of ionic dissociation and on the superficial density stated to exist by the author in 1901 is now confirmed by experiment. The superficial density can be represented by $(\Delta/a)^{2/3}$ (where Δ = density of the substance, a = its atomic weight), and if d = the number of atoms (or molecules in a compound), then $d = (\Delta/a)^{2/3}$. If, further, ρ = time taken by the leaves of a spectroscope to fall through ten divisions, when connected with a negatively electrolysed substance under the influence of ultra-violet rays, then the capacity of ionic dissociation is represented by $(\Delta/a)^{2/3} 1/\rho$.

Tables are given showing that the electric properties of metals depend chiefly on their capacity of ionic dissociation, and also that whilst the metals can be arranged in a voltaic series from + to −, with increasing hardness and surface density, in a similar series for dielectric substances, such as water, glycerol, etc., the values for the surface-tension and density decrease from + to −. Z. K.

Electrochemical Behaviour of Cobalt. R. SCHILDBACH (*Zeitsch. Elektrochem.*, 1910, **16**, 967—979).—The difference of potential between cobalt and a *N*-solution of the chloride (measured in an atmosphere of nitrogen) is −0·293 volt and −0·339 volt for 0·1*N*-cobalt chloride. For the sulphate the corresponding values are −0·316 and −0·339 volt, compared with the normal hydrogen electrode, the sign being that of the cobalt electrode. These values were obtained with cobalt powder; the massive metal gives rather more positive values, −0·288 volt in *N*-cobalt sulphate, for example. Cobalt powder charged with hydrogen gives considerably more negative values at first, which gradually change until the equilibrium potential is reached. When unpolarised cobalt is placed in a cold solution of one of its salts, its potential is more positive than the equilibrium value, −0·12 volt, for example, but the equilibrium value is reached fairly quickly.

From neutral solutions, in an atmosphere of hydrogen, cobalt is deposited with quantitative current efficiency. The difference of potential between the electrode and the electrolyte is, however, much larger than the equilibrium value. The difference increases with the current density, and diminishes as the temperature rises, almost vanishing at 90°; it is very much increased by the addition of small quantities of acid to the solutions, and this effect is especially marked at low temperatures. In its electrochemical behaviour, generally, cobalt occupies an intermediate position between iron and nickel. T. E.

Zinc Amalgams and the Clark Element. ERNST COHEN and P. J. H. VAN GINNEKEN (*Zeitsch. physikal. Chem.*, 1910, **75**, 437—493).—It is shown both by electromotive and dilatometer experiments that the 10% zinc amalgam has a transition point at 42·9°, and a second transition point at 20°. On the basis of these results and the previous measurements of Cohen and Inouye (compare Abstr., 1910, ii, 37), the equilibrium diagram for zinc–mercury is constructed, and applied to explain the behaviour of the Clark cell.

If a 10% zinc amalgam is placed in one limb of the Clark cell in the fused state and allowed to cool, above 42·9° there is a heterogeneous amalgam, consisting of a solution and of mixed crystals containing very little mercury. Below 42·9° these mixed crystals unite with the liquid phase to form a second series of mixed crystals, richer in mercury. This transition is fairly rapid, and is certainly complete in one day at 25°. Below 20° the mixed crystals just referred to combine with the liquid phase to form still another series of mixed crystals; this change is very slow. At 0° nine days are required to complete it, and at temperatures from 10—15° it takes very much longer. This agrees with the observations of Willows (*Phil. Mag.*, 1899, [5], **48**, 433), who found that at room temperature the amalgam sometimes required six weeks to reach its final state. A second complication below 20° is the time taken to establish the equilibrium concentration of the mixed crystals, but this is a faster change than the other just described. The results of previous observers with the Clark cell are discussed in the light of these observations. G. S.

Behaviour of Iron and Nickel Anodes in Various Electrolytes. EUGENE P. SCHOCH and C. P. RANDOLPH (*J. Physical Chem.*, 1910, **14**, 719—737).—The conditions under which a nickel anode becomes passive in sulphate and chloride electrolytes were investigated by Schoch (Abstr., 1909, ii, 371). In view of subsequent publications, the authors adopt the theory that the passivity is due to oxide formation and not to protection of the anode surface by a layer of gaseous oxygen. The film of oxide necessary to produce all the characteristic effects may be less than is optically perceptible. When the anode becomes active again at a higher voltage, as with chromium and manganese, the ions produced contain oxygen as chromat-ions, etc. Experiments carried out with nickel in six different electrolytes and iron in sixteen electrolytes lead to the conclusion that both modes of anode action, that is, metal dissolution and oxide formation, are specifically influenced by the particular anions present.

The electrolytes, arranged in increasing order of their tendency to effect oxidation, are: (1) halogens, (2) sulphates, (3) acetates, (4) perchlorates, (5) nitrates, (6) chromates, chlorates, bromates, iodates, hydroxides, the last five being classed together, although iodates have perhaps the greatest activity.

On breaking circuit, a passivised anode quickly returns to its original condition in acidic electrolytes and slowly in neutral electrolytes. In the latter case, the restoration of the active surface is immediately effected by boiling, but in alkaline solutions the original solution potential of the metal cannot be attained even by boiling.

In mixed electrolytes each anion exercises an influence proportional to its concentration. The dependence of metal dissolution on the specific nature of the anion indicates that some individual interaction takes place between anions and anode, or between anions and nascent metal ions. Alkaline acetate solutions are able to convey currents of greater density than sulphates on account of the anodic depolarisation resulting from oxidation of the acetion to methyl alcohol.

The effect of these experiments on the problem of the corrosion and passivising of iron is indicated, and the conclusion is drawn that "chromating," etc., will not protect iron from the action of a natural water containing sulphates or chlorides. R. J. C.

Migration of Ions in the Water Voltameter. FRANZ STREINTZ (*Zeitsch. Electrochem.*, 1910, **16**, 980. Compare Abstr., 1910, ii, 928). —Using more accurate values of the transport numbers of sulphuric acid, the agreement between the observed and calculated changes of level in the voltameter becomes very much closer. T. E.

Electrophoresis of Lamp-black. WALTHÈRE SPRING (*Bull. Soc. chim. Belg.*, 1910, **24**, 416—420).—A criticism of the results obtained by Reychler (Abstr., 1910, ii, 1030), and of his views on the detergent action of soap. The methods adopted by Reychler for the purification of the lamp-black were not so thorough as those used by the author, and hence the different results. T. S. P.

Influence of the Spark on the Frequency of Electrical Vibrations. D. ROSCHANSKY (*Physikal. Zeitsch.*, 1910, **11**, 1177—1181). —The author discusses from a theoretical point of view the variation in the form of electrical discharge in its dependence on the length of the spark-gap and the electrode-material. If the metals, which have been investigated, are arranged in the order of the symmetry of the discharge, the series magnesium, bismuth, cadmium, zinc, aluminium, copper, and silver is obtained. This is the same order as was found by Wien for the effect of the various metals on the displacement of the resonance curves. H. M. D.

Method for Making Two Substances React in the Electric Arc. E. A. SALMON (*Compt. rend.*, 1910, **151**, 1057—1058).—The electrodes employed are pierced with canals parallel to their axes; the reacting substances enter the arc through one electrode, and the products of the reaction escape through the other. The electrodes are freely movable in a quartz jacket.

The formation of cyanogen from carbon and nitrogen has been shown by this apparatus, and also the rapid decomposition of water vapour when the electrodes are of copper. W. O. W.

Magnetisation at Very Low Temperatures. PIERRE WEISS and H. KAMMERLINGH ONNES (*Arch. Sci. phys. nat.*, 1910, [iv], **30**, 341—355, 449—475).—The study of the variation of magnetism with temperature has been continued down to temperatures not far removed from the absolute zero. A comparison of the magnetisation at the ordinary temperature and at low temperatures for several high values of the field shows that this ratio is practically independent of the field.

The law of corresponding states is found to hold good very accurately for magnetite at temperatures near to the critical point, but at very low temperatures the divergence is greater.

Vanadium, chromium, and Goldschmidt's manganese are not appreciably more magnetic at the temperature of liquid or solid hydrogen than at the ordinary temperature, whilst manganese, prepared by electrolysing the pure chloride with a mercury cathode, heating in hydrogen to expel mercury, and fusing in a magnesia cylinder in hydrogen, is markedly ferromagnetic. The powdery material before fusion may be compressed to form a cylinder, and then shows only paramagnetic properties.

The following ratios are found between the intensities of magnetisation at the temperature of liquid hydrogen and at the ordinary temperature: nickel, $I_{20\cdot2^\circ\mathrm{abs.}}/I_{17\cdot3^\circ} = 1\cdot0548$; iron, $I_{20\cdot3^\circ\mathrm{abs.}}/I_{20^\circ} = 1\cdot0210$; magnetite, $I_{20\cdot3^\circ\mathrm{abs.}}/I_{15\ 8^\circ} = 1\cdot0569$. C. H. D.

Sublimation of Ammonium Chloride. RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1910, **75**, 369—370).—Scheffer's theory of the ammonium chloride equilibrium (compare Abstr., 1910, ii, 484) is substantially the same as, and leads no further than, that of the author (compare Abstr., 1909, ii, 23). G. S.

Calorimetric Investigation of Chlorine at Low Temperatures. TADEUSZ ESTREICHER and M. STANIEWSKI (*Bull. Acad. Sci. Cracow*, 1910, 349—351).—A weighed quantity of chlorine, contained in a closed, thin-walled, glass bulb-tube, was cooled to −192°, −108°, and −80°, and then immersed in a water calorimeter at room temperature. From the observed thermal changes, it is found that the specific heat of solid chlorine between −192° and −108° is 0·1446. This gives 5·13 for the atomic heat of solid chlorine. The specific heat of liquid chlorine between −80° and 15° is 0·2230.

From these data and the observations between −108° and 15° the authors have obtained 22·96 cal. for the latent heat of liquefaction of solid chlorine. This result is obtained on the assumption that the melting point is −103·5°. H. M. D.

The Heat of Vaporisation of Certain Liquefied Gases. TADEUSZ ESTREICHER and AL. SCHNERR (*Bull. Acad. Sci. Cracow*, 1910, 345—348).—The heats of vaporisation of liquid sulphur dioxide, hydrogen chloride, bromide and iodide, chlorine, ammonia, and hydrogen sulphide have been measured. The apparatus used has been described previously (Abstr., 1904, ii, 478). The vaporised gases were absorbed by suitable reagents, and to prevent superheating, the liquids were brought to a state of steady ebullition by means of a small secondary heating coil before the current was passed through the much larger primary coil.

The following results were obtained:

	SO_2.	HI.	HBr.	HCl.	Cl_2.	NH_3.	H_2S.
Temperature ...	−11·16°	−37·2°	−69·86°	−84·3°	−35·8°	−33·4°	−61·37°
Molecular heat of vaporisation	6106·7	4331·8	3939·1	3600·3	4371·9	5461·9	4494·8 cals.
Trouton's constant	23·3	18·5	19·4	19·1	18·4	22·75	21·3

The values of the Trouton constant for these liquefied gases are therefore approximately normal. H. M. D.

Specific Gravities at the Melting Point in Relation to Constitution. JOHN C. EARL (*Chem. News*, 1910, **102**, 265).—On the assumption that the carbon, hydrogen, and oxygen atoms in combination are spheres of equal size at the respective melting points of the substances containing them, the density of a compound containing these elements only may be calculated from the formula: density $=$ molecular weight$/[n \times 4\pi/3 + (2n+2)0{\cdot}894]$, where n represents the number of atoms in the molecule at the melting point. It is stated, however, that in many cases the formula does not hold. G. S.

Measurement of the Viscosity of Liquids and of Lubricants. OSCARRE SCARPA (*Gazzetta*, 1910, **40**, ii, 261—285).—The usual Poiseuille viscometers are inaccurate, because the capillaries are too short and too wide, so that the flow may not follow Poiseuille's law, or, when comparisons are being made, the flow may follow different laws according to the time of outflow. The author further shows that the following sources of error are not negligible: (1) the variation in pressure due to the change in level of the liquid during the flow, even when an external pressure is applied; (2) the different densities of the liquids investigated (where the flow is caused by the liquid itself without external pressure; (3) capillary phenomena associated with the movement and change of shape of the meniscus during the flow. It is possible to calculate the relative values which the size of bulb, length and diameter of the capillary must have in order that some of these errors shall be negligible.

In the new viscometer now described, a capillary 5—10 cm. in length and about 0·02 cm. in diameter is employed. In it, bulbs of the following sizes are blown in close proximity to each other: (*a*) 1 c.c.; (*b*) 5 c.c.; (*c*) 10 c.c.; (*c′*) 1 c.c. The bulb used for a particular experiment is chosen from *a*, *b*, and *c*, according to the viscosity of the liquid. The capillary ends either in a U-tube 30 cm. long and 2 cm. in diameter, or is suspended by means of a cork in a wide, cylindrical tube. The negative pressure employed to cause the flow of the liquid is produced in an aspirator of 15 litres capacity, the air in which is in connexion with a pressure regulator. This consists of a burette having a flask-like expansion at the top, its capacity being about 1 litre. The vessel is nearly filled with water, and by drawing off known volumes of it from the burette, or adding them through a tap funnel at the top, the pressure inside the apparatus can be varied as desired. In measuring a viscosity, the time, t_1, occupied by the liquid in emptying the bulb is observed, the flow being caused by the algebraic sum of the pressure (P) applied to it and its own mean difference of level. Both ends of the viscometer are then connected with the atmosphere, and the time, t_2, which the liquid takes to flow in again under the pressure due to its own difference of level alone is noted. If V be the volume of the bulb, R the radius of the capillary, and L its length, then $\eta = \pi R^4/8VL.P \times t_1t_2/t_1 + t_2 = t_1t_2/t_1 + t_2 \times$ constant, if the same pressure P be always established. The value of the constant for a particular apparatus can be determined most readily by measuring $t_1t_2/t_1 + t_2$ for a liquid (such as water) of which the absolute coefficient of viscosity is known with accuracy. A mathematical discussion is given of the magnitude of various errors and of the conditions necessary for avoiding them. The three bulbs mentioned above are designed to suit the measurement of viscosities ranging from one-tenth to ten times that of water at 20°. For oils, the author maintains these sizes of bulbs, but uses a capillary 10 cm. long having a diameter of the order of 0·05 cm.

With this viscometer the author has carried out measurements of the viscosity of some common lubricants (steam turbine oil, bearing oil, cylinder oil) at different temperatures, and obtains values differing considerably from those given by the Engler viscometer generally used. From a comparison of the curves plotted from the two sets of results, he shows that great errors are committed when the Engler results are extrapolated to higher temperatures. The incorrectness of the Engler viscometer in these cases is due to the fact that when the liquid is very viscous its flow in that viscometer does not follow Poiseuille's law.

R. V. S.

Efflux pressure of Isomorphous Mixtures of *p*-Dihalogen derivatives of Benzene. NICOLAI N. NAGORNOFF, S. F. SCHEMTSHUSCHNY, and NICOLAI S. KURNAKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1168—1179 [*]).—A short survey of the thermal and other physical properties of mixtures of *p*-dihalogen benzene derivatives, temperature–pressure and concentration–hardness curves, as well as tables of melting points and vapour pressures of the dihalogen derivatives, being given. The measurements of the efflux pressure were carried out in Gagarine's dynamometer, and the results are given in a series of tables and curves. The pressure-concentration curve of the continuous isomorphous mixtures of *p*-dichloro- and *p*-chlorobromobenzene, m. p. 64·5°, has a maximum at 11·15 kilogram/mm.^{2} at the composition 10 mol. % of dichlorobenzene, whilst the maximum for the *p*-dibromo- and chlorobromo-benzene curve lies at 17·50 kilogram/mm.^{2} at the composition 75% (mol. %) of dibromobenzene. The behaviour of a 50% mixture of dibromo- and dichloro-benzene is entirely different from that of chlorobromobenzene, and the individuality of the latter compound is well shown on the pressure curve. Still more strongly marked is the individuality of bromoiodobenzene in the systems of the latter with dibromo- and di-iodobenzene respectively. The maxima of the curves lie at 25·9 kilogram/mm.^{2} at 50% dibromobenzene and at 51·7 kilogram/mm.^{2} and 90% (mol. %) di-iodobenzene respectively. The maximum for the dichloro-chloroiodo-benzene curve lies at 16·8 kilogram/mm.^{2} and 90%

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[*] and *Zeitsch. physikal. Chem.*, 1910, **75**, 578—584.

chloroiodobenzene. The measurement of the efflux pressure is a very delicate method of establishing the existence of a definite chemical compound in a homogeneous solid medium, which is the characteristic of isomorphous mixtures. Z. K.

The Viscosity of the Dispersoids. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1910, 7, 301—304).—An expression is deduced for the viscosity of a system consisting of finely divided solid particles suspended in a liquid medium. If η is the viscosity of the liquid medium, η' that of the suspensoid, and f is the ratio of the volume occupied by the solid substance to the total volume, this may be written: $\eta' = \eta(1 + 9f/2)$. According to this, the increase in viscosity due to the suspended solid is determined by the percentage amount of this, and is independent of the degree of dispersion.

Since many colloidal substances reduce the viscosity of water to a much larger extent than that which would be expected according to this formula, it follows that the disperse phase in such systems is not present in the solid state. It is also improbable that the observed reduction in viscosity can be accounted for on the assumption that the disperse phase consists of liquid particles. The nature of these highly viscous emulsions or emulsoids appears to be determined by another factor which prevents the free motion of the disperse phase assumed in the deduction of the above formula for the viscosity. H. M. D.

Absorption of Carbon Dioxide and Sulphur Dioxide by Caoutchouc and by Blood Charcoal. ALBERT REYCHLER (*J. Chim. Phys.*, 1910, 8, 617—629. Compare Abstr., 1910, ii, 272).—The absorption of carbon dioxide or sulphur dioxide by fine Para sheet (presumably not vulcanised) follows the linear law characteristic of simple solution phenomena. If C and c are the number of mols. of either oxide per kilo. of caoutchouc and per litre of gas respectively, the ratio C/c is a constant.

Carbon dioxide is rapidly absorbed at 20°, and the value of C/c is 1·06. Sulphur dioxide at 18·5° is much more soluble, the value obtained, $C/c = 25{\cdot}8$, being in good agreement with that previously given by the author, namely, 26·0 at 18°. The figures obtained by Chappuis (1883) at 0° also support the solution theory, the constant C/c having the value 38·5. Although Wo. Ostwald has suggested that these results are equally in accord with an adsorption formula, $C = \text{const.} \times c^{1{\cdot}02}$, the author prefers to suppose that the exponent is 1·00 instead of 1·02, and that there is no indication of adsorption.

The blood charcoal used was the commercial product, which was not calcined, but was exposed in a vacuum for some time before use. The value of C/c with carbon dioxide at 20° is sufficiently constant (about 4·4) to justify the suggestion that the relation of the charcoal to the gas is that of a solvent.

In the case of sulphur dioxide, however, a complication arises from the fact that the absorption of this gas by the uncalcined charcoal is accompanied by the liberation of carbon dioxide and sometimes water vapour. The absorption equation is of the form $C = A + m.c$, where A and m are constants depending on the concentration of the gas. The constant A is supposed to be a measure of the amount of a chemical change whereby combined carbon dioxide is replaced by combined sulphur dioxide, and the constant *m* is the solution constant; thus *A* increases with the concentration of the sulphur dioxide, whereas *m* decreases. A quantitative verification of the hypothesis is not possible in view of the unknown character of the chemical compounds in question, and the secondary influence which the compounds may exert on the solubilities.

It is supposed that the charcoal used was already chemically saturated with carbon dioxide, so that the further absorption of this gas followed a simple solution law. R. J. C.

Adsorption Experiments with Varying Degree of Dispersion of the Adsorbent. KNUD ESTRUP (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 299—301).—The adsorption of potassium permanganate by precipitated barium sulphate has been investigated.

Solutions of barium chloride and potassium sulphate were prepared of such a strength that 10 c.c. of each, when mixed together, gave one gram of barium sulphate. In one series of experiments, 10 c.c. of the potassium sulphate solution were diluted with water and a solution of potassium permanganate to 90 c.c. before addition of the equivalent quantity of the barium chloride solution. With increasing concentration of the potassium permanganate, the amount of this adsorbed increases, and the relationship between the adsorbed and dissolved amounts of permanganate is that required by an exponential formula.

In a second series, the potassium sulphate solution (10 c.c.) was diluted with water and permanganate solution in such a way that the concentration of the permanganate was constant, although the total volume varied from 50 c.c. to 500 c.c. These solutions were then mixed with corresponding solutions of barium chloride, in which the original 10 c.c. had been diluted with water until the total volume amounted to from 50 c.c. to 500 c.c. With precipitation under these conditions it was found that the amount of permanganate adsorbed by one gram of barium sulphate diminishes at first with increasing dilution, and then increases. The minimum adsorption corresponds with solutions which are approximately *N*/18.

In a third series similar to this, the permanganate was not added until five minutes after precipitation of the barium sulphate. A similar influence of concentration is found in these circumstances, but the adsorbed quantities are, of course, much smaller. H. M. D.

Dissociation of Iodine Vapour. GUNNAR STARCK and MAX BODENSTEIN (*Zeitsch. Elektrochem.*, 1910, **16**, 961—966).—The iodine is heated in a large quartz glass bulb connected by a capillary tube to a quartz glass manometer on the principle of the Bourdon gauge. The bulb is heated uniformly by means of a specially arranged electric furnace, and the temperature is measured by a thermocouple placed inside the bulb. Measurements are made at four concentrations of iodine vapour, and at temperatures from 800° to 1200°. The mean values of the equilibrium constant $K^1 = p_{I^2}/p_{I_2}$ (the pressures being expressed in atmospheres) are: at 800°, 0·0114; at 900°, 0·0474; at 1000°, 0·165; at 1100°, 0·492; at 1200°, 1·23. By means of the equation $d\log K/dT = -U/RT^2$ the heat of the reaction $2I = I_2$ is calculated. The mean value (at constant pressure) is 36,860 cals. Taking the molecular heat at constant pressure of monatomic iodine as 5 and that of iodine molecules as $6{\cdot}5 + 0{\cdot}0038T$, the heat of reaction $Q = 35480 + 3{\cdot}5T - 0{\cdot}0019T^2$, 35480 being the value at absolute zero. Introducing these values into Nernst's equation gives $\log K^1 = -7762/T + 1{\cdot}75\log T - 0{\cdot}000416T + 0{\cdot}422$. The values of K^1 calculated from this equation agree very closely with those found experimentally. Brill (Abstr., 1907, ii, 233) had previously found an entire lack of agreement between the requirements of Nernst's theory and Victor Meyer's measurements of the dissociation of iodine.

The value of the chemical constant of iodine atoms (taking that of iodine molecules as 4) is 2·2, which, with the exception of hydrogen, is the lowest value yet observed. T. E.

The Capillary Rise of Salts. Zdenko H. Skraup, A. von Biehler, R. Lang, E. Philippi, and J. Priglinger (*Monatsh.*, 1910, **31**, 1067—1158. Compare Abstr., 1910, ii, 934).—When experiments with very dilute solutions are carried out in closed vessels, there is always a slight deposit of dew on the interior of the vessel, showing that the dilute solutions in the strips of filter paper possess a higher vapour pressure than the solution itself.

Experiments with water alone showed that the paper is less moist in the upper layers than in the lower; this could also be seen to be the case with solutions, but no definite evidence could be obtained to show that the concentration of the solution was different at different heights.

Paper containing ash is more adsorbent than ashless paper, the increased adsorbing power not being due to chemical processes, but rather to some mechanical influence of the ash. Restoring the ash to a paper which has been washed free from it restores the original adsorbing power.

Rise in temperature diminishes the times necessary for the capillary rise to become complete, and also slightly increases the adsorption. The ordinary variations in room temperature have practically no effect on the adsorption.

Addition of indifferent substances to a solution has an effect on the time taken by the solute to rise and also on the height attained. With mixtures of alcohol and water the time of rise is greatest for the mixture showing the greatest contraction. The rise of the solute is affected in different ways by the addition of alcohol; it is not appreciably altered in the case of acids and salts, but considerably diminished in the case of the basic hydroxides, the diminution being the greatest in mixtures containing about 50% of alcohol. Glycerol behaves similarly to alcohol, except that it increases the rise of sodium hydroxide.

Salts may be divided into two chief classes. The salts of the first class comprise those of the alkalis and alkaline earths, and rise to almost the same height as the water; those of the other class rise much lower than the water, for example, 40 mm. as compared with 100 mm.

In the following summary all the results refer to experiments in air saturated with water vapour.

Salts of the First Class.—The capillary rise is independent of the concentration of the solution, as proved by experiments with potassium and ammonium iodide, potassium ferro- and ferri-cyanide, potassium nitrate, sodium nitrite, and various chromates of the alkali and alkaline-earth metals. A remarkable phenomenon in connexion with these salts is that their concentration in the upper zone of the filter paper is three or four times greater than the concentration of the solution, and greater than in the lower zones of the filter paper. With potassium cyanide, as also with the alkali carbonates, borax, and sodium phosphate, increase in dilution diminishes the rise, so that salts which are appreciably hydrolysed are also adsorbed.

Valency, or atomic weight of the metal, has in itself no influence on the time of rise, which depends rather on the general chemical character of the salt. Lithium salts show themselves more closely related to the alkaline-earth metals than to the alkali metals.

Salts of the Second Class comprise those of the heavy metals and of aluminium. The capillary rise decreases with the dilution. Cations of similar nature rise to the same height, for example, ferro-, mangano-, cobalto-, nickelo-, zinc and cadmium ions, ferri- and aluminium ions. Cations of the same metal, but with different valencies, show different rises; with iron and cerium the ion of lesser valency shows the greater rise, whereas with tin the opposite holds good. In general, the anion has no great influence on the height to which the cation rises, but with the acetates of copper, lead, silver, and iron, the anion rises higher, and the cation lower, than is the case with the sulphates, chlorides, and nitrates.

In many cases the anion and cation have practically the same rise, and, in general, the anion in the salt rises higher than the same anion in the acid. In ferric, aluminium, and tin salts, the capillary rise of the anion is the same as for the free acids, but it cannot be assumed that this is due to complete hydrolysis at the dilutions used, unless it is assumed at the same time that the condition of a solution in capillary vessels is different from what it otherwise is. In chromium salts the anion rises lower and the cation higher than is the case with the corresponding iron and aluminium salts, which is in agreement with the fact that chromium readily forms complex salts. Owing to the strong hydrolysis of both stannous and stannic salts, the cations show the same rise. In the case of ceric nitrate, the filter paper shows two zones containing cerium, separated by a zone from which cerium is almost completely absent.

The cation of copper ammonia sulphate rises much lower than the cupric ion, whereas the complex ions in potassium ferric oxalate and malonate rise higher than the ferric ion in ferric oxalate, as does also the complex ion of potassium silver cyanide compared with the silver ion. Chromium nitrate and chromiumhexammine nitrate behave similarly, whereas blue chromium chloride, hexa-aquochromichloride, and green chromium chloride show considerable differences with respect to the rise of the anion.

With the complex ammonia compounds of cobalt and platinum, in some cases considerable differences in constitution had very little effect on the capillary rise, whereas in other cases slight differences in constitution had a considerable influence.

Experiments on the influence of one salt on the capillary rise of another show that no conclusions can be drawn as to the existence of double salts in solution; the mutual influences are very variable.

Strong acids are not influenced by the addition of alkali salts, whereas the capillary rise of the alkali hydroxides is diminished. The capillary rise of salts of the heavy metals is increased by the addition of the corresponding acids, whereas that of the acid is hardly affected by the addition of the salt. T. S. P.

Piezochemical Studies. VII. Influence of Pressure on Solubility. ERNST COHEN, KATSUJI INOUYE, and C. EUWEN (*Zeitsch. physikal. Chem.*, 1910, **75**, 257—304).—The measurements were made by the method already described (compare Cohen and Sinnige, Abstr., 1909, ii, 796) slightly modified in certain details, and an accuracy of 0·03 per cent. is claimed for the results. The solubility of sodium chloride at 24·05°, in grams per 100 grams of water, under different pressures is as follows: 35·90, 36·25, 36·55, 37·02, 37·36 at 1, 250, 500, 1000, and 1500 atmospheres respectively. For mannitol, at the same temperature, the results are as follows: 20·66, 20·92, 21·14, 21·40, and 21·64 grams at 1, 250, 500, 1000, and 1500 atmospheres respectively. G. S.

Solutions from the Point of View of General Dynamics. I. E. VOLCHONSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1194—1197). —A theoretical and mathematical discussion of the question. Z. K.

Solutions. REGINALD O. HERZOG (*Zeitsch. Elektrochem.*, 1910, **16**, 1003—1004).—Setting out from a relationship found by Einstein (*Ann. Physik*, 1906, [iv], **19**, 303), according to which $D = RT/6\pi N\eta\rho$, where D is the diffusion coefficient, η the viscosity of the solvent, ρ the diameter of a dissolved molecule, and N the number of actual molecules in a gram-molecule of a perfect gas, the author eliminates ρ by assuming that the dissolved substance occupies the same volume as it does when solid. Calling the volume of one gram of the solid v, and supposing that when dissolved it yields n molecules of molecular weight M, he finds $M = 4\pi N\rho^3/3v$. Eliminating ρ from these equations and putting in the values of the constants at 20°, using $N = 7{\cdot}05 \times 10^{23}$, he obtains $M = 11{\cdot}64/D^3v$. The molecular weights of a number of sugars calculated by this formula from their diffusion coefficients in aqueous solution are in surprisingly close agreement with the real values. The molecular weight of albumin is found to be 73,000. The diffusion coefficient of an electrolyte is connected with the mobilities of its ions by the formula $1/D = (1/u + 1/v)/2RT$; introducing this value of D into the above equation for aqueous solutions of acids at 25°, $u\sqrt{Mv} = 117$; for ten acids the actual values vary from 122 to 149. T. E.

Solubility of Gases in Aqueous Solutions of Glycerol and of *iso*Butyric Acid. KARL DRUCKER and E. MOLES (*Zeitsch. physikal. Chem.*, 1910, **75**, 405—436).—An apparatus suitable for determining the solubility of slightly soluble gases, and also for using small quantities of solvent, is described. The solubility of hydrogen and of nitrogen in mixtures of *iso*butyric acid and water, and of glycerol and water, has been measured at 25°. The ratio of the solubility of hydrogen in water and in glycerol is 6 : 1; for nitrogen the ratio is 8 : 1.

In connexion with the solubility measurements in glycerol-water mixtures, other properties of this binary system, such as the total vapour-pressure curve, the density, refraction, viscosity, specific heat, and heat of mixing, have either been determined directly or are taken from the work of previous observers. The proper methods for comparing the results are fully discussed, and it has been found most satisfactory to express the concentrations in parts by weight, and to compare the deviations between the experimental curve and that represented according to the mixture rule (the latter being, of course, a straight line) by drawing perpendiculars from the former on the latter as shown in detail in the paper. The above method brings out the analogies in the curves for different physical properties.

In the case of the water-*iso*butyric acid system, the solubility of the gases does not deviate greatly from Henry's law in the region where the mixture is opalescent. G. S.

Growth of Crystal Spheres. D. N. ARTEMÉEFF (*Zeitsch. Kryst. Min.*, 1910, **48**, 417—433).—A review is given of the literature on the growth and regeneration of damaged and broken crystals. Spheres were cut from crystals of various soluble salts, and these were suspended in saturated solutions of the same salt. The drusy, crystalline growths which formed on the surface were examined on the goniometer, and the crystal forms observed are recorded.

L. J. S.

The Rate of Dissolution of Selenite at Different Crystalline Surfaces. STANISLAW TOŁŁOCZKO (*Bull. Acad. Sci. Cracow*, 1910, 209—218).—The apparatus used in these experiments was that previously employed by Bruner and Tołłoczko (Abstr., 1907, ii, 935), and measurements of the rate of dissolution were made at the three surfaces (010), (110), and (111). In the case of each surface, the rate of dissolution is found to be a linear function of the velocity of flow of the solvent over the surface of the crystal. The actual rate of dissolution varies with the crystallographic nature of the surface, but the relative rates are practically independent of the flow of solvent. The relative dissolution velocities v_{010}, v_{110}, and v_{111} are represented by 1 : 1·76 : 1·88.

Experiments were also made to ascertain whether the differences in the rates of dissolution at the different surfaces are due to differences in solubility or to variations in the thickness of the diffusion layer. With this object a crystal of selenite of known weight and dimensions was introduced into a solution saturated by exposure to the surface (010). The solution, provided with stirring apparatus, was immered in a thermostat at 25° for a period of two months. At intervals the weight and dimensions of the small complete crystal and the electrical conductivity of the solution were determined, but no definite changes were observed. It appears, therefore, that the differences in the rates of dissolution are not due to differences in solubility. H. M. D.

The Rates of Growth and Dissolution of Crystals in Relation to the Reversibility of these Processes. STANISLAW TOŁŁOCZKO and J. TOKARSKI (*Bull. Acad. Sci. Cracow*, 1910, 219—234. Compare preceding abstract).—Measurements have been made of the rate at which crystals of copper sulphate increase in size when brought into contact with slightly supersaturated solutions, and of the rate at which dissolution takes place in contact with solutions containing somewhat less of the dissolved salt than that corresponding with saturation. The method employed was similar to that which has been used in previous investigations of this nature, and separate sets of observations were made for the two crystalline surfaces (110) and $(1\bar{1}0)$.

The rate of dissolution as well as that of crystallisation varies considerably with the surface examined. For the surface $(1\bar{1}0)$ the rates of dissolution and crystallisation under comparable conditions are equal, and this indicates that the processes are strictly reversible. On the other hand, the rate of dissolution is much greater than the rate of crystallisation in the case of the surface (110), and micrographic examination of the dissolving surface has shown that this is probably due to the fact that irregular etching takes place when dissolution occurs. No irregularities of this nature were observable in the case of the surface $(1\bar{1}0)$.

The cause of the difference in the rates of the dissolution and crystallisation processes at different surfaces is examined, and the conclusion is drawn that this is due to variations in the thickness of the diffusion layer at these surfaces. H. M. D.

Solid Colloidal Systems in Metallography. CARL BENEDICKS (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 290—299).—A summary is given of the author's views relating to the nature of the different micrographic structures which are found in iron carbon and iron nickel alloys. Troostite is said to represent a solid colloidal solution of cementite in ferrite, and as such it approximates more closely to perlite than to martensite in its properties. Similar colloidal systems are probably formed in other technical alloys, and evidence in favour of this is cited in the case of iron nickel alloys.

In opposition to von Weimarn, the author maintains that all solid solutions cannot be regarded as of the colloidal type, but that true solid solutions, in which the dispersity is of molecular character, are also capable of existence. Martensite is cited as an example of such a solution, and as such it differs widely from colloidal troostite.

H. M. D.

Equilibrium between Two Substances in a Mixed Binary Solution. VIII. E. VOLCHONSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1180—1194. Compare *ibid.*, 1909, **41**, 1763).—The equations $P=R(p-m)/(q-n)-R(x_c)$ and $P_1=R'(x_c)-R'(m-p)/(n-q)$ previously deduced are incorrect, and the correct forms are now shown to be $P=[R(p-m)/(q-n)-R(x_c)](p-m)$ and $P_1=[(m-p)/(n-q)\{R.(m-p)/(n-q)-R_\infty\}+x_{1c}\{R_\infty-Rx_{1c}\}](n-q)$. These equations might be simplified by assuming that for the system $BaSO_4$–H_2SO_4–H_2O the maximum work of the process is equal to the heat effect, that is, $A=u$

in the general thermo-dynamic equation $A - u = T.dA/dT$, but calorimetric experiments of the heat of decomposition of the acid barium sulphates, $BaSO_4,(H_2SO_4)_2,H_2O$ and $BaSO_4,H_2SO_4$, do not agree with those calculated from such equations.

At the ordinary temperature the solid phase of solutions containing 87·36% and 92·48% sulphuric acid respectively has the composition in each case, $BaSO_4,(H_2SO_4)_2,H_2O$, but at 93° the solid phase at the lower concentration consists of 94·94% $BaSO_4$, that of the higher concentration consists of 68·16% $BaSO_4$ and 31·26% H_2SO_4, the salt being anhydrous and crystallising in needles. As the temperature rises so the solubility of the compound $BaSO_4,(H_2SO_4)_2,H_2O$ increases, whilst that of the salt $BaSO_4,H_2SO_4$ decreases. The curve for the three solid phases $BaSO_4$, $BaSO_4,H_2SO_4$, $BaSO_4,(H_2SO_4)_2,H_2O$ is given. The temperature of decomposition of the last salt is about 53°, and its transformation into $BaSO_4,H_2SO_4$ and into $BaSO_4$ are both endothermic reactions. The compound $BaSO_4,H_2SO_4$ decomposes at about 158—160°, and its transformation into $BaSO_4$ is also an endothermic reaction.

Z. K.

Binodal Curves, Plait Points, and Tie Lines in Fifty Systems, each Consisting of Water and Two Organic Liquids. WALTER D. BONNER (*J. Physical Chem.*, 1910, **14**, 738—789).—Mixtures of water with a hydrocarbon, halogenated hydrocarbon, ether, ester, etc., were examined in conjunction with methyl, ethyl, and propyl alcohols and acetone as consolutes.

Bancroft's method of quantitative synthesis from pyknometers was adopted in order to obviate analyses. The consolute was added drop by drop to the stirred mixture contained in a long narrow tube at 0° until it became homogeneous as observed through a cathetometer telescope. In some cases the effect of the consolute was accentuated by addition of lamp-black, which floated at the surface of separation until homogeneity was attained.

For tie line determinations, the phases were allowed to separate or were separated by centrifuge, and their volumes, subject to correction for meniscus, were read off on the cathetometer. Tie lines and plait points (critical points) were determined by Lash Miller and McPherson's graphic method (Abstr., 1909, ii, 132). By these means a very extensive survey of the field was rapidly obtained, accurate to within a few per cent.

Rectangular co-ordinates are used instead of the more usual triangular diagram. The co-ordinates of the plait points show a certain stoicheiometric regularity. With alcohol as consolute, ethyl acetate, propionate, and *iso*butyrate fall into their natural sequence, as do the higher alcohols, hydrocarbons, and alkyl bromides. On passing from methyl to ethyl and propyl alcohol as consolute, the plait point travels further from the 100% water ordinate. The positions of the binodal curves, however, exhibit no regularity.

The systems hexane–water–carbinol and heptane–water–carbinol exhibit the peculiarity that the plait point is practically at the origin of co-ordinates, from which the tie lines therefore radiate. This indicates that when two phases are present, the upper phase consists of practically pure hydrocarbon, although the aqueous lower phase may also contain a considerable proportion of hydrocarbon.

Bancroft's exponential formula for the equilibrium in these systems has been tested by plotting the author's results in logarithmic co-ordinates.

In nineteen cases the formula holds, as a straight line graph is obtained. Of the remainder, twenty-five give concave or convex graphs and six irregular curves. In the nineteen cases which give a straight line, the meaning of the various constants in the exponential formula is discussed. R. J. C.

General Phase Rule and its Application to Systems of Capillary Chemistry. P. N. PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1034—1061).—The application of the phase rule to various disperse systems which belong to the domain of capillary chemistry is discussed from a theoretical and mathematical point of view. For the results obtained, the original must be consulted. Z. K.

Supersaturation Theory of Certain Apparently Rhythmical Reactions. RAPHAEL E. LIESEGANG (*Zeitsch. physikal. Chem.*, 1910, **75**, 371—372).—To Ostwald's view that the formation of concentric rings of silver chromate when silver nitrate diffuses into a gelatin film containing potassium dichromate is due to supersaturation phenomena, the objection has been raised that it is incompatible with the fact that two systems of concentric rings can be formed successively without apparent interference. This objection is now shown to have no weight, as the two systems of rings are at different levels in the gelatin film. Ostwald's view is further supported by the observation that a single salt, for example, trisodium phosphate, can be obtained crystallised in concentric rings in a gelatin film. G. S.

Mechanism of Irreversible Phenomena. RENÉ MARCELLIN (*Compt. rend.*, 1910, **151**, 1052—1055).—The author develops the equation:

$$\frac{dN}{dt} = M\left(e^{-\frac{1}{RT}\cdot\frac{d\psi_1}{dN}} - e^{\frac{1}{RT}\cdot\frac{d\psi_2}{dN}}\right)$$

to express the speed at which an unstable system reaches a condition of equilibrium. *e*, *t* *R*, and *T* have their usual significance; considering the speed of transformation as the resultant of the rates of evolution of two systems in contrary directions, ψ_1 and ψ_2 express the available energy of the two systems, whilst *N* is a variable indicating the degree of transformation (for example, the number of molecules of a superfused liquid transformed into crystals).

It is shown mathematically that the above expression is in accordance with the known laws for speed of crystallisation and for reactions in a homogeneous medium. The factor *M* depends on temperature, and will be determined experimentally. W. O. W.

Reactions in Heterogeneous Systems. The Influence of Alcohol. KASIMIR JABŁCZYŃSKI and ST. JABŁOŃSKI (*Bull. Acad. Sci. Cracow*, 1910, 287—294).—Experiments have been made to determine the influence of alcohol on the rate at which solid substances are acted on by aqueous solvents. The heterogeneous reactions examined were the rate of dissolution of magnesium and of calcium carbonate (in the form of marble) in dilute hydrochloric acid. When a portion of the water in the acid solution is replaced by alcohol, the rate of dissolution of the solid is in both cases retarded, and the retarding influence is found to be of the same magnitude as that found for the influence of alcohol on the rate of diffusion of electrolytes in aqueous solution. This result is interpreted in favour of the view that the velocities of reactions in heterogeneous systems are determined primarily by the rates of diffusion processes. H. M. D.

Dynamics of the Reaction between Alcohol and Sulphuric Acid. A Correction. ROBERT KREMANN (*Monatsh.*, 1910, **31**, 1031—1033).—A correction of an error of calculation (Abstr., 1910, ii, 700). T. S. P.

Kinetics of the Formation of Methyl Hydrogen Sulphate and of Methyl Ether. ROBERT KREMANN and H. NEUMANN (*Monatsh.*, 1910, **31**, 1051—1056).—An investigation of the velocity of formation of methyl hydrogen sulphate from methyl alcohol and sulphuric acid, and of methyl ether from methyl hydrogen sulphate and methyl alcohol. The measurements and calculations were made in a manner similar to that described for the corresponding ethyl compounds (Abstr., 1910, ii, 700, 945).

The velocity of formation of methyl hydrogen sulphate is much greater than that of ethyl hydrogen sulphate, whereas the temperature quotient, determined from experiments at 40° and 50°, is somewhat smaller, namely, 2·6 instead of 3·0. The velocity constants are satisfactory, and are the greater the higher the concentration of the sulphuric acid used.

The constants calculated from the experiments on the velocity of formation of methyl ether decrease very considerably during the course of the reaction, owing to the retarding effect of the water produced (compare with ethyl ether). T. S. P.

Velocity of Saccharification of Starch. II. HENRI VAN LAER (*Bull. Acad. roy. Belg.*, 1910, 707—718. Compare Abstr., 1910, ii, 839).—The results recorded by Brown and Glendinning (Trans., 1902, **81**, 388) and V. Henri (*Lois générales de l'action des diastases*, Paris, 1903), which respectively negative and affirm the view that the hydrolysis of starch by diastase takes place in accordance with the logarithmic law, are considered critically, and it is shown that the discrepancy between them is not due to (*a*) difference in temperature at which the experiments were made, (*b*) nature of the diastase used, or (*c*) difference in the limit of hydrolysis found.

It is further shown that the limit of hydrolysis reached depends on the activity, and, therefore, on the quantity of diastase used, and is less for starch yielding an opalescent mucilage than for soluble starch giving a limpid mucilage, such as that prepared under pressure as described previously (*loc. cit.*). T. A. H.

Inversion of Menthone. CARL TUBANDT [with K. MOHS, W. TUBANDT, and H. WEINHAUSEN] (*Annalen*, 1910, **377**, 284—314. Compare Abstr., 1905, ii, 424; 1907, ii, 670).—The work on the inversion of menthones by various acids in different solvents has been repeated and extended. As traces of water have an appreciable effect on the rate of inversion, the alcohols and other solvents were dehydrated by means of calcium.

The experiments with sulphosalicylic acid have been repeated; in each case an acid was used which had been completely dehydrated by continued heating at 80° until the constant for the acid had reached its maximum.

The following values were obtained for sulphosalicylic acid at 20°, where c = molar concentration of the catalyst, and K = value for $K+K_1$ (compare Abstr., 1907, ii, 671):

Ethyl Alcohol	*c.*	0·1	0·05	0·025	0·01	0·005
	K.	292	126	53·8	19	7·8
*iso*Butyl Alcohol	*c.*		0·05	0·025	0·0125	
	K.		139	60·6	26	

With ethyl alcohol and benzene (90% by volume), c = 0·025, K = 29·5.

These results show that with c = 0·01, hydrogen chloride is about eight times as efficient as sulphosalicylic acid, although as catalysts in the process of esterification the two acids have much the same value (Goldschmidt and Udby, Abstr., 1907, ii, 853).

With sulphosalicylic acid, as with hydrogen chloride, the rate of inversion increases more rapidly than the concentration of the catalyst. The addition of benzene to ethyl alcohol diminishes the rate of inversion, whereas when hydrogen chloride is used the addition of benzene facilitates inversion.

Inversion under the influence of acid is influenced to a marked extent by traces of moisture, but moisture has but little effect when bases are used. The following values are given:

Hydrogen chloride at 20°: Ethyl alcohol, c = 0·01, aq. = 0·1, depression of $K+K_1$ = 32%; *iso*butyl alcohol, c = 0·005, aq. = 0·01, depression = 36%; c = 0·005, aq. = 0·005, depression = 72%; ethyl alcohol and benzene (90%), c = 0·005, aq. = 0·01, depression = 36%.

Sulphosalicylic acid at 20°: Ethyl alcohol, c = 0·1, aq. = 0·01, depression = 40%; c = 0·05, aq. = 0·01, depression = 39%; c = 0·05, aq. = 0·05, depression = 75%; c = 0·05, aq. = 0·2, depression = 91%; c = 0·025, aq. = 0·01, depression = 40%; c = 0·025, aq. = 0·05, depression = 75%; *iso*butyl alcohol, c = 0·05, aq. = 0·01, depression = 41%; c = 0·05, aq. = 0·05, depression = 77%; ethyl alcohol and benzene (90%), c = 0·025, aq. = 0·01, depression = 43%.

The effects of small amounts of water are thus much more marked than in the case of esterification (Goldschmidt and Udby, *loc. cit.*; Kailan, Abstr., 1906, ii, 659; Lapworth, Trans., 1908, **93**, 2187), and it is suggested that the most accurate method of estimating small amounts of water in various solvents is by determining the rate of inversion of menthone in the solvent. The effect of moisture is the more marked in the case of *iso*butyl alcohol than in that of ethyl alcohol, and the effect of a given quantity of water appears to be independent of the concentration of the catalyst.

The addition of small amounts of alcohol to indifferent solvents increases to an appreciable degree the rate of inversion when acid catalysts are employed; thus the addition of 0·1 mol. of methyl alcohol to a 0·005*N*-solution of hydrogen chloride in benzene raises the constant some ten times. Different alcohols have much the same effect when 0·1 mol. is added, but when mixtures of benzene and 1 vol. % of the alcohol are used, the effects are the more pronounced the smaller the mol. wt. of the alcohol. With increasing amounts of alcohol the rate of inversion is increased rapidly, until a well-defined maximum is reached at 3%, and the addition of more alcohol produces a lowering of the constant—a lowering which is at first rapid, but gradually slows down.

It has been shown already (Abstr., 1907, ii, 673) that the addition of chlorides increases the catalytic power of hydrogen chloride. This has been confirmed; perfectly anhydrous lithium chloride, aniline hydrochloride, and calcium chloride all produce an acceleration both in anhydrous alcohol and in alcohol containing small amounts of water. The effect is the more marked the greater the concentration of the salt; thus, with 0·01*N*-hydrogen chloride, $K + K_1 = 0·0147$, with 0·002*N*-lithium chloride this is raised to 0·0157, and with 0·05*N*-lithium chloride to 0·0233. The addition of anhydrous aniline sulphosalicylate, on the other hand, retards the inverting action of sulphosalicylic acid in ethyl-alcoholic solution. In the case of the chlorides, it is found that the presence of an appreciable amount of a salt tends to diminish the retarding effects of small amounts of water, a result which may be due to combination between the salt and the water. The addition of mercuric chloride to the hydrogen chloride solution lessens the inverting power of the acid, for example, with 0·01*N*-hydrogen chloride the constant is 0·0147, and this is reduced by 0·1*N*-mercuric chloride in absolute ethyl alcohol to 0·0023, and a similar diminution is noticed when aqueous alcohol is used (compare Le Blanc and Noyes, Abstr., 1891, 388).

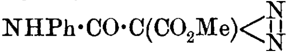
The following table gives the values of the temperature-coefficients:

Solvent.	Catalyst.	K_{30}/K_{20}.	K_{20}/K_{10}.
Ethyl alcohol	0 01*N* to 0·04*N*-EtONa	2·38	2·57
Ethyl alcohol + water (40 vol. %)	0·02*N*-EtONa	2·31	2·48
Ethyl alcohol + benzene (60 vol. %)	0·02*N*-EtONa	2·67	2·96
Ethyl alcohol + benzene (90 vol. %)	0·01*N*-EtONa	2·99	3·29
Ethyl alcohol + ether (80 vol. %)	0·01*N*-EtONa	2·69	2·98
*iso*Butyl alcohol	0·01*N*-EtONa	2·53	—
Ethyl alcohol	0·01*N*-HCl	2·87	3·10
Ethyl alcohol + benzene (90 vol. %)	0·005*N*-HCl	—	3·19
Ethyl alcohol	0·05*N*-Sulphosalicylic acid	—	3·09

Unlike most unimolecular reactions, the temperature-coefficient is small, and tends to diminish with rise of temperature. The relationship $\log K_1/K_2 = A^{T_1 - T_2}/T_1T_2$ holds good.

The view that in the case of acid catalysts the inversion is complicated by combination between the acid and ketone is supported by the fact that when the concentration of the acid is kept constant, the value of $K + K_1$ tends to decrease with the amount of ketone present. Further support is found in the fact that in the esterification of an acid by the hydrogen chloride catalytic method, the addition of a small amount of menthone to the mixture retards the process of esterification, for example, the value of *Kc* (Goldschmidt and Udby, *loc. cit.*) falls from 0·314 (ethyl alcohol without menthone) to 0·287 in the presence of 0·5 mol. menthone; similar results are obtained when methyl and *iso*butyl alcohols are used as solvents. J. J. S.

Intramolecular Transformations. V. Influence of the Solvent on the Velocity of Reaction and the Equilibrium. OTTO DIMROTH [and, in part, HEINRICH SCHNEIDER] (*Annalen*, 1910, **377**, 127—163. Compare Abstr., 1910, i, 518).—The author's ultimate goal in these researches is a position from which, not only the products of a reaction, but also their proportions can be predicted. In a simple substitutive or additive reaction, the isomerides which may be, but not those which actually are, produced can be predicted from the structural formula of the reacting substance; in order to foretell what isomerides actually are formed, it is necessary to know which of the concurrent reactions is the most rapid, and, if two or more isomerides are produced simultaneously, also to know the ratio of their velocities of formation. The velocity of reaction is not conditioned solely by chemical affinity; the course of a reaction is retarded by chemical resistances. Following Nernst, the author gives the relation—the velocity of reaction is the quotient of the driving force and the chemical resistance. Before this relation can be applied in a scientific manner, however, a large amount of pioneer work is necessary, and one of the first problems to be attacked is the influence of the medium on the course of a reaction.

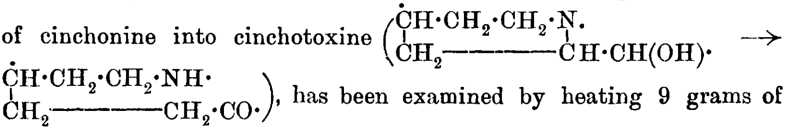
The simplest, and therefore the most rational, method of procedure is the study of a unimolecular reaction. The author has examined the behaviour of methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate and of its neutral isomeride,  $NHPh\cdot CO\cdot C(CO_2Me)<\begin{matrix}N\\ \|\\ N\end{matrix}$ (*loc. cit.*), in methyl, ethyl and benzyl alcohols, ethyl formate, acetate and nitrate, acetonitrile, acetone, chloroform, and nitrobenzene, and has measured the solubilities at 10° of the two isomerides, and also *k*, the velocity constant of the transformation at 10°. The results show clearly that the opinion held previously, namely, that the velocity of transformation increases as the dielectric constant of the solvent diminishes, is no longer tenable. A new relation is established: the velocity of transformation of the aci- ("enolic") modification is so much the smaller the greater the solubility of the aci-modification; in fact, the two quantities are approximately inversely proportional, for their product only varies from 0·1 to 0·32, whilst the solubilities vary from 218 grams (per litre) in methyl alcohol to 3·2 grams in ethyl nitrate, and the values of *k* vary from 0·00053 to 0·055.

In order to throw a clearer light on this dual rôle of the solvent, the influence of the latter on the state of equilibrium is considered. Attention is drawn to a little known relation deduced by van't Hoff from the law of mass action. This relation, which is applicable to two mutually interconvertible isomerides, whether tautomeric or desmotropic, in dilute solution, but does not apply to polymerides, is expressed by the equation: $C_a/C_b = G.L_a/L_b$, where C_a and C_b are the concentrations of the two isomerides, L_a and L_b are their solubilities, and G is a constant which is independent of the nature of the solvent, being equal to $K'p_b/p_a$, where p_a and p_b are the partial pressures, and K' the equilibrium constant of the two isomerides in the space above the solution. It follows from this relation that when G has been calculated from the equilibrium constant and the solubilities of a pair of isomerides in any suitable solvent, the state of equilibrium of the isomerides in any other solvents can be calculated from the solubilities of the two forms in these solvents.

Another relation of great importance is deduced from the preceding equation. A solution, saturated at a definite temperature with respect to each of two mutually interconvertible isomerides A and B, is in contact with the two solid phases. When $G=1$, $C_a/C_b=L_a/L_b$, and the system is in equilibrium. When $G<1$, then $C_a/C_b<L_a/L_b$; consequently A must change into B, which in turn must crystallise, more of A must dissolve, change into B, and separate as the latter, the result being that finally B is the only solid phase left. Conversely, when $G>1$, A will be the solid phase left. Therefore under the conditions mentioned the direction of the transformation is determined by the value of G, and is quite independent of the nature of the solvent. This result is frequently contrary to experience. For example, Bamberger has shown that α-nitroformaldehydehydrazone is changed into the β-isomeride in aqueous or alcoholic solution, the converse change occurring in benzene, chloroform, or light petroleum. In such cases a partial or total polymerisation must have occurred, which would nullify the conditions on which the relation is based. The accuracy of van't Hoff's reasoning has been established by the author by means of a pair of isomerides which fulfil all of the conditions required in the preceding system. These isomerides are the neutral methyl (or ethyl) 5-amino-1-phenyl-1 : 2 : 3-triazole-4-carboxylate and the acidic methyl (or ethyl) 5-anilino-1 : 2 : 3-triazole-4-carboxylate. The latter can be titrated by potassium hydroxide in the presence of the former; the velocity of transformation, which is so small at the ordinary temperature or even at 50—60° that the solubilities of the two isomerides can be readily determined, is accelerated by an acid catalyst without disturbing the state of equilibrium. In ether, ethyl alcohol, toluene, benzene, nitrobenzene, or chloroform, the average value of G is 2·25 for the ethyl ester, and 0·34 for the methyl ester. In accordance with van't Hoff's deduction it is shown experimentally that, independently of the nature of the solvent, the residual solid phase is the neutral isomeride in the case of the methyl ester and the acid isomeride in the case of the ethyl ester. Moreover, no relation is obvious between the dielectric constants of the solvents and the equilibrium constants of either pair of isomerides.

Having shown that the equilibrium is dependent on the solubilities of the reacting substances, the author discusses the conclusion which can be drawn from this relation with regard to the connexion between the velocity of reaction and the solubility. At present it is only possible to state the relation: $k_b/k_a=GL_a/L_b$, where k_a and k_b are the velocity constants of the opposed reactions. How far the individual velocity constants are functions of the solubility of A and B cannot be stated from this indeterminate equation, but the k values must be either inversely proportional to the solubilities of the reacting substances (that is, $k_a = h_1/L_a$ and $k_b = h_2/L_b$, where h_1 and h_2 are proportionality factors satisfying the relation $h_1/h_2 = G$), or directly proportional to the solubilities of the resulting substances (that is, $k_a = i_1 L_b$ and $k_b = i_2 L_a$, where again $i_2/i_1 = G$). von Halban assumes the latter relation in his experiments on the decomposition of triethylsulphonium bromide (Abstr., 1909, ii, 722), but the author's experiments on methyl 5-hydroxy-1-phenyl-1 : 2 : 3-triazole-4-carboxylate, mentioned above, indicate that more probably the former relation represents the connexion between the velocity constants and the solubilities. Unfortunately, a pair of isomerides has not yet been found by which the equation $k_a = h_1/L_a$ can be experimentally tested and the constancy of h_1/h_2 in all solvents ascertained. C. S.

Peculiar Relation between the Strengths of Acids and their Activity. PAUL RABE and ANDREW McMILLAN (*Ber.*, 1910, 43, 3308—3310).

—The catalytic action of acids in accelerating the conversion of cinchonine into cinchotoxine  $\left(\begin{matrix}\mathrm{CH\cdot CH_2\cdot CH_2\cdot N.}\\ |\qquad\qquad\qquad |\\ \mathrm{CH_2}\text{————}\mathrm{CH\cdot CH(OH)\cdot}\end{matrix}\right. \longrightarrow \left.\begin{matrix}\mathrm{CH\cdot CH_2\cdot CH_2\cdot NH\cdot}\\ |\\ \mathrm{CH_2}\text{————}\mathrm{CH_2\cdot CO\cdot}\end{matrix}\right)$, has been examined by heating 9 grams of cinchonine, 108 c.c. of water, and five equivalents of an acid (hydrochloric, oxalic, tartaric, formic, phosphoric, succinic, and acetic) at 98° for definite times (eight, sixteen and a-half, and fifty hours), the amount of cinchotoxine produced being determined by extracting the cooled, basified mixture with ether, in which cinchotoxine is extremely soluble. It is found that the velocity of conversion diminishes as the dissociation constant of the acid increases. This remarkable result is receiving further attention. C. S.

Auto-oxidisable Substances and Systems of Physiological Interest. I. and II. TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1910, 24, 90—93, 94—96).

—The uptake of oxygen by commercial preparations of lecithin is much increased by the addition of ferric chloride. The same is true for cuorin. The action can be shown when the ferric chloride is diluted, so that only one part in six millions is present. Other metallic salts act similarly, but never so powerfully; copper, silver, and cobalt salts are, after iron, the most effective. The order of efficiency of the metals in this catalytic action is quite different in the case of linseed oil. W. D. H.

Chemical Composition of Matter. III. EDUARD MULDER (*Rec. trav. chim.*, 1910, [ii], 14, 453—454. Compare Abstr., 1909, ii, 34).

—Supposing that units of matter may be condensed in their centres of gravity, *A* and *B*, at unit distance apart, and that their energy is also concentrated at the same points, whilst the mass and energy of the ether penetrating them is concentrated at points *A'* and *B'* at infinitely small distances from *A* and *B* respectively, experience shows that there would be attraction along *AB*. A difference of pressure at the points *AA'* and *BB'*, that is, between ordinary matter and ether must be admitted, as well as a mean intensity of energy. The problem to be solved is as to the transformations which take place before the attraction manifests itself. T. A. H.

Calculation of Molecular Dimensions from Radiometer Observations. P. DEBYE (*Physikal. Zeitsch.*, 1910, **11**, 1115—1121).—In a recent paper (*Ann. Physik*, 1910, [iv], **32**, 809), Knudsen has measured the pressures which are produced as a result of radiometer action between two parallel plates which are at different temperatures and are surrounded by a gas at low pressure. A formula was deduced, by means of which the observed radiometer pressures can be represented satisfactorily when the pressure of the gas is sufficiently small, but for higher pressures the calculated pressures are higher than those observed. The author shows that the divergences are probably due to the invalid assumption, that all the molecules which leave the hot plate reach the cold plate with velocities corresponding with the higher temperature. As a consequence of molecular collisions, a certain fraction of the molecules will not reach the cold plate in this condition. This fraction increases with the pressure of the gas, and is determined by the ratio of the distance between the plates to the free path of the molecules. A new formula, which takes this effect into account, has been deduced, and this is found to agree better with the experimental observations.

From the deviations between the observed pressures and those calculated by Knudsen's formula, the diameters of the gaseous molecules can be calculated. The values obtained for hydrogen and oxygen are $2·9 \times 10^{-8}$ and $3·9 \times 10^{-8}$ cm. respectively. These values are a little greater than those obtained from the constant b of van der Waals' equation. H. M. D.

The Attraction Constant of a Molecule of a Substance and its Chemical Properties. RICHARD D. KLEEMAN (*Phil. Mag.*, 1910, [vi], **20**, 905—921).—In previous papers (compare Abstr., 1910, ii, 932) an expression has been obtained for the force of attraction between the molecules of a liquid. This attractive force, which gives rise to surface tension and latent heat of vaporisation, is supposed to be the same as that which causes chemical combination. According to this, the attraction constant $\Sigma\sqrt{m}$, representing the sum of the square roots of the weights of the atoms in a molecule, should be related to the chemical properties of a substance.

Such relationships have been found in the case of a large number of organic substances. The values of $T_c/\Sigma\sqrt{m}$, in which T_c is the critical temperature, have been calculated, and it is claimed that the values of this factor are approximately constant for certain comparable series of compounds.

Other expressions, which do not involve the critical or other corresponding temperature, are similarly related to the chemical properties. Such are: $v/(\Sigma\sqrt{m})^{\frac{3}{4}}$, $\lambda/(\Sigma\sqrt{m})^{\frac{1}{3}}$, $E/(\Sigma\sqrt{m})^{\frac{1}{3}}$, $L/\Sigma\sqrt{m}$, and $p/(\Sigma\sqrt{m})^{\frac{1}{4}}$, where v is the molecular volume, λ the surface tension, E the potential energy of the surface film, L the latent heat of vaporisation, and p the pressure of the saturated vapour corresponding with a temperature, T, which has the same value on the reduced scale for the different substances. H. M. D.

Wash-bottle with Divided Liquid Layer. FRANZ MICHEL (*Chem Zeit.*, 1910, **35**, 1228).—An eprouvette into the neck of which is ground a glass cap provided with inlet and exit tubes, the inlet tube being expanded at the lower part to a pipette-like form which fits the contracted part of the apparatus but loosely, leaving an annular space of 1—2 mm. When required for use, the cap is removed, and the required amount of the washing liquid introduced. The tube is then replaced; glass beads are now placed in the upper part of the bottle until they reach 2—5 cm. above the liquid, and the bottle is then closed. On passing a current of gas, the column of liquid is divided into two parts, as a gaseous space forms below the contracted part of the apparatus. The next gas bubbles are then forced through the narrow space, and pass through the interstice of the glass beads. The apparatus, therefore, serves the purpose of two separate wash-bottles. If it is desired to mix the two liquids, the passing of the gas is temporarily stopped, which causes the liquid to ascend into the inlet tube, and on again passing the gas, or by blowing through the tube, the two layers are re-formed. L. DE K.

Lecture Apparatus for Demonstrating, by means of the Electric Arc, the Formation of Oxygenated Compounds from Atmospheric Air. HENRI VAN ERP (*Rec. trav. chim.*, 1910, [ii], **14**, 447—452).—The apparatus is a small, triangular electric furnace, constructed in asbestos board, and provided with hollow copper electrodes, cooled by water circulating inside them. Air is caused to pass across the arc formed between the two electrodes, and is then passed through a wash-bottle containing a solution of potassium hydroxide, in which after a time the presence of nitrite and nitrate may be demonstrated. The method of constructing the apparatus is described in detail in the original, which also contains an illustration. T. A. H.

Inorganic Chemistry.

Nature of the Decomposition of Hydrogen Peroxide by Light. A. Tian (*Compt. rend,* 1910, 151, 1040—1042).—By submitting solutions of hydrogen peroxide in conductivity water to the action of ultra-violet light from a quartz-mercury lamp, the author finds that the reaction for its decomposition is a unimolecular one, and proceeds in accordance with the equations : $H_2O_2 = H_2O + O$; $2O = O_2$. The decomposition by light therefore resembles that induced by catalysts, and is different from the decomposition by heat, which is a bimolecular reaction. Under the conditions of the experiment, the reverse action occurred to an extent not exceeding the formation of 0·00005 gram of hydrogen peroxide per litre. W. O. W.

Catalytic Decomposition of Hydrogen Peroxide in a Homogeneous Medium. Eugen Spitalsky (*J. Russ. Phys. Chem. Soc*, 1910, **42**, 1085—1159*).—A discussion of the nature of catalysis, in which it is shown that the velocity and, to some extent, the direction of all oxidising-reducing actions, and particularly that of hydrogen peroxide, are greatly affected by the concentration of the hydrogen ions of the reacting mixture, and that the condition of the latter at any given moment, and whatever the concentration of the hydrogen ions, can be completely defined by the effective concentration of the hydrogen peroxide at that moment. In the catalysis of hydrogen peroxide by dichromate there is a simultaneous reversible formation of various intermediate compounds of varying stability, of which those having the least number of molecules of the hydrogen peroxide attached to the catalyst are comparatively less stable; hence, towards the end of the reaction when the concentration of hydrogen peroxide is less, the velocity of the reaction is greatest.

The measurements were made gasometrically, the experiments being performed in Bredig and Walton's apparatus (Abstr., 1903, ii, 282), and Riesenfeld and Weich's criticisms (Abstr., 1908, ii, 951) of the gasometric method are shown to be entirely without foundation.

Many of the results have already been published (Abstr., 1907, ii, 338, 942).

Since chromic acid or the dichromate in acid solution is reduced by hydrogen peroxide to chromic oxide, it was necessary, in order to complete the experiments on the catalytic decomposition of hydrogen peroxide by chromates, to investigate how far this process occurs in the catalytic experiments described, and what is its relation to the activity of the catalyst. In very dilute solutions all the best ordinary methods for the estimation of chromic acid are wholly inapplicable, but the following very accurate and convenient method is employed. To about 10 c.c. of a solution containing 0·0108 mol. CrO_3, 30 c.c. of sodium hydrogen arsenate solution containing 0 004 gram-mols. NaH_2AsO_4 per litre are added, then 30 c.c. of hydrochloric acid. The mixture is left for twenty minutes, after which two drops of methyl-orange or indigo solution are added as indicator, and the mixture titrated with an equivalent solution of potassium bromate. The method is recommended as a general one in analysis, and as a more accurate and cheaper substitute for iodometric methods.

In the presence of a large excess of hydrogen peroxide, chromic acid is at first rapidly reduced, although the reaction is not instantaneous, after which the hydrogen peroxide is catalytically decomposed under the influence of the chromium tri- and sesqui-oxides, but the relative proportion of the two last formed finally does not alter with the concentration or quantity of hydrogen peroxide employed, the reaction being one of chemical equilibrium between the two oxides, a fact which was confirmed by the measurement of the concentration of the hydrogen ions in various mixtures.

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* The fresh matter is published also in *Zeitsch. anorg. Chem.*, 1910, **69**, 179—208.

Contrary to Riesenfeld's assumption (*loc. cit.*), it is shown that the form of curves obtained for the decomposition of hydrogen peroxide in the presence of dichromate is best explained by the fact that, after the reduction of the dichromate and the establishment of equilibrium between the two oxides, the catalytic decomposition of the hydrogen peroxide proceeds without any further change in the catalyst, or, if any change does occur, it is a reversible one, and only depends on the concentration of the hydrogen peroxide at the given moment. The catalytic properties of chromic acid in no way depend on its previous history, and the effect of the fresh acid is identical with that of the acid after having been used several times; it is evident therefore that no irreversible changes take place. The curves and the general characteristics of the reaction are closely analogous to those of fermenting processes. Z. K.

Catalysis of Hydrogen Peroxide. EUGEN SPITALSKY (*Ber.*, 1910, **43**, 3187—3201).—A reply to the criticisms of Riesenfeld (Abstr., 1908, ii, 951). It is also shown that the usual method of determining the velocity of the catalytic decomposition of hydrogen peroxide by measuring the rate at which oxygen is evolved gives the same results as the direct titration of the hydrogen peroxide with potassium permanganate. T. S. P.

The Colours of Colloidal Sulphur. RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1910, **7**, 307—308).—If drops of a 20% citric acid solution are placed on a thin layer of a solidified solution containing gelatin and sodium thiosulphate, the precipitation of sulphur which results from the diffusion of the acid is accompanied by the development of colour effects. In transmitted light the colour is a deep lilac-blue. The colour is not due to interference, but appears to be determined by the size of the colloidal particles. After about twenty-four hours, the colour effects disappear, and this is supposed to be due to the conversion of S_μ into S_γ. H. M. D.

Reduction of Phosphoryl Chloride by Hydrogen under the Influence of the Electrical Discharge. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1910, **151**, 876—878. Compare Abstr., 1910, ii, 121).—When the vapour of phosphoryl chloride mixed with pure dry hydrogen is submitted to the action of the silent electrical discharge, the armatures slowly become coated with a yellow solid. If this is removed by hot water and dried in a vacuum, it is obtained as an easily oxidised, reddish-yellow powder having the composition P_2O. It appears to be identical with the oxide obtained by the action of phosphine on phosphoryl chloride in presence of hydrogen bromide (Abstr., 1898, ii, 216; 1901, ii, 502), the existence of which has been questioned by other investigators. The action is stated to take place in accordance with the equation: $2POCl_3 + 4H_2 = P_2O + 6HCl + H_2O$.

The reaction was carried out in an apparatus of fused silica which is described in detail. The use of glass for the purpose is inadmissible. W. O. W.

Safety Explosives Employed in Mines. J. TAFFANEL (*Compt. rend.*, 1910, 151, 873—876).—It is shown experimentally that the gases formed by the detonation of safety explosives of the securite type contain a much greater proportion of carbon monoxide when the charge is enveloped in the usual paraffined wrapper than when the explosive is uncovered, or wrapped in ordinary paper or asbestos. The presence of the secondary flame accompanying explosion appears to depend largely on the presence of an oxidisable envelope, or of coal dust. It is not seen when asbestos paper is employed, and the use of the latter, therefore, enables heavier charges to be fired with safety. W. O. W.

Bromo- and Hydrobromo-derivatives of Silicon. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1910, 151, 1055—1057).—Four kilograms of the crude product arising from the action of hydrogen bromide on silicon at a red heat were fractionally distilled under diminished pressure. About 90% of the liquid consisted of silicon tetrabromide, the remainder containing tribromosilicomethane with a small quantity of *dibromosilicomethane*, SiH_2Br_2, a spontaneously inflammable liquid, b. p. about 75°, and probably *bromosilicomethane*, SiH_3Br, b. p. 30—40°.

The product of the action of the silent electric discharge on tribromosilicomethane yielded on fractionation silicon tetrabromide, hexabromosilicoethane, colourless crystals, m. p. 95°, b. p. 265°, an *octabromide*, Si_3Br_8, crystals, m. p. 133°, a *decabromide*, Si_4Br_{10}, m. p. 185° (decomp.), together with an uninvestigated yellow residue.

Silicon tetrabromide differs from the tetrachloride in not undergoing reduction when mixed with hydrogen and submitted to the silent electrical discharge. W. O. W.

The History of "Potash" and of its Name. EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1910, 34, 1217—1219, 1226—1228, 1235—1237).—Historical. L. DE K.

The Isomorphism of Potassium and Sodium Compounds. ERNST SOMMERFELDT (*Zeitsch. anorg. Chem.*, 1910, 69, 47—51).—The question of the possible isomorphism of potassium and sodium compounds has been studied in the double sulphates, blödite, $Na_2Mg(SO_4)_2,4H_2O$, and leonite, $K_2Mg(SO_4)_2,4H_2O$, the crystals being examined by the ultramicroscope.

Crystals of blödite become turbid if containing more than 0·8% K_2SO_4, the number of particles increasing with the time, whilst leonite only shows similar particles when as much as 11·6% Na_2SO_4 is present.

According to Ostwald, the crystallisation of a supersaturated solution is only brought about by a foreign salt if the latter is isomorphous with the salt in solution. The crystallisation of a supersaturated solution of potassium sulphate on the addition of a crystal of ammonium sulphate may be explained by the dissolution of the crystal, displacing potassium sulphate. In accordance with this explanation, a readily soluble salt, such as potassium iodide, also brings about the crystallisation of potassium sulphate. Ostwald's criterion may, therefore, sometimes give misleading results.

C. H. D.

A Characteristic Behaviour of Alkali Phosphate. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1910, **69**, 475—478).—It was noticed that the addition of sodium hydroxide to an American meat juice caused it to set into a crystalline mass. When exposed to the air, the juice deposits crystals of potassium dihydrogen phosphate, and the addition of sodium hydroxide no longer causes crystallisation to occur in the liquid.

W. D. H.

Some New Compounds of Nitrogen and Hydrogen with Lithium. I. FRANZ W. DAFERT and R. MIKLAUZ (*Monatsh.*, 1910, **31**, 981—996. Compare Abstr., 1909, ii, 882).—Metallic lithium combines with pure, dry nitrogen at the ordinary temperature, amorphous *lithium nitride*, Li_3N, being formed; the presence of relatively small quantities of oxygen or hydrogen, however, will completely prevent the reaction. Lithium is not attacked by dry air at the room temperature.

Lithium nitride has m. p. 840—845°; the fused substance rapidly attacks iron, nickel, copper, platinum, porcelain, and other silicates. At 870° it will eat through any containing vessel. It penetrates through vessels of magnesia as through a filter.

When heated at 220—250° in a current of hydrogen, a new compound, *trilithiumammonium*, Li_3NH_4, is formed from the amorphous nitride. If this compound is heated above 340° in an atmosphere of hydrogen, part of its hydrogen is expelled, to be absorbed again on cooling. If the temperature is raised to 480°, pure *trilithiumamide*, Li_3NH_2, is formed. This latter compound is also formed directly by the action of hydrogen on crystallised lithium nitride which has been obtained by heating lithium at 460° in a current of nitrogen; the reaction is so vigorous that the amide is obtained as a fused mass.

Trilithiumammonium is an extremely hygroscopic substance, evolving hydrogen and ammonia under the action of water. Trilithiumamide possesses similar properties; it is not sensitive towards light.

T. S. P.

Photo-Halides. II. WILLEM REINDERS (*Chem. Weekblad*, 1910, **7**, 993—1005. Compare Abstr., 1910, ii, 1062).—The author advances arguments in favour of the theory that the photo-halides are absorption compounds of colloidal silver and normal halides. He does not consider that there is any evidence to support the theory that they are sub-halides.

A. J. W.

"Ripening" of Silver Halide Emulsions. RAPHAEL E. LIESEGANG (*Zeitsch. physikal Chem.*, 1910, **75**, 374—377).—The increase in size of the particles of silver halides, the so-called "ripening" of photographic plates, may be accounted for in two ways: (1) by the association of small particles, a process analogous to the coagulation of colloids, and (2) by the gradual increase in size of the larger particles at the expense of the smaller, owing to the greater solubility of the latter.

The first process must be associated with a kind of diffusion which could not take place in a solidified gelatin film, and the observation that ripening proceeds rapidly in such a dried film supports the latter view. Further evidence in favour of this explanation is adduced.

G. S.

Calcium Silicates in Cement. L. Sz. Szathmáry (*Zeitsch. Kryst. Min.*, 1910, **48**, 448; from *Vegyészeti Lapok*, 1907, **2**, No. 7, and *Bányászati és Kohászati Lapok*, 1908, **46**, 635—652).—Several calcium silicates have been prepared synthetically, but some of them are probably of the nature of solid solutions. Which of these are present in cements the author leaves undecided. The calcium aluminate, $2CaO,Al_2O_3$, is probably a constituent of cement. Incidentally, the following analysis is given of [impure] wollastonite from Csiklova, Hungary.

SiO_2.	CaO.	Fe_2O_3.	CO_2.	H_2O.	Total.
44·95	49·49	0·58	4·31	0·58	99·91

L. J. S.

The Alloys of Tellurium with Cadmium and Tin. Matsusuke Kobayashi (*Zeitsch. anorg. Chem.*, 1910, **69**, 1—9; *Mem. Coll. Sci. Eng. Kyoto.*, 1910, ii, 353—363).—Mixtures of cadmium and tellurium, fused in glass or porcelain tubes in an atmosphere of carbon dioxide, have been submitted to thermal analysis. The freezing-point curve has a maximum at about 1041°, corresponding with the compound TeCd, but it is not possible to prepare this compound in a pure condition under ordinary pressure, owing to the volatility of cadmium. The two eutectic points lie so near to the freezing points of cadmium and tellurium respectively as to be indistinguishable from them.

The freezing-point curve of mixtures of tellurium and tin also has a maximum at 780°, corresponding with the formula TeSn. The eutectic point between this compound and tellurium lies at 393° and 86% Te. The compound TeSn has D_{19} 6·472, and does not form solid solutions with tin or tellurium (compare Fay, Abstr., 1907, ii, 880; Biltz and Mecklenburgh, Abstr., 1909, ii, 1022).

The thermal results are confirmed by microscopical examination.

C. H. D.

Falk's White Lead. Julius F. Sacher (*Chem. Zeit.*, 1910, **34**, 1261—1263. Compare Abstr., 1910, ii, 712, 1067).—When lead carbonate, lead oxide, and lead acetate are kneaded together, the product is not $5PbCO_3,2Pb(OH)_2,PbO$, but a mixture in varying proportions of normal lead carbonate and white lead. The mixtures only become white when air, containing carbon dioxide, has access, otherwise a yellow or red colour persists. True white lead, examined microscopically, is always amorphous, and pure normal lead carbonate is always crystalline, different preparations differing only in the size of their crystals.

The decomposition of white lead by hydrogen sulphide, observed by Falk, carbon dioxide being liberated, is due to the presence of lead acetate, the acetic acid set free decomposing a further quantity of carbonate. C. H. D.

Formation of Colloidal Copper. André Rassenfosse (*Bull. Acad. roy. Belg.*, 1910, 738—741).—Copper sulphate in sulphuric acid is reduced by various organic liquids, forming at first probably violet cuprous sulphate, and finally colloidal copper.

When a few drops of alcohol are placed in a solution of copper sulphate in sulphuric acid, a violet zone which gradually becomes brown is formed between the two liquid layers. On gently warming, it disappears to re-appear on cooling, but at 45° it becomes yellow. The solution is stable, and is not affected by filtration or by treatment in a centrifugal machine, but when submitted to an electric current deposits a deep reddish-brown, granular, pulverulent copper, quite different from the coherent deposit obtained from a solution of copper sulphate in sulphuric acid.

Similar results, with some difference in details, are shown when methyl alcohol, ether, acetone, acetic acid, or chloroform is added to such a solution, and a solution of copper phosphate in phosphoric acid shows similar behaviour. T. A. H.

Corrosion of Copper and Iron Alloys by Water Containing Salt and Air. Oxidation of Copper at High Temperatures. Willem P. Jorissen (*Zeitsch. angew. Chem.*, 1910, 23, 2305—2306).—A specimen of delta metal from the keel of a ship, which had been attacked by sea-water, was found to contain 41·1% of cuprous oxide, no cupric oxide being present; the zinc had completely disappeared. Cuprous oxide was also formed from copper which had been kept for two years either in sea-water or in a solution of sodium chloride of the same chlorine content. When copper is partly immersed in distilled water, cuprous oxide is formed on the submerged part, whereas cupric oxide is formed on the other part.

Cuprous oxide is formed when air is continually circulated over copper heated to a temperature above that at which dissociation of cupric oxide takes place.

Analyses are given of (*a*) a piece of iron which had been in the ground for years, (*b*) iron used to protect a copper alloy in a pump from corrosion, (*c*) iron used for the same purpose in a ship's condenser, (*d*) some Dutch bronze cannons fished up from the Straits of Messina. T. S. P.

Occluded Gas in Alloys of Copper. G. Guillemin and B. Delachanal (*Compt. rend.*, 1910, **151**, 881—883. Compare Abstr., 1909, ii, 144).—Results of analyses are given showing the total volume of occluded gas and the percentage of carbon dioxide, carbon monoxide, methane, hydrogen, and nitrogen in different specimens of brass, bronze, aluminium bronze, phosphor-bronze, and tin.

Forgeable brass contains hydrogen, carbon dioxide, and carbon monoxide; the latter predominates in unsound ingots containing blow-holes. The presence of hydrogen does not impair the mechanical properties of brass. The small amount of gas in phosphor-bronze consists chiefly of carbon dioxide and hydrogen. Commercial tin contains hydrogen, carbon dioxide, and carbon monoxide.

W. O. W.

The Tempering of Bronzes. L. GRENET (*Compt. rend.*, 1910, **151**, 870—871).—The connexion between the temperature at which bronze is annealed after tempering and the hardness of the product appears to be the same as in the case of steel. W. O. W.

The Formation of Cuprous Iodide from the Physicochemical Standpoint. P. P. FEDOTÉEFF (*Zeitsch. anorg. Chem.*, 1910, **69**, 22—37).—The reaction occurring between copper and iodine in presence of water has been studied : $Cu + I_2 \longrightarrow CuI_2 \rightleftarrows CuI + I$. Equilibrium at 20° is only reached after fifteen to thirty hours' shaking. The quantity of iodide dissolved increases with the proportion of iodine. In solutions in equilibrium with solid iodine, the concentration of the dissolved iodine increases with that of the copper. Isothermals for the two systems (cuprous iodide and iodine respectively as solid phase) are drawn, and it is shown that in all the saturated solutions the ratio $Cu : 4I$ is maintained. The range of composition within which cupric iodide is stable is increased by raising the temperature.

Assuming that the complex ion present is I'_3, the ratio I'_3/I' at $20° = 0{\cdot}964$. As the cation does not enter into the equilibrium, the general conclusion is drawn, that in aqueous solution of iodine in iodides the iodine is equally divided between the simple and the complex ions. The formula of cupric iodide in a solution saturated with iodine is $Cu\!<\!\begin{matrix}I\\I_3\end{matrix}$. The number of complex ions increases with rising temperature.

The solubility-product $Cu^{\bullet} \times I' = L = 5{\cdot}06 \times 10^{-12}$ (Bodländer and Storbeck, Abstr., 1902, ii, 607), so that $K = (Cu^{\bullet\bullet})^2(I')^4/L^2(I_2) = 4{\cdot}18 \times 10^{-14}$.

The potential of the iodine electrode at 20° is $e_0 = 0{\cdot}900 + 0{\cdot}029\log(I_2)/(I')^2$; and of the $Cu^{\bullet\bullet}/Cu^{\bullet}$ electrode at 20°, $e_0 = 0{\cdot}476 + 0{\cdot}058\log(Cu^{\bullet\bullet})/(Cu^{\bullet})$. C. H. D.

Double Sulphates formed by Lanthanum and Cerium Sulphates with the Alkali Sulphates. BARRE (*Compt. rend.*, 1910, **151**, 871—873).—The solubility of lanthanum and cerium sulphates in aqueous solutions of potassium, sodium, and ammonium sulphates at different concentrations has been determined. The existence of the following double salts has been revealed by the solubility curves and confirmed by analyses :

$La_2(SO_4)_3,K_2SO_4,2H_2O$; $La_2(SO_4)_3,5K_2SO_4$; $La_2(SO_4)_3,Na_2SO_4,2H_2O$;
$La_2(SO_4)_3,(NH_4)_2SO_4,2H_2O$; $2La_2(SO_4)_3,5(NH_4)_2SO_4$;
$La_2(SO_4)_3,5(NH_4)_2SO_4$. $Ce_2(SO_4)_3,K_2SO_4,2H_2O$;$2Ce_2(SO_4)_3,3K_2SO_4,8H_2O$;
$Ce_2(SO_4)_3.5K_2SO_4$; $Ce_2(SO_4)_3,Na_2SO_4,2H_2O$;
$Ce_2(SO_4)_3,(NH_4)_2SO_4,8H_2O$; $Ce_2(SO_4)_3,5(NH_4)_2SO_4$.

Lanthanum and cerium sulphates are more soluble in a solution of ammonium sulphate than in one of sodium or potassium sulphate.
W. O. W.

Nature of the Oxides Causing the Colour of Oriental Sapphires. AUGUSTE VERNEUIL (*Compt. rend.*, 1910, **151**, 1063—1066).—The opinion that the colour of oriental sapphires is due to ferric oxide is based on analyses by Vauquelin, Forchhammer, and others. The author having previously described the preparation of artificial sapphires from fused alumina coloured by ferric and titanic oxides (Abstr., 1910, ii, 212), now shows that the latter is present in the natural stones; three sapphires of different origin being found to contain 0·03—0·058% of titanic acid. The conclusion is drawn that the colour of sapphires is due to titanium, present as an oxide or as a titanate of iron. W. O. W.

Catalytic Properties of Asbestos. P. A. TSCHEISHWILI (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 856—862).—An acid solution of *N*/20-potassium permanganate filtered through asbestos is reduced in each of the first eight filtrations, after which it is no longer reduced on filtration. Ten c.c. loses in this way 0·025 c.c. for each filtration, and the results obtained are exactly the same for asbestos from various sources, and whether it has only been treated with acids and water or whether it has been ignited before such treatment. The precipitate formed on the asbestos has no catalytic influence on the reduction of the permanganate, and it does not consist of manganese peroxide.

It is much more convenient to use asbestos in the filtration of permanganate solutions, and allow 0·025 c.c. as correction, than to use glass wool, through which a clear filtrate, cannot be obtained. Z. K.

The Rusting of Iron. V. ANDSTRÖM (*Zeitsch. anorg. Chem.*, 1910, **69**, 10—21. Compare Moody, Trans., 1906, **89**, 720; Friend, Proc., 1910, **26**, 179; Lambert and Thomson, Trans., 1910, **97**, 2426). —Thin strips of soft iron are enclosed with water (the oxygen and carbon dioxide in which have been estimated) in flasks, closed by ground stoppers sealed by mercury. After shaking for a definite time, the rust formed is collected on a filter, that present as an incrustation on the strips being added, and the iron in the filtrate is also estimated.

The quantity of iron removed by corrosion is independent of the proportion of carbon dioxide in the water, and is proportional to the amount of dissolved oxygen, the ratio of iron to oxygen corresponding with Fe_3O_4. The dissolved portion of the iron corresponds with $Fe(HCO_3)_2$. These results are shown in the form of curves. When very little oxygen is present, but the solution contains large quantities of carbon dioxide, corrosion only proceeds very slowly.

The results are interpreted as indicating that rusting is principally due to the action of oxygen, probably with intermediate formation of hydrogen peroxide. C. H. D.

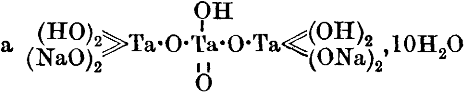
Dissociation of Ammoniacal Ferrous Chlorides and the Formation of Ferrous Nitride. FERNAND GIRARDET (*Bull. Soc. chim.*, 1910, [iv], **7**, 1028—1034. Compare Lang and Rigaut, Trans., 1899, **75**, 883; Jackson and Derby, Abstr., 1900, ii, 596).—The interaction of ammonia with ferrous chloride is reversible between −18° and 350°, and a study of the tensions of dissociation of the products indicates that two compounds of this type exists, represented by the formulæ $FeCl_2,6NH_3$ and $FeCl_2,2NH_3$. The former is stable only at low temperatures. Above 350°, the chloride is decomposed and ferrous nitride is formed, the optimum temperature for this reaction being 480°. In preparing ferrous nitride, it is best to heat the chloride to 480°, and then introduce ammonia gas. Full experimental details and tables of dissociation tensions are given in the original.

T. A. H.

Chemical Constitution of Iron-pyrites and Pyrolusite. L. BENEDEK (*Zeitsch. Kryst. Min.*, 1910, **48**, 447—448; from *Magy. Chem. Folyóirat*, 1908, **14**, 85—81).—Iron-pyrites when heated to a red-heat in an atmosphere of carbon dioxide loses half of its sulphur, and ferrous sulphide (FeS) remains. At 300—400° in water vapour half the sulphur is also lost, after which the ferrous sulphide is decomposed with the production of ferrous oxide and hydrogen sulphide. These reactions indicate, in the author's opinion, that the iron in iron-pyrites is ferrous.

Pyrolusite (MnO_2) when heated in an atmosphere of hydrogen passes first into Mn_2O_3, at 280° into Mn_3O_4, and finally into MnO. L. J. S.

Preparation of Tantalic Acid from West Australian Fergusonite. Sodium Tantalate. EDGAR WEDEKIND and W. MAASS (*Zeitsch. angew. Chem.*, 1910, **23**, 2314—2316).—A specimen of fergusonite from West Australia contained 54·22% Ta_2O_5, 1·80% Cb_2O_5, 27·73% Y_2O_3, 3·20% Ce_2O_3, and 0·36% ThO_2, and owing to the high tantalum content the authors have used it to prepare tantalum pentoxide and derivatives. The acid and basic constituents were separated essentially according to the method of Krüss and Nilson (Abstr., 1887, 706), the residue then consisting essentially of tantalic, columbic, and titanic acids; 7·5 grams of the residue were then carefully added to 15 grams of sodium carbonate fused in a platinum crucible, after which a further 4 grams of sodium carbonate and 1·6 grams of sodium nitrate were added. The cold fusion was extracted with 750 c.c. of water, filtered, and left overnight; 6·4 grams of sodium tantalate crystallised out. The finest crystals were picked out, the remainder dissolved in much hot water, and, after cooling, the tantalum precipitated as tantalic acid by means of carbon dioxide (compare Weiss and Landecker, Abstr., 1909, ii, 942). The tantalic acid was dried at 100°, mixed with a little fuming nitric acid, evaporated to dryness, and then converted into pentoxide by ignition.

Sodium tantalate forms colourless, hexagonal crystals, which give an alkaline solution. Analysis gives $Na_4Ta_3O_{10}H,12·32H_2O$, agreeing with Rose's empirical formula $Na_8Ta_6O_{19},25H_2O$; $10·5H_2O$ are lost at 105—110°, a further molecule at 190°, and the last molecule in the blow pipe. It is probably an acid sodium salt of a tritantalic acid of the formula  $\begin{matrix}(HO)_2\\(NaO)_2\end{matrix}{>}Ta{\cdot}O{\cdot}\overset{OH}{\underset{\underset{O}{\|}}{Ta}}{\cdot}O{\cdot}Ta{<}\begin{matrix}(OH)_2\\(ONa)_2\end{matrix},10H_2O$, the anhydrous tantalate obtained on heating being a hexatantalate. T. S. P.

Gold Tellurides. GIOVANNI PELLINI and E. QUERCIGH (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 445—449).—The freezing-point curve of the system gold–tellurium has been determined, the alloys being fused in an atmosphere of carbon dioxide. The curve has a single maximum, corresponding with the compound $AuTe_2$, melting at 464°. There are two eutectic points, at 12 and 47 atomic % Au and at 416° and 447° respectively. There is no indication of the formation of solid solutions. The compound $AuTe_2$ occurs in nature as calaverite. As such a compound is not obtained by the action of tellurium on solutions of gold salts, it is probable that the mineral has been formed by a process of fusion. C. H. D.

Halogen Compounds of Rhodium. Mlle. G. GOLOUBKINE (*Bull. Soc. chim. Belg.*, 1910, **24**, 388—396).—Spongy rhodium readily dissolves in a solution of hydrochloric acid saturated with chlorine, or in a solution of hydrobromic acid saturated with bromine, giving the corresponding halogen compounds. The preparation of the bromine compounds is described.

One gram of spongy rhodium is heated with 24 grams of 40% hydrobromic acid containing 7 grams of bromine in a sealed tube at 80—100° for forty-eight hours. The contents of the tube are distilled under diminished pressure, the residue treated with a little water, and again distilled to remove all hydrobromic acid. The bromide remaining is dissolved in water, and the solution evaporated in a vacuum over sulphuric acid, the final drying of the product being carried out in a vacuum over fused potassium hydroxide. If the spongy rhodium used contains zinc or bismuth, the resulting impure bromide is reduced in a current of hydrogen; the zinc or bismuth bromide sublimes, leaving pure rhodium, from which the pure bromide is obtained by the treatment already detailed.

Rhodium tribromide, $RhBr_3,2H_2O$, is a blackish-red substance, which is very soluble in water. When heated at 100—140° it loses, not only water, but also hydrogen bromide. With potassium hydroxide the solution gives a precipitate of the *hydroxybromide*, $Rh(OH)_2Br,2H_2O$, and from the filtrate, dark red crystals of *potassium rhodobromide*, K_2RhBr_5, are obtained.

Potassium, sodium, rubidium, ammonium, and *barium rhodobromides* are prepared by adding a slight excess of rhodium bromide to the solutions of the bromides of the metals mentioned. The solution is evaporated to dryness, and the excess of rhodium bromide extracted with alcohol, leaving the rhodobromide undissolved. They possess the general formula M'_2RhBr_5, and are readily soluble in water; most of them are dark red in colour, the sodium salt being brick-red.

A warm concentrated solution of potassium iodide produces a black precipitate of *rhodium iodide*, RhI_3, from a solution of rhodium bromide. Dilute solutions give no precipitate in the cold.

T. S. P.

Mineralogical Chemistry.

Iron-pyrites from Hungary. A. Liffa (*Zeitsch. Kryst. Min.*, 1910, **48**, 441—442; from *Földtani Közlöny*, 1908, **38**, 276—294, 405—423).—Crystallographic descriptions are given of iron-pyrites from various Hungarian localities. Crystals (penetrated by quartz) from Csungány gave on analysis by K. Emszt:

Fe.	As.	Ni.	S.	SiO_2.	Total.
45·36	trace	0·05	51·61	2·84	99·86

L. J. S.

Blomstrandine from the Urals. Otto Hauser and H. Herzfeld (*Centr. Min.*, 1910, 756—764).—Some black crystals, supposed to be æschynite, embedded in pegmatite from Miask, proved on analysis to be the blomstrandine of Brögger (Abstr., 1907, ii, 885). Approximate goniometric measurements are given; D 5·00:

Ta_2O_5.	Cb_2O_5.	TiO_2.	SnO_2.	WO_3.	ZrO_2.	UO_2.	ThO_2.
1·30	15·08	34·07	0·20	trace	0·50	3·24	7·93

Y_2O_3.	$(Ce,La,Di)_2O_3$.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	PbO.	Loss on ignition.	Total.
26·66	4·69	1·36	1·73	0·16	1·04	0·28	0·35	0·96	99·55

The ratio of meta-columbates to meta-titanates is here 1 : 1, whilst in the Norwegian mineral this is 1 : 2 and 1 : 4. L. J. S.

Nephrite from the Harz. J. Uhlig (*Jahrb. Min.*, 1910, ii, 80—103).—Small veins, the largest of them 20 cm. in thickness, of nephrite occur in the gabbro-serpentine rocks of the Radauthal, near Harzburg. The material is pale green, greyish-green, or light grey, but of a darker green colour (due to enclosed chlorite) in a few strings. Under the microscope it is seen to consist of a felted mass of actinolite needles with occasional chlorite. At times, however, the actinolite fibres have a parallel arrangement, giving rise to a finely fibrous texture; this ("Fasernephrit") is the material recently described from the same locality under the name nephritoid (J. Fromme, Abstr., 1910, ii, 314). Analysis I, of light grey material, corresponds approximately with the actinolite formula $Mg_3Ca(SiO_3)_4$:

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	Cr_2O_3.	FeO.	NiO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O (125°).	H_2O (Ign.)	Total.	Sp. gr.
I.	56·51	0·02	1·80	—	trace	4·38	0·03	0·06	12·72	21·32	—	—	0·28	2·70	99·82	2·94
II.	49·17	0·11	6·52	0·59	—	7·07	0·07	0·80	22·91	10·14	0·08	0·30	0·43	2·10	100·29	3·30

Another small vein of much the same appearance consists of a compact felted mass of pyroxene needles and scales, together with some prehnite and garnet. This pyroxene gave analysis II, agreeing approximately with the diopside formula $Ca(Mg,Fe)(SiO_3)_2$.

L. J. S.

Zeolites from Nadap, Hungary. Béla Mauritz (*Zeitsch. Kryst. Min.*, 1910, **48**, 439—441; from *Földtani Közlöny*, 1908, **38**, 190, 231, and *Ann. hist.-natur. Musei Nation. Hungarici*, 1908, **6**, 537—545, 546—554).—Cavities and crevices in weathered andesite in the neighbourhood of Nadap, comitat Fejér, contain the crystallised zeolites, epistilbite (not before recorded from Hungary), heulandite, chabazite, and stilbite, together with calcite, amethyst, iron-pyrites, and fluor-spar. Crystallographic descriptions are given of each of these zeolites, and analyses of the heulandite (I and II) and stilbite III and IV):

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	SrO.	Na_2O.	K_2O.	Li_2O.	H_2O.	Total.
I.	56·57	16·93	—	6·91	0·93	1·68	1·25	trace	16·15	100·42
II.	56·71	17·30	—	7·05	0·88	1·80	1·37	trace	15·87	100·98
III.	55·79	17·05	trace	7·82	—	1·46	0·20	—	18·65	100·97
IV.	55·78	16·70	trace	7·86	—	1·56	0·26	—	18·79	100·95

L. J. S.

Analyses of Hungarian Minerals. Alexander von Kalecsinszky (*Zeitsch. Kryst. Min.*, 1910, **48**, 446—447; from *Jahresber. k. ungarisch. geol. Anstalt,* for 1907, 1909, 294—314).—A report on the work of the chemical laboratory of the Hungarian Geological Survey includes many analyses of limestones, coals, and clays, and the following analyses (I) of kaolinite from Kovászó, and (II) of magnesite from Jolsva:

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Moisture.	Loss on ignition.	Total.
I.	48·71	35·16	1·10	0·34	1·26	3·15	10·37	100·09

	$MgCO_3$.	$CaCO_3$.	FeO.	H_2O.	Insol.	Total.
II.	72·25	25·43	2·01	0·34	0·26	100·29

L. J. S.

Behaviour of Gabbro Magma in Fusions. Hans Andesner (*Jahrb. Min.*, 1910, *Beil.-Bd.*, **30**, 467—494).—Hornblendite from Kals, Tyrol, was used in the experiments; this is a schistose rock composed largely of hornblende, together with some zoisite, quartz, rutile, and apatite, and having practically the same bulk composition as a gabbro. When fused alone the glassy product has much the characters of a basalt, and under the microscope shows crystals of magnetite, plagioclase, and augite. In other experiments, the amphibolite was fused with various proportions of olivine, quartz, tungstic acid, nephelite, alumina, or anorthite. The microscopical structure of the products are described in detail. The minerals formed include magnetite, plagioclase, olivine, augite, nephelite, spinel (picotite), and corundum; the last two of these being produced when an excess of alumina is present. L. J. S.

Meteorites. Walter Andre Wahl (*Zeitsch. anorg. Chem.*, 1910, **69**, 52—96).—An analytical comparison of meteoric stones and minerals with terrestrial rocks and minerals shows that the former are distinguished by containing a relatively larger proportion of oxygen. The different classes of siderolites differ principally in their state of oxidation; thus, those containing only metallic iron and olivine may be derived from those containing iron, pyroxene, and olivine by oxidation, a part of the iron being oxidised to ferrous oxide and then converting the metasilicate into an orthosilicate:

$$Fe_n + a(Fe,Mg)SiO_3 + b(Fe,Mg)_2SiO_4 + O_m = Fe_{n-m} + (a+b)(Fe,Mg)_2SiO_4.$$

When still less oxygen is present, silica is found in the form of tridymite. The difference between enstatite-chondrites and ordinary chondrites is also shown to be one of the degree of oxidation. The presence of calcium sulphide in certain meteorites is explained in the same way.

Chondrites of loose structure are to be regarded as fragmentary, of the nature of tuffs. The various forms of chondrulitic structure may be explained by the breaking up of a silicate magma into spray in a hot atmosphere and the crystallisation of the drops from outside inwards. The consolidation of the tuffs is brought about by heat, and may be imitated artificially. The structure of the original mass is represented by eucrite. Explanations are given of the other derived structures, including veins and breccias. C. H. D.

Meteoric Stone of Mern, Seeland. ARISTIDES BREZINA (*Jahrb. Min.*, 1910, ii, Ref. 207—208; from *Danske Vidensk. Selsk. Skrifter*, 1909, [vii], 6, (3), 113—125).—This stone fell on August 22nd, 1878, at Mern, near Praesto, in Seeland. Its original weight was 7½ pounds. It is described as the representative of a new type, "veined crystalline enstatite-spheroidal-chondrite." The constituents are olivine, rhombic pyroxene, clinoenstatite, nickel-iron, troilite, and chromite. The chemical composition is:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	K_2O.	Na_2O.	H_2O.	CO_2.	S.	Fe.
39·81	2·70	12·23	15·46	0·46	1·35	0·06	2·47	2·47	13·00

The iron is in part present as sulphide, and of the sulphur, 2·38% is liberated as hydrogen sulphide when the material is treated with hydrochloric acid. 45·20% is insoluble in hydrochloric acid. Traces of phosphoric acid and manganese are present. L. J. S.

Physiological Chemistry.

Putting into Action of the Human Machine. JULES AMAR (*Compt. rend.*, 1910, **151**, 892—894).—A subject set to do muscular work immediately on rising from sleep showed a sudden temporary diminution in his respiratory quotient. This reached a minimum at 0·82 after four minutes from the commencement of the experiment; after four minutes' rest it had risen to 0·99, but at the end of four minutes' further exertion it fell to 0·86. W. O. W.

The Question of the Oxidation of the Products of Zymin Fermentation during Respiration. LEONID IWANOFF (*Biochem. Zeitsch.*, 1910, **29**, 347—349).—Polemical in reply to Kostytschew (Abstr., 1910, ii, 148). W. J. Y.

The Isoelectric Constants of the Constituents of Blood-corpuscles, and their Relationship to Hæmolysis by Acids. LEONOR MICHAELIS and DENGO TAKAHASTU (*Biochem Zeitsch.*, 1910, **29**, 439—452).—The methods employed were those repeatedly used by

Michaelis and his collaborators in the previous investigations on proteins, namely, the determinations of the hydrogen ion concentration in which coagulation most readily takes place, and the method of electrical cataphoresis. They also determined the hydrogen ion concentration in which hæmolysis takes place. The coagulation optimum for the stroma substance of all the species of blood investigated was $[H^{\cdot}] = 1 \cdot 10^{-5}$. The isoelectric constant of oxyhæmoglobin is $[H^{\cdot}] = 1 \cdot 8 \times 10^{-7}$. Red blood-corpuscles in isotonic solution remain intact, when $[H^{\cdot}] = 1 \cdot 10^{-5}$. On further addition of acids, hæmolysis takes place. On the assumption that the coagulation optimum concentration of hydrogen ions represents the isoelectric point, the conclusion is drawn that the hæmoglobin is only held intact in the corpuscles when they are negatively charged. S. B. S.

Influence of Electrolytes and Non-electrolytes on the Permeability of Red-Blood Corpuscles. Miroslav Miculicich (*Zentr. Physiol.*, 1910, 24, 523—527).—The effect was ascertained of the separate addition of a number of salts and non-electrolytes on the time of complete hæmolysis of defibrinated ox-blood by urethane, alcohol, and saponin. The substances were added in such a concentration that the resulting mixtures were isotonic with 0·97% sodium chloride. By employing different salts of the same base, the anions were arranged into a comparative group for each hæmolysin, in order of the length of time required for hæmolysis. In a similar manner by using different salts of the same acid, the cations were arranged into a similar group. It was found that with very few exceptions the order of grouping of both anions and cations was the same for urethane and alcohol, but differed markedly in the case of saponin. This is explained by the fact that saponin brings about hæmolysis in a different manner from the other two. The differences in the times of hæmolysis observed with the various salts is attributed to the different influence of the electrolytes on the permeability of the blood-cells to the hæmolysin. Differences were also obtained in the cases of non-electrolytes. W. J. Y

Permeability of Red Corpuscles in Physiological Conditions, especially to Alkali and Alkali-earths. G. Gryns (*Proc. K. Akad. Wetensch. Amsterdam,* 1910, 489—491).—Hamburger's data and conclusions (Abstr., 1910, ii, 1080) on this subject are questioned. W. D. H.

The Influence of Oxidation in Living Cells according to Researches on the Red Corpuscles. Otto Warburg (*Zeitsch. physiol. Chem.*, 1910, 69, 452—462).—Experiments on the red corpuscles of the goose suspended in Locke's solution confirm the views of Overton and H. Meyer on the importance of the lipoid membrane in oxidation and narcosis. The general result of the action of various reagents, the solubilities of which in water and oil are given, is that the occurrence of a lipoid phase influences chemical changes which diminish oxidation more than the occurrence of a watery phase. W. D. H.

Hæmolysis by Ammonia, Sodium Hydroxide, and Sodium Carbonate. OSCAR GROS (*Biochem. Zeitsch.*, 1910, **29**, 350—366).—The relationship between the concentration of the ammonia and carbonate, and the time necessary for complete hydrolysis can be represented by the equation $c^m.t = k$ (where c = concentration, t = time, k = constant), in which the exponent m varies between 0·65 and 0·71. The ammonia or carbonate appears to be adsorbed by the corpuscle, and the amount adsorbed regulates the rate of hydrolysis. This relationship only holds so long as the amount of ammonia present is large compared with that used in hæmolysis or by-reactions. When small quantities of ammonia are employed, so that the time necessary for complete hæmolysis is large, nearly all the ammonia is adsorbed, and the rate of hæmolysis is proportional to the amount of ammonia, and inversely proportional to the concentration of blood-corpuscles. In the case of sodium hydroxide, the reaction equation is $C^{1 3}.t = k$. It was only possible to investigate this reaction in low concentrations.

S. B. S.

A Proof of the Presence of Toxic Substances in the Blood of Animals after Thyroidectomy. PAUL TRENDELENBURG (*Biochem. Zeitsch.*, 1910, **29**, 396—407).—It has been shown by Reid Hunt (Abstr., 1905, ii, 847) that mice which have been fed on thyroid gland or on blood from cases of Basedow's disease (exophthalmic goitre) are able to withstand injections of acetonitrile many times as large as the amount required to kill normal mice.

A similar resistance is now obtained by feeding mice on the blood of cats from which the thyroid gland has been removed. The conclusion is drawn that this is due to the presence of toxic substances in the blood of the cats, and thus adds support to the hypothesis that the thyroid gland functions as a remover of these poisons. W. J. Y.

The Behaviour of Chlorine in Serum. PETER RONA (*Biochem. Zeitsch.*, 1910, **29**, 501—508).—The author has employed the method originally used by him for investigating the state of sugar in the blood. He has placed serum in dialysing membranes and surrounded them with salt solutions of varying concentrations, and thereby found a concentration which does not alter on dialysis. This concentration corresponds with the amount of free sodium chloride in the serum. From the results the conclusion is drawn that the whole of the chloride in serum is free, and not united to the protein. Nevertheless, the chlorine in the serum directly determined was less than that found by the dialysis method. The difference, although small, was appreciable, and the author ascribes it to the fact that the real concentration of chloride in the serum is greater than the apparent, owing to the fact that the proteins occupy a definite volume in the serum. S. B. S.

The Origin of the Hydrochloric Acid in the Gastric Tubules. MABEL P. FITZGERALD (*Proc. Roy. Soc.*, 1910, *B*, **83**, 56—93).—An historical account is given of the various micro-chemical tests which have been employed by many workers in order to locate the seat of formation of the hydrochloric acid of the gastric juice.

Although evidence connects this origin with the parietal cells of the gastric tubules, hitherto no certainty of this has been attained, neither has it been proved that hydrochloric acid exists in a demonstrable form in the secretion of the glands before this reaches the free surface of the mucosa.

Solutions containing potassium ferrocyanide 1·5% and ammonium ferric citrate 2·25% were injected into rabbits and guinea-pigs, and the animals killed from three to thirty hours after the first injection. This mixture readily formed Prussian blue with hydrochloric acid of a much less concentration than that contained in the gastric juice, but gave no reaction with sodium phosphate or carbon dioxide. Microscopical sections from the stomach showed the presence of Prussian blue in the lumina of the gland tubules, and in the canaliculi in the parietal cells. Hydrochloric acid was thus shown to be already in the free state in the secretion, as it appears in the canaliculi. No definite evidence was obtained of the occurrence of free hydrochloric acid in the cytoplasm of the parietal cells, although a faint blue coloration occasionally observed in them seemed to indicate its presence. The source of the hydrochloric acid in the parietal cells is attributed to the chlorides, which were shown to be present in greater abundance than in the chief cells or the adjacent tissue elements. W. J. Y.

Oxalic Acid Metabolism. Julius Pohl (*Zeitsch. exp. Path.*, 1910, **8**, 308—311).—The contention of Tomaszewski (Abstr., 1910, ii, 425) that oxalic acid is oxidised by the animal organism is denied. Oxalic acid which was injected into dogs was recovered unchanged from the urine, whilst oxalic acid was not destroyed by incubation with a paste made by grinding the liver of a rabbit.

Parabanic acid was injected into a dog, and was subsequently found in the urine partly unchanged and partly changed into oxalic acid. The two acids were estimated as follows: a portion of the urine was boiled with ammonia to convert the parabanic acid into oxalic acid, and the total amount of the latter determined as calcium salt. Another portion was precipitated with normal lead acetate to remove the oxalic acid, and the parabanic acid in the filtrate converted into oxalic acid with ammonia and determined as such.

It is suggested that parabanic acid is possibly a source of the oxalic acid normally found in the animal organism, and that at an intermediate stage oxaluric acid is formed. W. J. Y.

Protein Metabolism of the Dog, and the Effect of Feeding with Protein and Protein Cleavage Products on the Secretion of Bile, with Special Reference to Time Relationships. Adam Loeb (*Zeitsch. Biol.*, 1910, **55**, 167—235).—The quantity of bile depends on the quantity and kind of protein administered; casein and gliadin are less effective than flesh. It therefore appears that it is not formation of urea, but its work in dealing with the nitrogen-free residue, that causes in the liver the increase of bile formation. Peptone increases bile formation. The excretion of sulphur in the bile is in the first four hours after a meal about twice as great as in the next four hours. The excretion of ammonia in the urine falls after a meal, and is at the maximum in the night. This depends on changes in the alkalinity of the body which accompany the secretion of digestive juices. In the period of digestion, also, relatively more acid equivalents in the form of sulphates and phosphates are excreted than in the period of rest. The fixed alkali behaves in the same way. The flow of bile somewhat elevates excretion of ammonia; in abundant protein feeding, ammonia is excreted in absolutely higher, but relatively lower, amount. After feeding there is a decrease in the excretion of phosphates. On a protein-rich diet, a greater amount of the nitrogen is excreted in the first third of the day than on a protein-poor diet; the same is true for protein cleavage products. In a dog with a biliary fistula, nitrogenous equilibrium and even retention can be maintained on abiuretic protein products, provided the nitrogen given is above the protein minimum. The excretion of "neutral sulphur" in such a dog is higher during the digestive period than during rest, but the relationship of this to the sulphur in the food was not determined. The output of sulphates on a protein-rich diet is most marked during the digestive period, and this increase appears more rapidly than that of nitrogen excretion.

W. D. H.

Digestion and Absorption of Nucleic Acid in the Alimentary Canal. E. S. London and Alfred Schittenhelm (*Zeitsch. physiol. Chem.*, 1910, **70**, 10—18).—Previous work on this question has mainly consisted of investigations *in vitro*. The present experiments were carried out *in vivo* in dogs with fistulæ. Nucleic acid is neither altered nor absorbed in the stomach, but chemical changes occur in the intestine; a small amount of purine bases is liberated, but the greater part of the nucleic acid is split into dialysable compounds, which contain organically-united purine substances. Following Levene's work these are nucleosides or nucleotides, but they were not identified more closely. The absorption of such compounds occurs in the lower jejunum and ileum. The digestive juices contain no purine bases on a purine-free diet. W. D. H.

The Inhibition by Cholesterol of the Irritating Action of Oleic Acid. F. W. Lamb (*J. Path. Bact.*, 1910, **15**, 129).—In a study of the absorption of triolein and oleic acid in the frog's intestine, the investigation was complicated by the irritating effect of these substances; this may be obviated by mixing oleic acid with an equimolecular amount of cholesterol. Powell White obtained similar results on subcutaneous injection of the same substances.

W. D. H.

The Action of Drugs on the Cerebral Vessels. Walter E. Dixon and William D. Halliburton (*Quart. J. exp. Physiol.*, 1910, **3**, 315—318).—The experiments were performed on the carefully isolated brains of dogs; these were perfused with Ringer's solution at constant pressure, and the rate of outflow noted by a drop record. The cerebral blood vessels respond towards drugs in the manner similar to the pulmonary and coronary vessels. Adrenaline, pilocarpine, and muscarine, drugs well recognised as acting on nerve-endings, cause some dilatation, although they always produce marked constriction of systemic vessels. It is probable that the dilator action is confined to the larger blood vessels, and it is suggested that the action is due to an effect on vaso-dilator nerves. Barium, lead, veratrine, and pituitary extract cause some constriction, the inference being that these drugs here, as elsewhere, act directly on muscle. The constriction with pituitary extract is slight and transient, and is followed by dilatation. W. D. H.

The Synthetic Formation of Amino-acids in the Liver. GUSTAV EMBDEN and ERNST SCHMITZ (*Biochem. Zeitsch.*, 1910, **29**, 423—428).—On perfusion of a glycogen-poor liver with *p*-hydroxyphenylpyruvic acid, tyrosine could be isolated in the form of the dinaphthalenesulphonyl derivative, and, after perfusion of *p*-phenylpyruvic acid, phenylalanine could be isolated in the form of a carbamic acid. Leucic acid on perfusion gave rise apparently to leucinecarbamic acid. Furthermore, by simple perfusion of a glycogen-rich liver, part of the glycogen appears to give rise to alanine; lactic acid and pyruvic acid being apparently formed as intermediate products.

S. B. S.

A Synthesis with Acetic Acid in the Artificially Perfused Liver. OTTO NEUBAUER and OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1910, **70**, 1—9).—In the artificially perfused dog's liver, if the liquid contains *dl*-aminophenylacetic acid, there is formed *d*-acetylaminophenylacetic acid in addition to phenylglyoxylic and *l*-mandelic acids.

W. D. H.

Probable Function of Cholesterol in the Production of Uric Acid in the Animal Organism. F. TRAETTA-MOSCA and F. APOLLONI (*Gazzetta*, 1910, **40**, ii, 368—377. Compare following abstract).—When a mixture of calf's liver and cholesterol or phytosterol to which a little ammonia has been added is incubated in presence of toluene for two days, uric acid is formed. Neither the liver alone, nor cholesterol, nor putrefying liver yields any uric acid in these circumstances. When the liver has been boiled, no production of uric acid from the mixture can be observed. The authors suppose that by oxidation of the cholesterol, α-hydroxy*iso*butyric 'acid is formed, and that this combines with 2 molecules of urea to produce uric acid. The reaction is effected by ferments contained in the liver.

R. V. S.

Importance of α-Hydroxy*iso*butyric Acid in the Formation of Uric Acid from Cholesterol by means of Calf's Liver. F. TRAETTA-MOSCA and GOLDA MIZZENMACHER (*Gazzetta*, 1910, **40**, ii, 378—388. Compare preceding abstract).—In confirmation of the hypothesis that α-hydroxy*iso*butyric acid is formed as an intermediate product when uric acid is producted from cholesterol and calf's liver in presence of ammonia, the authors find that when α-hydroxy*iso*butyric acid is mixed with calf's liver, physiological saline solution, and ammonia, and the mixture incubated for two days in presence of toluene and chloroform, uric acid is produced. The reaction proceeds better in an atmosphere of carbon dioxide than in air. When no hydroxy*iso*butyric acid is added, smaller quantities of uric acid are formed. Urea added to the mixture does not increase the amount of uric acid produced. The ammonia seems to play a leading part in the reaction. When the liver has been previously boiled, no uric acid is formed. The addition of glycerol, sodium butyrate, or fermentation lactic acid instead of hydroxy*iso*butyric acid does not lead to an increased formation of uric acid. The estimations of uric acid were effected by the Ludwig-Salkowski method. R. V. S.

Differentiation of the Tryptic and Proteolytic (Autolytic) Actions of the Liver. FRIEDRICH SIMON (*Zeitsch. physiol. Chem.*, 1910, **70**, 65—84).—The course of digestion of various proteins under the influence of trypsin and the autolytic enzyme of the liver are compared; the points to which special attention is paid are the amounts of coagulable nitrogen, uncoagulable nitrogen, and ammonia at various stages. The two enzymes manifest differences, the principal one being that the digestion of the insoluble protein goes on longer in autolytic than in pancreatic digestion, and there is also, perhaps, a temporary activity of synthetic processes noticeable in the former case. W. D. H.

The Influence by Salt Ions of Autolysis. LEO BRÜLL (*Biochem. Zeitsch.*, 1910, **29**, 408—413).—In concentrations of *N*/10, the chlorides of the alkaline earths increase the autolysis more than do the salts of the alkalis in the same relative concentration. The action of calcium chloride is more marked than that of the other chlorides of the alkaline earths. Loeb's solution does not increase the rate of action. S. B. S.

The Stimulating Action of Lipoids on the Action of Liver Diastase. EUGENIO CENTANNI (*Biochem. Zeitsch.*, 1910, **29**, 389—394).—Lipoids of egg-yolk, blood, intestine, etc., increase the rate of action of the natural liver diastase from which lipoids had been removed by ether. The lipoids of yeast exerted no action. The lipoids of the liver itself also increased the action. The activating action is not due to the reaction, or to dialysable constituents, and the activating substance is not destroyed by prolonged boiling. The dialysable lipoid substances are, however, also capable of reactivating the diastase of the parenchyma which had been extracted with ether. S. B. S.

Glycolysis. The Oxidative Destruction of Sugar by the Action of Organic Preparations. WALTHER LÖB and GEORG PULVERMACHER (*Biochem. Zeitsch.*, 1910, **29**, 316—346).—The organic preparation which stimulated the oxidative destruction of sugar, either by hydrogen peroxide or oxygen, was prepared by precipitating the alcoholic extract of pancreas with iron salts (ferric or ferrous), It was thought, from the experiments of Minkowski and Cohnheim, that the secretion by the pancreas was an active agent in stimulating the peroxydase of the iron containing blood-pigment; hence the employment of the preparation mentioned. Its action was studied in some detail under varying conditions. Pepsin and pancreatin digestion do not destroy the oxidative properties. It is not entirely stable to heat, although different preparations vary in this respect. Amongst the sugar products isolated were formaldehyde (very small quantities), small amounts of carbon dioxide, and also formic acid and polyhydroxy-acids. Pentose was also found in relatively large quantities. It has not yet been determined whether similar preparations other than those derived from the pancreas exert a like action.

S. B. S.

Physiology of Glands. XVI. The Internal Secretion of the Thyroid and its Formation under the Influence of Nerve-Stimulation. LEON ASHER and MARTIN FLACK (*Zeitsch. Biol.*, 1910, **55**, 83—166).—The internal secretion of the thyroid increases the excitability of the depressor nerve, and the activity of adrenaline in raising arterial pressure. The secretory nerves of the thyroid are contained in the laryngeal (especially the superior) nerve. If these nerves are stimulated, the depressor nerve action and the action of adrenaline are increased. Removal of the thyroid abolishes the effect. Injection of iodothyrin does not produce these results, but injection of thyroid extract does; thyroid extract contains other active substances. The great elevation of blood pressure produced by a combination of an excitation of the thyroid's secretory nerves and an injection of adrenaline does not occur when the depressor nerves are cut. The secretion of the thyroid and injection of thyroid extract have in themselves no effect on pulse or blood-pressure. The bearing of these observations on Basedow's disease is discussed.

W. D. H.

The Inhibition of the Action of Chemical Muscle-stimuli by Non-electrolytes. VELYEN E. HENDERSON (*Zentr. Physiol.*, 1910, **24**, 519—523).—Non-electrolytes, such as dextrose, sucrose, and mannitol, in the presence of sodium salts were found to inhibit the exciting action of guanidine and oxalic acid on muscle. Moreover, the convulsions of the muscle produced in a mixture of the stimulant and sodium chloride ceased on the addition of the non-electrolytes. The same results were obtained when Ringer's solution was employed in place of sodium chloride. The action is attributed to an exosmosis of the active ions in the presence of the non-electrolyte. W. J. Y.

The Inhibitory Influence of Magnesium on the Direct Excitability of Frog's Muscle, and the Antagonistic Effects of Sodium and Calcium on this Influence. DON R. JOSEPH and SAMUEL J. MELTZER (*Chem Zentr.*, 1910, ii, 237; from *Zentr. Physiol.*, 1910, **24**, 7—8).—Solutions of magnesium sulphate diminish the direct and indirect excitability of frog's muscles to induction shocks. Sodium restores the direct, and calcium after or together with sodium restores the indirect excitability. If the magnesium salt is injected into the lymph sac, the sodium of the lymph prevents the inhibition of the direct excitability, and the simultaneous injection of calcium chloride restores the indirect excitability. W. D. H.

The Influence of Different Substances on the Gaseous Exchange of the Surviving Muscular Tissue of Frog's. IV.—IX. TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1910, **24**, 23—61, 62—71, 72—74, 75—79, 80—85, 86—89. Compare Abstr., 1910, ii, 54, 523).—The investigations were conducted on the lines of the author's previous work. Thirty-eight organic acids were investigated; although many lessen the gaseous exchange, none act in the specific way, namely, by lessening the output of carbon dioxide, which was previously found to be the result of oxalic, malonic, and succinic acids. Succinic acid produces the most marked effect. Various narcotics and antiseptics lessen the gaseous exchange in varying degrees without altering the respiratory quotient; among the antiseptics, phenol has the greatest, and boric acid the least, effect. Fumaric, malic, and citric acids in very small concentrations increase the amount of anoxybiotic carbon dioxide products; the question arises whether specific enzymes are responsible for their production. Potassium fluoride lessens the gaseous exchange, and, like the organic acids, specially affects the substances that yield carbon dioxide; potassium chloride, bromide and iodide are indifferent substances in this relation. Potassium chlorate has no effect, but the bromate, and especially the iodate, are toxic to muscle. The bromine compounds of succinic, fumaric, and maleic acids act like the dicarboxylic acids in raising the respiratory quotient; in the metabolism of muscle, these acids probably enter the muscle substance. W. D. H.

The Chemical Conditions Necessary for the Maintenance of the Normal Cell Structure. I. and II. ERIK MATTEO PROCHET WIDMARK (*Skand. Archiv. Physiol.*, 1910, **23**, 421—429; **24**, 13, 22). —I. Weighed portions of muscular tissue from frogs, finely minced, were allowed to soak in isotonic saline solutions to which varying quantities of solutions of calcium, strontium, barium, and magnesium chlorides were added. The loss of weight undergone by the tissue owing to this treatment was estimated. In the case of calcium chloride, the tissue undergoes its maximal loss of weight (37%) when the calcium chloride attains the concentration of 15 millimols. per litre. Similar results were obtained with barium and strontium chlorides, but the action of magnesium chloride is very much less marked.

II. To account for shrinking of the cell after treatment with calcium salts, it is suggested that the calcium precipitates the phosphates in the interior of the cell. No evidence of this hypothesis could, however, be obtained experimentally, as muscular tissue, from which the greater part of the phosphorus had been removed by washing with isotonic saline solution, also showed loss of weight on treatment with calcium salts. Furthermore, if citrates are added in addition to the calcium salts to prevent precipitation of phosphate, loss of weight also took place. S. B. S.

The Reducing Action of the Tissues. Walter Strassner (*Biochem. Zeitsch.*, 1910, **29**, 295—310).—The author has measured the reducing action of tissues on methylene-blue, using the method of Knecht and Hibbert (titanium chloride method) for estimating the dye. The author draws the conclusion that the reducing action is due to the sulphhydryl group in the tissues, in spite of the facts that heating, autolysis, and hydrocyanic acid diminish the reducing action. He shows, however, that hydrocyanic acid also diminishes the reducing action of thiolacetic acid, and suggests that autoxidation or heating may destroy the sulphhydryl group. Starvation, phosphorus poisoning, and other actions which produce fatty tissues diminish the reducing capacity of the tissues, which is unaffected, however, by poisoning with mercuric chloride, chloral hydrate, and other drugs.

S. B. S.

The Staining of Fat by Nile-blue Sulphate. J. Lorrain Smith (*J. Path. Bact*, 1910, **15**, 53—55).—When the fat in the human tissues is neutral, Nile-blue sulphate colours it red; but if the fat contains much fatty acid, the globules take a colour compounded of blue and red in variable proportions. The blue staining of the fatty acid is due to the union of the colour base (oxazine) with the acid in the form of a soap-like compound. As a rule, lipoids contain fat in a neutral form, but hydrolysis readily occurs, and so blue staining may be obtained. The red substance, as Thorpe showed (Trans., 1907, **93**, 324), is not present in the Nile-blue sulphate in dry powder, but it appears in aqueous solutions of the dye, because the oxazine base spontaneously oxidises into oxazone; in the same way, it imparts a red colour to liquid neutral fat. Some confusion has arisen in the work of recent investigators, as they have regarded the oxazine base and the oxazone as the same thing, and in accordance with this assumption they have applied to the double staining of fat the theory of metachromatism by the base set free in aqueous solution by hydrolytic dissociation. Such conclusions are unwarranted.

W. D. H.

The Resorption of Cholesterol and Cholesteryl Esters. H. A. Klein and Adolf Magnus-Levy (*Biochem. Zeitsch.*, 1910, **29**, 465—471).—The authors investigated the amount of cholesterol in the fæces of a dog on a fixed diet to which were added cholesterol and cholesteryl oleate. It was found that a somewhat larger proportion of the former was resorbed than of the latter. Various data are given as to the amount of cholesterol in eggs, butter, brain, and other substances, and the suggestion is made that the synthesis of cholesterol in the animal body can be investigated by estimating the amount formed in fowl's eggs when the birds are kept on diets containing varying amounts of cholesterol. S. B. S.

The Occurrence of Deoxycholic Acid in Gall Stones. William Küster (*Zeitsch. physiol. Chem.*, 1910, **69**, 463—465).—The occurrence of deoxycholic acid in the gall stones of oxen was regarded as probable, seeing that it is so easily derived from cholic acid by reduction. Evidence is adduced to show that this is the case. W. D. H.

The Alteration in the Excretion of Amino-acids or Substances Titratable with Formaldehyde as a Cause of the Increase in the Cal. : N Ratio after Great Loss of Blood. DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1910, 69, 482—490).—The amount of amino-acid nitrogen in the urine (dog and rabbit) is increased by great loss of blood, both absolutely and relatively to the total nitrogen. The condition does not again become normal until three weeks later. A second bleeding produces a still more marked effect. There is no special effect on ammonia excretion. The increase in the Cal. : N ratio (energy quotient) is, in part at least, due to the rise of amino-acid excretion. W. D. H.

The Influence of Prolonged Inanition on the Excretion of Amino-acids or Substances Titratable with Formaldehyde. DIONYS FUCHS (*Zeitsch. physiol. Chem.*, 1910, 69, 491—495).—In the later stages of inanition the amount of amino-acid nitrogen in the urine rises absolutely, but not relatively, to the total nitrogen; the ante-mortem rise of total nitrogen is therefore not to be attributed to the increased excretion of amino-acids. Lactic acid and other fatty acids increase at this stage, and ammonia usually falls. W. D. H.

A Yellow Substance in the Urine. L. DE JAGER (*Zeitsch. physiol. Chem.*, 1910, 70, 60—64).—A yellow precipitate is produced in the urine by the addition of hydrochloric acid and formaldehyde. It contains neither urobilin nor urochrome, but appears to be a compound of urea. W. D. H.

The Detection and Formation of Aromatic Substances in the Body. II. The Behaviour of Indole and Scatole in Rabbits. FERDINAND BLUMENTHAL and ERNST JACOBY (*Biochem. Zeitsch.*, 1910, 29, 472—487).—To account for the presence of indole in the urine of starving rabbits, which has been assigned, amongst other causes, to hæmorrhage, to delay of fæces in the intestine during starvation, and consequent putrefaction, etc., the authors have tested the contents of the intestines of rabbits when fed and during starvation. They find that the tests with ether or benzol extracts of fæces are untrustworthy, probably owing to extraction of urobilinogen and other causes, but that satisfactory results are obtained with the Ehrlich, vanillin, and heliotropin reactions with the aqueous distillates from fæces. In the case of fasting animals, the contents of the large, but not of the small, intestine contain indole, and in the case of fed animals the latter also sometimes contains phenol. After injection of indole and scatole, indole substances are found in the contents of the alimentary tract. In view of Jaffe's investigations on the supposed indole-3-carboxylic acid in normal urines, the urines of fed and starving rabbits were also investigated, and indole-yielding substances (obtained on distillation of the urine) were found in the urine of both, but more especially in those urines in which the indican reaction was positive.
S. B. S.

The Oxydase Reaction in Myeloid Tissues. JOHN SHAW DUNN (*J. Path. Bact.*, 1910, 15, 20—30).—The oxidising property of leucocytes was first pointed out by Vitali in 1887, when he showed that pus added to tincture of guaiacum produces a blue reaction without the addition of hydrogen peroxide; this property is destroyed by heat. The precipitate obtained by adding alcohol to a chloroform extract of pus has the same power, so also have organs rich in granular leucocytes, such as bone-marrow, but not purely lymphocytic organs like lymph glands or thymus (Brandenburg). The blood in myelogenous leucæmia has the same property, and as it belongs only to granular leucocytes, the reaction may be used in diagnosis (E. Meyer).

In the present research it is shown that the synthesis of indophenol from *a*-naphthol and *p*-phenylenedimethyldiamine is produced with great rapidity, as shown by the microscopic examination of blood films, by the polynuclear and eosinophile leucocytes, fairly rapidly by hyaline leucocytes, and by the myelocytes of marrow and in leucæmic blood. It is produced less readily by basophile leucocytes, but not by lymphocytes, red corpuscles, or by normal tissue elements, with the exception of parotid and lachrymal gland epithelium. The occurrence of the reaction in large hyaline leucocytes confirms Ehrlich's view that they originate in bone-marrow. The oxidising substance exhibits considerable resistance to heat, and its effects can therefore be observed in most cases in tissues submitted to the paraffin method of imbedding, but it is desirable in the investigation of the more embryonic forms of myeloid cells that unfixed films or sections should be examined also. W. D. H.

The Wassermann Reaction in Rabbits Infected with the Trypanosomes of Nagana, and the Effect of Treatment with Arsenophenylglycine (Ehrlich). CARL H. BROWNING and I. MCKENZIE (*J. Path. Bact.*, 1910, **15**, 127—128).—No safe conclusion as to the action of pathogenic protozoa can be based on the Wassermann reaction in the case of rabbits; for instance, normal rabbits may give a positive reaction. This and other irregularities are fairly common in the lower animals. Arsenophenylglycine is a therapeutic agent of high efficiency in trypanosome infections in rabbits.

W. D. H.

The Behaviour of *p*-Hydroxyphenyl-lactic Acid and *p*-Hydroxyphenylpyruvic Acid in the Animal Body. YASHIRO KOTAKE (*Zeitsch. physiol. Chem.*, 1910, **69**, 409—419).—*l*- and *dl*-*p*-Hydroxyphenyl-lactic acids are almost completely unchanged in the body, and are excreted unchanged in the urine; *p*-hydroxyphenylpyruvic acid is almost completely destroyed. This agrees well with Neubauer's work and views on alcaptonuria. W. D. H.

The Physiological Action of an Ergot base, and of 4-β-Aminoethylglyoxaline. FRIEDRICH KUTSCHER (*Chem. Zentr.*, 1910, ii, 327—328; from *Zentr. Physiol.*, 1910, **24**, 163—165).—The bases precipitable by silver nitrate from extract of ergot are separable into two fractions, one precipitable by ammonia and silver nitrate, the other precipitable by silver nitrate and barium hydroxide. From the first fraction, the picrolonate and the chloride (as hygroscopic crystals) were prepared; this base gives Pauly's diazo-reaction, but not the biuret reaction. It causes lowering of the blood-pressure in rabbits, heart slowing, and stoppage of respiration; a few milligrams are fatal. In this it differs from histidine, which is physiologically inactive, and from 4-β-aminoethylglyoxaline, which causes a rise of blood-pressure, and is much less toxic. W. D. H.

[Poisonous Action of Sodium Chloride on Sea Urchin's Eggs.] Otto Warburg (*Zeitsch. physiol. Chem.*, 1910, **69**, 496—497; *Biochem. Zeitsch.*, 1910, **29**, 414—415).—Polemical in regard to the work of Jacques Loeb and Wasteneys (Abstr., 1910, ii, 1096).
W. D. H.

The Behaviour of Lead Compounds in the Human Stomach. Thomason (*Chem. Zentr.*, 1910, ii, 328—329; from *Sprechsaal*, 1910, **43**, 325—327).—The effect of dilute (0·15 to 0·25%) hydrochloric acid on white lead and lead glaze at body temperature in the presence and absence of foods and pepsin was investigated. The percentage solubility of white lead in the stomach increases with a lessening of the food present; the solubility of lead is inversely proportional to the amount of protein, and directly proportional to the amount of hydrochloric acid present. W. D. H.

Toxicity of Some Inorganic and Organic Arsenic Compounds and Tolerance to these Poisons. L. Launoy (*Compt. rend.*, 1910, **151**, 897—899).—The percentage of arsenic was determined in a number of compounds of the element, and the toxic dose for guinea-pigs found when the substances were administered by injection through the peritoneum. The following list shows the weight of arsenic in grams per kilogram of body-weight required to kill the animal in one to ten days: sodium arsenate, 0·006—0·012; sodium thioarsenate, 0·00875; sodium thiotrioxyarsenate, 0·00991; sodium cacodylate, 0·09125; sodium thiocacodylate, 0·07131; sodium methylarsinate, 0·0254; sodium thiomethylarsinate, 0·0256; atoxyl, 0·0418; thioatoxyl, 0·0221; acetylatoxyl, 0·0461; acetylthioatoxyl, 0·0266; colloidal arsenic, 0·0083.

It was not found possible to establish tolerance to arsenic by prolonged administration of atoxyl in small doses. W. O. W.

Chemistry of Vegetable Physiology and Agriculture.

Biochemistry of Micro-organisms. IV. The Fermentation of Formic Acid by Bacillus Kiliense. HARTWIG FRANZEN and G. GREVE (*Zeitsch. physiol. Chem.*, 1910, 70, 19—59. Compare Abstr., 1910, ii, 799).—Protocols are given in full to illustrate the action of the *Bacillus Kiliense* in the fermentation of formic acid; its activity is compared with that of the bacilli previously investigated.

W. D. H.

New Method for Detecting Reducing and Oxidising Properties of Bacteria. W. H. Schultze (*Centr. Bakt. Par.*, 1910, i, **56**, 544—551).—Reductase-agar is prepared as follows: Concentrated aqueous sodium hydroxide is added drop by drop to 100 c.c. of boiling water containing 1 gram of *a*-naphthol until the latter is dissolved. On cooling, more sodium hydroxide is added until the solution again becomes clear and light brown in colour. The solution is then mixed with a 1% solution of *p*-nitrosodimethylaniline (equal vols.), filtered, and mixed with about two-thirds the volume of ordinary nutritive-agar (liquid) and poured into Petri dishes.

Oxydase-agar is prepared by adding a well-filtered mixture of equal volumes of 1% *a*-naphthol solution (prepared as described above) and 1% *p*-phenylenedimethyldiamine hydrochloride to liquefied nutritive-agar (about 3 parts). As the preparation becomes blue in a few hours, it must always be freshly prepared.

The oxydase-agar may be employed for showing the oxidising action of liquids, such as saliva, etc. N. H. J. M.

Mobilisation of the Phosphoric Acid of Soils under the Influence of Bacteria. S. A. Sewerin (*Centr. Bakt. Par.*, 1910, ii, **28**, 561—580).—The experiments were made with soil (1100 grams) to which finely-ground phosphorite (10 grams) was added. After being sterilised, the soil was inoculated and kept for two months, and the soluble phosphoric acid determined. During the whole time air was passed through the flasks, and the amount of carbon dioxide produced estimated.

As regards the production of soluble phosphoric acid, the results were negative, the amount of readily soluble phosphoric acid being diminished. There was a considerable production of carbon dioxide, ten to twenty times as much as in sterilised soil.

The disappearance of readily soluble phosphoric acid is attributed partly to its assimilation by the bacteria and partly to purely chemical changes. This does not exclude the possibility that a smaller amount of insoluble phosphoric acid may have been rendered soluble.

N. H. J. M.

The Formation of Trimethylamine by Bacterium prodigiosum. D. Ackermann and H. Schutze (*Chem. Zentr.*, 1910, **2**, 756; from *Zentr. Physiol.*, 1910, **24**, 210—211).—Trimethylamine can be obtained from cultures of *B. prodigiosum* grown on potatoes. Its parent substances are choline and lecithin. By the addition of choline or lecithin, the yield of trimethylamine is increased up to twenty-fold. Betaine has no influence. In cultures on peptone-agar, no trimethylamine is formed, but it occurs when choline is added. *B. vulgatus* on potatoes yields no trimethylamine even if choline is added also. W. D. H.

Action of the Bulgarian Ferment on Proteins and Amino-compounds. Jean Effront (*Compt. rend.*, 1910, **151**, 1007—1009).—The Bulgarian ferment contains an enzyme capable of effecting a more profound decomposition of casein than results from the action of pepsin or trypsin. The liberation of ammonia has been demonstrated when the ferment acts on asparagine, milk, or Witte's peptone in presence of calcium carbonate, in the latter case the amount set free corresponding with 40% of the total nitrogen.

In the author's opinion the value of the Bulgarian ferment in the treatment of gastro-intestinal disorders depends on its ability to decompose proteins rather than on the lactic acid it produces.

W. O. W.

Biological Degradation of Carbohydrates. AUGUSTE FERNBACH (*Compt. rend.*, 1910, **151**, 1004—1006).—Starch is readily hydrolysed by *Tyrothrix tenius* whether the micro-organism is present *in vitro* or as a maceration. The successive products are maltose, dextrose, and dihydroxyacetone. When the organism is cultivated in a medium containing glycerol, the triol undergoes oxidation to dihydroxyacetone, methylglyoxal, and two decomposition products of the latter, namely, acetic acid and formaldehyde. These are also met with in the later stages of the hydrolysis of starch and sucrose, and probably arise from the action of bacterial secretions. W. O. W.

The Behaviour of Yeast Gum in Autolysis and in Alcoholic Fermentation. ERNST SALKOWSKI (*Zeit. physiol. Chem.*, 1910, **69**, 466—471).—After autolysis and alcoholic fermentation, yeast still contains much of the gum, but quantitative experiments are not given to determine the amount which disappears. W. D. H.

Chemical Disinfectants. SHERIDAN DELÉPINE (*J. Soc. Chem. Ind.*, 1910, **29**, 1344—1354).—The factors influencing the efficiency of a large number of substances used as disinfectants as regards (1) their power of inhibiting the activity of bacteria, (2) their bactericidal action, are enumerated and discussed.

It is pointed out that certain substances even in minute amounts have the property of arresting the multiplication and other activities of bacteria, and may be called antiseptics, but that the same materials in larger quantities may kill bacteria and are then appropriately named disinfectants. Illustrations are given of substances, such as mercuric chloride, which may act in both ways, time of exposure and concentration of solution, apart from the nature and resisting power of the bacteria, being the chief factors which determine whether the substance is merely inhibitory or lethal. It is well known that different bacteria show different powers of resistance towards disinfectants, and that, in general, the spores of a bacillus are far more resistant both to heat and to bactericidal agents than the bacillus itself, but it is also the case that different individuals in a pure bacillus culture exhibit different powers of resistance. A series of tests with phenol on cultures of *Bacillus coli* showed that younger cultures were more resistant than older ones, although after some time the resistance became almost constant or diminished very slowly. The drying of *Bacillus coli* by exposure to air at 14—18° had little effect on its resistance to phenol until about the seventeenth day, when the resistance began to diminish. The material associated with the bacteria and the disinfectant has an important influence on the efficiency of the latter. It is shown that certain substances, which when present in sufficient quantity act as disinfectants, act as stimulants to the growth of bacteria when present in minute amounts.

T. A. H.

The Importance of the Temperature Factor in the Determination of the Rate of the Activity of Certain Disinfectants. R. R. Fasson, C. W. Ponder, and G. Sims Woodhead (*J. Path. Bact.*, 1910, **15**, 131—133).—The experiments were made with emulsified disinfectants derived from coal-tar (cresols, etc.), as compared with carbolic acid. Dose and time of action are important factors in estimating their activity, but temperature also must be taken into account. At lower temperatures the activity of the emulsion is raised more rapidly than that of the solution, but at the higher temperatures used the activity of the emulsion is no longer increased in proportion to the increase in the activity of the carbolic acid. W. D. H.

The Sterilisation of Chalk Waters by the Use of Minute Quantities of Bleaching Powder. G. Sims Woodhead (*J. Path. Bact.*, 1910, **15**, 130—131).—The activity of bleaching powder in the destruction of bacteria of the *Coli* group is very great, and large quantities are quite unnecessary. The amount of chlorine necessary to kill the whole of the non-sporulating bacilli in Cambridge water is usually one part per seven million parts of water. Various details on the method are added. W. D. H.

The Disinfecting Power of Complex Organo-mercury Compounds. I. Aromatic Mercurycarboxylic Acids. Walther Schrauth and Walter Schoeller (*Zeitsch. Hyg. Infect.*, 1910, **66**, 497—504).—The disinfecting power of a number of derivatives of sodium hydroxy-*o*-mercuribenzoate, $OH{\cdot}Hg{\cdot}C_6H_4{\cdot}CO_2Na$, was compared in order to ascertain the effect of the introduction of various groups on this property. It was found that by substituting the hydroxy-group by groups having a stronger affinity for silver, such as iodine, cyanogen or veronal, the disinfecting power was decreased. With sulphur, it was still further decreased, whilst the power was almost entirely lost in compounds in which both valencies of the mercury were attached to the benzene ring, such as in sodium mercuridibenzoate, $Hg(C_6H_4{\cdot}CO_2Na)_2$. W. J. Y.

The Pentosan Content of Various Fungi. J. L. Wichers and Bernhard Tollens (*J. Landw.*, 1910, **58**, 238—242).—Various fungi growing on wood were examined and found to contain pentosans and, in some cases, methylpentosans. The amount varied from 2·5% in *Trametes odorata* to 6·7% in *Lenzites flaccida*; methylpentosans were found also in *Xylaria polymorpha* and *Fomes fomentarius*. Estimations made at the same time by the quicker method of Böddener and Tollens (see this vol., ii, 75), always gave rather lower results. E. J. R.

Occurrence of Aucubin in Garrya spp. Henri Hérissey and C. Lebas (*J. Pharm. Chim.*, 1910, [vii], **2**, 490—494).—The glucoside aucubin was first isolated from *Aucuba japonica* (Abstr., 1902, i, 634), and has since then been recorded by Bourdier (*Thèse*, Paris, 1908) in *Plantago* spp. In the present investigation, it was isolated, not quite pure and in small amount, from the stem and leaves of *Garrya elliptica*, *G. macrophylla*, and *G. Thureti*. T. A. H.

The Carbohydrates of White Pepper. K. H. Böddener and Bernhard Tollens (*J. Landw.*, 1910, **58**, 229—231).—It has already been shown that white pepper, in addition to its 54% of starch, 1% of ethereal oil, and 4 to 9% of piperin, contains also pentosans and methylpentosans, or at least substances that give furfuraldehyde and methylfurfuraldehyde on distillation with hydrochloric acid. The authors have endeavoured to investigate further these pentosans, but without success. The methods used for separating the piperin and the starch with its transformation products removed also the greater part of the pentosans, so that the amount remaining after the final purification was too small for separation. E. J. R.

The Root of the Kermek (Statice, Plumbaginaceae). G. Povarnin and A. Sekreteff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1024—1034).—The root of the kermek (*Statice Gmelini*) contains tannides 15·70%, sugars 2·03%, soluble substances 30·15%, non-tanning substances 14·45%, water 10·76%, ash 4·23%, resins 0·34%, some amine (probably alkaloids), a trace of gallic acid, possibly some phloroglucinol, and a glucotannide. Kermek and similar tanning roots should be analysed as far as possible without access of air: The tanning substances in the root are readily oxidised, and consist of at least two tannides, red and yellow, which can be distinguished by the differently coloured lead, calcium and barium salts; the tannides also give characteristic reactions with silver and cadmium nitrates, formic acid and concentrated sulphuric and hydrochloric acids. On dry distillation, the tannides yield pyrogallol.

Violuric acid is recommended as a reagent for the detection of basic substances in plants. Z. K.

The Death of Plants at Low Temperatures. A. A. Richter (*Bull. Acad. Sci. St. Petersburg*, 1910, 1251—1260).—*Aspergillus niger* when exposed to very low temperatures ceases to evolve carbon dioxide, and loses all the properties of living protoplasm, neither does it regain these at 18—19°; but it revives rapidly at 30—34°, even if it had previously been frozen at the temperature of a mixture of ether and solid carbon dioxide. Z. K.

Effect of Road Tarring on Vegetation. Marcel Mirande (*Compt. rend.*, 1910, **151**, 949—952. Compare Abstr., 1910, ii, 884).—The vapour of hydrocarbons arising from tar or asphalt exercises an injurious action on vegetation, producing blackening of the leaves, characteristic of death of the protoplasm. The effects observed are not due to actual contact with particles of tar, since these, in common with solid hydrocarbons, such as naphthalene or anthracene, have very little action when applied to plants in the state of fine powder. W. O. W.

Influence of Different Volatile Substances on Higher Vegetation. HENRI COUPIN (*Compt. rend.*, 1910, **151**, 1066—1067).—The author classifies forty-seven aliphatic and aromatic volatile substances into five groups, according to their relative toxicity towards germinating wheat.

The action of the same compound differs in intensity with different plants. The grains are more open to attack at the earlier stages of germination than when the aerial organs have attained development.

W. O. W.

The Presence of Arginine and Histidine in Soils. Pyrimidine Derivatives and Purine Bases in Soils. OSWALD SCHREINER and EDMUND C. SHOREY (*J. Biol. Chem.*, 1910, **8**, 381—384, 385—393).—In soils, the products of cleavage of proteins of vegetable origin can be separated out. Those identified in the present research were arginine and histidine in variable proportions, cytosine, xanthine, hypoxanthine and picolinecarboxylic acid. W. D. H.

Calcium or Sodium Nitrate [as Manure]. PAUL WAGNER *Bied. Zentr.*, 1910, **39**, 729—731; from *Mitt. deut. landw. Ges.*, 1910, St. 8, 107—109).—In field experiments with mangolds, winter rye, and barley, somewhat higher yields were obtained with sodium nitrate than with calcium nitrate, whilst in the case of sugar beet, potatoes, and oats, the yields were rather higher when calcium nitrate was employed. N. H. J. M.

Manurial Action of Ammonium Sulphate in Conjunction with Sodium Chloride. BERNHARD SCHULZE (*Bied. Zentr.*, 1910, **39**, 731—733; from *Mitt. deut. landw. Ges.*, 1910, St. 30, 452—458).—It is shown by field experiments that when sodium chloride is applied along with ammonium sulphate, the manurial value of the ammonium salt becomes about equal to that of sodium nitrate.

N. H. J. M.

Employment of Nitrogenous Manures for Sugar Beet. B. ERBEN, FR. PRACHFELD, and W. VILIKOVSKY (*Bied. Zentr.*, 1910, **39**, 782—783; from *Mitt. landw.-botan. Versuchsstat. Tabor*).—Moderate amounts of sodium nitrate increased the yield of roots, whilst larger amounts only increased leaf production. Calcium nitrate gave almost the same results as sodium nitrate.

Calcium cyanamide only increased the yield slightly, and liquid manure had less effect than sodium nitrate.

In moderate amounts, nitrogenous manures had no, or very slight, injurious effect on the amount of sugar in the roots, and had no effect on the amounts of non-sugars. N. H. J. M.

Analytical Chemistry.

Photochemical Reactions in Laboratory Work. KURT GEBHARD (*Chem. Zeit.*, 1910, **34**, 1269).—The author points out that whilst a slightly acid solution of potassium iodide in starch mucilage remains colourless in the dark, it rapidly becomes coloured in the light, due to liberation of iodine, although in presence of a fourth substance liberation of iodine may occur more rapidly in the dark than in the light. This and observations recorded by others (for example, Gibbs, Abstr., 1909, i, 640, and Batik, 1910, i, 543) indicate that as the result of unsuspected photochemical reactions, errors may often be caused in ordinary laboratory work. T. A. H.

Several Acids Suitable for Use as Standards in Acidimetry. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1910, **44**, 487—493).—*p*-Nitrotoluene-*o*-sulphonic acid (Kastle, this vol., i, 30), and *p*-amino-*o*-sulphobenzoic acid and potassium *o*-nitro-*p*-sulphobenzoate (Hart, Abstr., 1881, 1144) are recommended as standards for use in acidimetry. The last two are anhydrous, and can be thoroughly dried without risk of decomposition. *p*-Nitrotoluene-*o*-sulphonic acid, although crystallising with $2H_2O$, is a definite and very stable compound. All these substances are stable in the air, are not hygroscopic or deliquescent, and give very sharp end-reactions with phenolphthalein. E. G.

Use of Metallic Potassium in Estimating the Halogens in Benzene Derivatives. C. H. MARYOTT (*Amer. J. Sci.*, 1910, [iv], **30**, 378—380).—Stephanoff (Abstr., 1907, ii, 50) proposed to estimate the halogens by treatment with alcohol and metallic sodium. The author did not get satisfactory results, but on substituting potassium for sodium, a complete reduction was effected. About 0·4 gram of the substance is placed in an Erlenmeyer flask, and 10—15 c.c. of alcohol-benzene mixture are added (1 vol. of 98% alcohol with 2 vols. of benzene free from sulphur compounds). About ten times the theoretical amount of potassium is now added gradually in small pieces. When the action slackens, two extra c.c. of alcohol are added, and when the potassium has completely dissolved, the whole is shaken with water. The aqueous layer is then acidified with nitric acid, and the halogen is precipitated with silver nitrate as usual.
L. DE K.

Estimation of Total Sulphur in Urine. W. DENIS (*J. Biol. Chem.*, 1910, **8**, 401—403).—Benedict's method (Abstr., 1909, ii, 827), in which the oxidising agent is a mixture of copper nitrate and sodium or potassium chlorate, was compared with Folin's sodium peroxide method. The former method leads to spattering and loss, due to too rapid evolution of nitrogen oxides. It can be modified, and the spattering avoided by mixing the copper salt solution with sodium chloride and ammonium nitrate; the results then are very near to those obtained by Folin's method. W. D. H.

Benedict's Method of Estimating the Total Sulphur in Urine. CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1910, **8**, 423—425. Compare Abstr., 1910, ii, 827).—Benedict's and Folin's methods gave practically the same results. The presence of sugar makes no difference, but albumin causes the oxidation by Benedict's method to be violent; it makes no difference in Folin's method. W. D. H.

Estimation of Sulphur in Organic Compounds. THEODOR ST. WARUNIS (*Chem. Zeit.*, 1910, **34**, 1285—1286).—0·2—0·4 Gram of the finely powdered substance is mixed in a spacious silver or nickel crucible with 10 grams of powdered pure potassium hydroxide and 5 grams of sodium peroxide by means of a silver wire. After covering the crucible with a lid, the mixture is heated for some fifteen minutes in an air-bath at 75—80°, and then heated over a gradually increased flame until it has melted completely. The mass is then allowed to cool, and dissolved in water, solution of bromine in hydrochloric acid is added, and the liquid filtered and boiled to expel the excess of bromine. In the filtrate, the sulphuric acid is estimated as usual.

A blank experiment should be made to allow for any sulphate present in the reagents or sulphuric acid absorbed from the gas employed. L. DE K.

Estimation of Sulphur and Phosphorus. CHARLES G. L. WOLF and EMIL ÖSTERBERG (*Biochem. Zeitsch.*, 1910, **29**, 429—438).—The authors have investigated various methods for the estimation of sulphur in tissues. They show that satisfactory results can be obtained by preliminary oxidation of the organic matter, and completion of this process by the reagent originally suggested by Benedict containing copper nitrate and potassium chlorate. They show also, that after destruction of the organic matter and precipitation of the sulphate in this way, the phosphorus can be estimated in the filtrate, so that only one sample is necessary for the estimation of both sulphur and phosphorus. S. B. S.

Remarks on the Iodometric Titration of Acids and Kjeldahl's Nitrogen Estimation. R. KOEFOED (*Zeitsch. physiol. Chem.*, 1910, **69**, 421—440).—Correct results are obtained by strictly adhering to the procedure given. The ammoniacal distillate is collected in a flask containing 15 c.c. of *N*-sulphuric acid until the total volume measures 100 c.c. When making the check, 15 c.c. of the acid are diluted up to 100 c.c. with water previously boiled. Ten c.c. of 5% potassium iodide, 2 c.c. of 2% starch solution (saturated with sodium chloride), and, finally, 4 c.c. of 4% potassium iodate are added. The iodine liberated, which represents the free acid, is then titrated with *N*/10-sodium thiosulphate, which operation should occupy just two minutes.

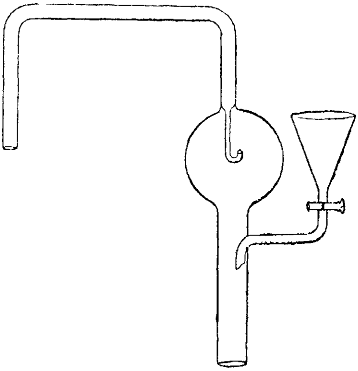
The author has tried the various chemicals from time to time proposed as standards, including glycine and hippuric acid after conversion into ammonium sulphate by Kjeldahl's process. The results which are tabulated, do not differ much, except those with glycine and hippuric acid, which give somewhat higher figures.

In most cases, Kjeldahl's original process (use of potassium permanganate) is recommended; in such cases where there is danger of formation of piperidine rings, the Gunning modification (use of potassium sulphate) is more appropriate. L. DE K.

Error in Estimating Nitrogen in Soil. EILHARD A. MITSCHERLICH and ERNST MERRES (*Chem. Zentr.*, 1910, ii, 495; from *Landw. Jahrb.*, 1910, 39, 345—367).—In soil sampling, a sample should be taken by means of a borer from each square metre; according to the soil, the error will vary from ±4 to 6%. The error due to changes during the drying of soils in the air can be avoided by adding tartaric acid. Soil extracts should be kept under carbon dioxide.

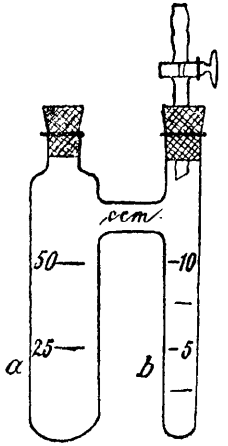
N. H. J. M.

Distillation Arrangement for Ammonia and Nitrogen Estimations. CARL MÜLLER (*Chem. Zeit.*, 1910, 34, 1308).—The apparatus (see figure) is placed on the distilling flask, and the reducing agent and the sodium hydroxide solution are admitted through the funnel. In this manner there is no loss of ammonia to be feared owing to gases given off, as these have to pass through the acid in the receiver. L. DE K.



Folin's Method for the Estimation of Urinary Ammonia Nitrogen. MATTHEW STEEL (*J. Biol. Chem.*, 1910, 8, 365—379. Compare Abstr., 1908, ii, 776).—In urines containing large quantities of ammonio-magnesium phosphate, there is in Folin's method an incomplete decomposition of this substance, and so the yield of ammonia is too low; the error may exceed 50%. Some alkali must be added which will liberate all the ammonia from the phosphate but not from other substances, such as urea. The plan adopted is to substitute sodium hydroxide for sodium carbonate. If plenty of sodium chloride is added also, urea and other substances are not decomposed. For the 3 grams of sodium carbonate employed by Folin, 0·5 to 1 gram of sodium hydroxide plus 15 grams of sodium chloride are substituted. W. D. H.

Nitrometer Appendage Flasks. FRANZ MICHEL (*Chem. Zeit.*, 1910, 34, 1237).—The H-vessel (see figure), which dispenses with the use of the pipettes and funnels, is used as follows: Tube *a*, which for nitrogen estimations carries two marks at 25 and 50 c.c. respectively, contains the alkaline hypobromite solution. Tube *b* also carries two marks of 5 and 10 c.c. respectively, and is intended for the substance to be tested. The diameters of the tubes are so chosen that their length is about equal. If a solid substance, such as an ammonium salt, has to be tested, a weighed quantity is placed in tube *b*, and water is added up to the desired mark. Liquids are introduced up to the desired mark, or may be delivered from a pipette. After closing the tubes (*a* with a rubber cork, *b* with a stopcock tube), the pressure in both tubes is equalised as usual. To start the reaction, the apparatus is inclined in such a manner that the liquid from *b* gradually enters *a*, and when the effervescence has ceased, the liquid is allowed to again enter *b*, and this operation is repeated a few times. When all the liquid is once more in tube *a*, the apparatus is placed in a horizontal position, *a* downwards, and well shaken. In this manner it is impossible for any liquid to enter the stopcock tube. L. DE K.



Application of Busch's "Nitron" Method to the Analysis of Chili Saltpetre. LEOPOLD RADLBERGER (*Chem. Zentr.*, 1910, ii, 685, 686; from *Osterr.-ung. Zeitsch. Zucker-Ind. Landw.*, 1910, **39**, 433—436).—Busch's method (Abstr., 1905, ii, 282) may be employed for estimating the quantity of nitrate in Chili saltpetre provided that this contains not more than the normal amount of perchlorate. If the salt contains a large amount of perchlorate, the results obtained by the process are untrustworthy.

W. P. S.

Analysis of Nitrates by Grandval and Lajoux's Method. Estimation of Nitrates in Water by a Sulphosalicylic Reagent. HUBERT CARON and DÉSIRÉ RAQUET (*Bull. Soc. chim.*, 1910, [iv], **7**, 1021—1025, 1025—1027).—In the first paper the modified form of Grandval and Lajoux's process introduced by Perrier and Farcy (Abstr., 1909, ii, 344) is criticised, and in the second the use of a solution of salicylic acid in sulphuric acid is suggested in place of phenol dissolved in sulphuric acid as a colorimetric reagent for nitrates.

It is stated that the coefficients of decolorisation quoted by Farcy (Abstr., 1909, ii, 616) do not agree with those calculated from the results given in his previous paper (Abstr., 1909, ii, 344). Further, the dry residue from the water is liable to absorb moisture, and unless this is guarded against, different results are obtained by different workers for the same proportion of nitrates. The results obtained vary also with the method used in preparing the solution of phenol in sulphuric acid, and the authors recommend the use of a reagent freshly prepared by dissolving 1 c.c. of the liquefied phenol, specified in the Codex Français, in 10 c.c. of sulphuric acid.

In the second paper, it is pointed out that several phenolic substances dissolved in sulphuric acid give colours with nitrates, and a solution of from 1 to 5% of salicylic acid in sulphuric acid is suitable for use in estimating nitrates in water. The process suggested is as follows: Evaporate 10 c.c. of the water to dryness with 1 c.c. of a 1% solution of sodium salicylate; add to the residue 1 c.c. of sulphuric acid, and, after mixing thoroughly for some minutes, add 10 c.c of water and 10 c.c. of ammonia, and compare the colour given with that furnished by a known nitrate solution similarly treated. The quantity, X, of nitrate in the water is given by the formula:

$$X = Ph/h' \times V'/V,$$

where h and h' are the respective heights of the two solutions giving the same tint in the colorimeter, V and V' the original volumes of the two solutions, and P the amount of nitrate in the standard solution.

T. A. H.

Estimation of Free Carbon Dioxide in Water. J. TILLMANS and O. HEUBLEIN (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 617—630).—Titration with calcium hydroxide solution yields trustworthy results, provided that phenolphthalein is used as the indicator. Rosolic acid is quite useless for the purpose, as the hydrogen carbonates of the alkalis and alkaline earths exhibit a strongly alkaline reaction towards this indicator.

W. P. S.

Acid Content of Moor Water. H. STREMME (*J. pr. Chem.*, 1910, [ii], **82**, 519—520).—It is pointed out that Endell in his paper on the acidity of moor waters (Abstr., 1910, ii, 1005) has worked according to the method first given by the author two years ago (*Zeitsch. prakt. Geol.*, 1908, 126).

T. S. P.

Separation of Alumina and Ferric Oxide. PHILIPPE BARBIER (*Bull. Soc. chim.*, 1910, [iv], **7**, 1027—1028).—The material is dissolved in the ordinary way, excess of sodium acetate added, and the acids neutralised by sodium hydroxide. A 10% aqueous solution of sodium hyposulphite is then added until the red coloration of the liquid just disappears. The mixture is boiled, when alumina is precipitated as a dense powder, which can be collected and weighed as usual. Iron can be estimated in the filtrate by any of the ordinary methods. Glucina is precipitated with the alumina if present, and can be separated by digesting the precipitate with ammonium carbonate solution during thirty-six hours, when the alumina remains undissolved, and the glucina can be recovered quantitatively by prolonged ebullition of the solution.

T. A. H.

Estimation of Manganese in Steel by the Volhard-Wolff Method. AUGUST KAYSSER (*Chem. Zeit.*, 1910, **34**, 1225—1226).——One gram of steel is boiled with 25 c.c. of hydrochloric acid, D 1·12. When solution is complete, a 1 gram tablet of compressed potassium chlorate is added, and the boiling continued until the odour of chlorine has passed off. The liquid is transferred to a flask, and, after precipitating the iron with zinc oxide, avoiding an excess, the hot solution is titrated with potassium permanganate solution (1·9 gram per litre; 1 c.c. = 0·1% of manganese in the sample). When dealing with samples rich in carbon, more potassium chlorate should be used.

L. DE K.

Method of Dissolving Tinstone. ADOLPH GILBERT (*Zeitsch. offentl. Chem.*, 1910, **16**, 441—442).—Natural tinstone is much more refractory than artificial stannic oxide towards fusion with alkali. If 0·5—1 gram tinstone is fused with 10—15 grams of sodium hydroxide in a silver crucible, a little finely-powdered wood charcoal being added (50 mg.), a reaction takes place with considerable development of heat, and solution is complete in three to five minutes. The heating must be continued in order to burn off the excess of carbon. All the tin passes into solution in water, iron oxide remaining insoluble. It is desirable to remove copper and sulphur by a preliminary roasting and extraction with hydrochloric or nitric acid. The quantity of carbon used is only a small fraction of that required to reduce the tin oxide.

The reaction has been described by Burghardt (Abstr., 1890, 1027), but has remained unnoticed in the literature. C. H. D.

Precipitation of Vanadic Acid as Silver Vanadate and Estimation of Phosphoric and Vanadic Acids in the Presence of One Another. GRAHAM EDGAR (*Amer. Chem. J.*, 1910, **44**, 467—472).—The solution of the alkali vanadate which may contain excess of alkali carbonate, but no other matters precipitable by silver nitrate, is acidified with nitric acid, and boiled to expel carbon dioxide. Dilute sodium hydroxide is then added to the boiling solution until the yellow liquid turns colourless. An excess of *N*/10-silver nitrate is added, and then ammonia to dissolve the precipitate formed, and the excess of ammonia is boiled off; a few fragments of porous tile should be added to prevent bumping. The silver vanadate is collected on a filter, and well washed, and then the excess of silver is estimated in the usual manner by acidifying the filtrate with nitric acid and titrating with *N*/10-ammonium thiocyanate with ferric nitrate as indicator. One c.c. of silver consumed = 0·00304 gram of vanadic acid.

In the presence of phosphoric acid, this is co-precipitated as trisilver phosphate with the vanadic acid. The latter is then estimated separately by dissolving the precipitate in sulphuric acid and reducing the vanadic acid by boiling with sulphur dioxide. The vanadium is titrated hot with *N*/20-permanganate and the phosphoric acid is found by an easy calculation. L. DE K.

An Indirect Method for Estimating Columbium and Tantalum. HARRY W. FOOTE and RALPH W. LANGLEY (*Amer. J. Sci.*, 1910, [iv], **30**, 393—400).—The process is based on the great difference between the densities of the oxides of columbium (4·552) and tantalum (8·716).

When applied to the mineral stibiotantalite, a sufficiency of the sample is treated with hydrofluoric acid, the solution is largely diluted with water, and the antimony and bismuth are removed by means of hydrogen sulphide; the precipitate is then treated further by the usual process. The filtrate is evaporated to dryness, and the residue heated with sulphuric acid to expel the fluorine. After diluting with water, the solution is made alkaline with ammonia, and the precipitate is collected, washed, ignited, and weighed After heating over a blast lamp for an hour, the density of the mixed oxides is determined and their composition ascertained by referring to a table. L. DE K.

A Recent Method for Separating Tantalum and Columbium.

HARRY W. FOOTE and RALPH W. LANGLEY (*Amer. J. Sci.*, 1910, [iv], **30**, 401—402).—Weiss and Landecker (Abstr., 1909, ii, 942) have stated that tantalic acid may be precipitated from its solution in sodium carbonate by means of a current of carbon dioxide; any columbic acid remains in solution, and may be separated by boiling with sulphur dioxide. The authors, however, agree with Rose and with Ostwald that the columbium is almost completely co-precipitated with the tantalum, and that, therefore, this process cannot be employed for their separation. L. DE K.

Estimation of Both Phenol and *p*-Cresol in Urine.

MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1910, **29**, 368—388). —The method is based on two determinations: (1) the total amount of bromine required to convert the phenol and *p*-cresol in the liquid into tribromophenol and tribromo-*p*-cresol, and (2) the quantity required to convert the phenol into tribromophenol and the cresol into dibromo-*p*-cresol.

Since 6 atoms of bromine are necessary for the formation of either of the tribromo-compounds, whilst that of dibromo-*p*-cresol only requires 4 atoms, the quantities of phenol and *p*-cresol present are readily calculated from the difference between the two determinations. For the first estimation, a modification of Koppeschaar's method is employed. Twenty to 30 c.c. of sulphuric acid (1 : 1) are added to a measured volume of the liquid contained in a stoppered flask, and a standard solution of potassium bromide and bromate (0·834 gram $KBrO_3$ and 2·97 grams KBr per 1000 c.c.) is run in from a burette, the liquid being continually agitated, until the precipitate collects together into a mass, and the liquid becomes coloured distinctly yellow. At this point, the volume that has been added is noted, and an eighth part of this volume is further run in. The mixture is then shaken at frequent intervals for one hour. It is then filtered through glass-wool into 25 to 30 c.c. of 5% potassium iodide solution, and the iodine liberated titrated with *N*/10 thiosulphate.

The second reaction is carried out with the same quantity of the original liquid, 30 c.c. of 25% hydrochloric acid are added, and the whole diluted to 500 c.c. The volume of the solution of potassium bromate and bromide required to produce a yellow coloration, as previously determined, is then run in, the liquid being gently rotated throughout, and the mixture left without shaking for fifteen minutes. Twenty-five to 30 c.c. of 5% potassium iodide are added, and the flask left for one hour in front of a light. The iodine liberated is titrated with thiosulphate. The method gives good results.

A new *tribromo-*p*-cresol* was obtained by the action of potassium bromide and bromate on *p*-cresol in the presence of hydrochloric acid, and the subsequent addition of potassium iodide; it crystallises from acetic acid in colourless needles, m. p. 139°. W. J. Y.

An Improvement in Scherer's Reaction for Inositol. Ernst Salkowski (*Zeitsch. physiol. Chem.*, 1910, **69**, 478—481).—A trace of inositol is dissolved in a few drops of nitric acid, a drop of 10% calcium chloride solution added, and then a drop of 1% platinum chloride solution; the whole is carefully evaporated in a porcelain capsule. A red colour develops; on the addition of water it becomes orange; the red returns on heating once more, with a blue tinge; on stronger heating, it becomes a dirty green. Performed in this way, the reaction is more delicate, and the colours more intense. W. D. H.

A Simple Method for the Estimation of Sugar in Blood. Leonor Michaelis and Peter Rona (*Zeitsch. physiol. Chem.*, 1910, **69**, 498).—Polemical against K. Moeckel and E. Frank (Abstr., 1910, ii, 1116). W. D. H.

Reischauer's Titration Process for the Estimation of Diabetic Sugar. Gustav Otto Goebel (*Apoth. Zeit.*, 1910, **25**, 614—615).—Into six separate test-tubes are introduced the usual quantity of Fehling's solution and water, and to each is added an increasing amount of the urine to be tested. After being heated in the boiling water-bath for fifteen minutes, they are cooled rapidly, shaking being avoided. They are now all tested for excess of copper in the following manner: 0·5 gram of potassium iodide dissolved in a little water is added, and, after gentle shaking, 5 c.c. of dilute sulphuric acid (1 : 5). Excess of copper will be noticed by the formation of cuprous iodide, and also free iodine, which may be recognised by adding starch solution; no notice should be taken of a blue colour appearing gradually.

The contents of the tube which show no excess of copper are those where about the right amount of urine has been added, and serve as a guide for a second trial, when a little less urine should be used.

L. de K.

Estimation of Sugar by Safranine. K. A. Hasselbalch and J. Lindhard (*Biochem. Zeitsch.*, 1910, **29**, 416).—The authors, in reply to Wender's criticism (Abstr., 1910, ii, 1116), maintain that their safranine method for the estimation of sugar (Abstr., 1910, ii, 905) is new, in that they so elaborated the details that the reaction can be used quantitatively, and not merely qualitatively. S. B. S.

Polarimetric Estimation of Lactose. H. Droop Richmond (*Analyst*, 1910, **35**, 516—517).—Of the many substances which have been proposed for the removal of proteins previous to the polarimetric estimation of lactose in milk, that most commonly used is mercuric nitrate, but the author finds that this reagent does not effect complete precipitation of all the proteins present. If the filtrate obtained from milk which has been treated with mercuric nitrate is further treated with phosphotungstic acid, a somewhat voluminous precipitate is obtained, and the optical activity of the solution is increased. In the case of milk itself, the difference in the polarisation, before and after treatment with phosphotungstic acid, is small, but with dried milks and other milk products the difference may amount to several units per cent. As, however, the use of mercuric nitrate is so convenient and involves such a small dilution, the author recommends that its use be continued in conjunction with the addition of phosphotungstic acid. The milk should be treated with mercuric nitrate in the usual manner; after the addition of 5% of phosphotungstic acid and 5% of sulphuric acid (1 : 1), the mixture is filtered, and the filtrate is examined in the polariscope. The readings observed are multiplied by 1·1. W. P. S.

Estimation of Lactose in the Presence of the Commonly-occurring Sugars. Julian L. Baker and H. F. E. Hulton (*Analyst*, 1910, 35, 512—514).—The method proposed depends on the fact that brewers' yeast ferments such sugars as dextrose, invert sugar, maltose, and sucrose, whilst lactose is not affected. The estimation is carried out by adding about 0·5 gram of washed brewers' yeast to 100 c.c. of a 2—3% solution of the mixed sugars, allowing fermentation to proceed for seventy hours at a temperature of 27°, then filtering and boiling the solution, and determining its copper-reducing power. If the sugar solution is non-nitrogenous, a small quantity of sterile yeast water or asparagine may be added. Lactose alone appears to be slightly attacked by the yeast, results of experiments showing that from 90—95% of the quantity present is found at the end of the fermentation process, but in the presence of other sugars the loss of lactose is much less. The fermentation must not be prolonged for more than seventy-two hours, as after this period of time bacteria develop, the solution becomes acid in reaction, and the lactose diminishes rapidly. The process is particularly suitable for the estimation of lactose in the presence of flour, for instance, in infants' and invalids' foods; when sucrose is also present, it is advisable to invert this sugar with invertase or citric acid, before proceeding with the estimation of the lactose. The method is not, however, applicable in the case of foods, etc., containing commercial sugars, such as dextrin-maltose, glucose, and the like, as these, even after fermentation in the presence of diastase, leave a residue which reduces Fehling's solution. W. P. S.

Estimation of Lactose in Milk. Vitoux (*Ann. Falsif.*, 1910, 3, 471—472).—It is shown that the process described by Denigès (treatment of the milk with sodium metaphosphate and hydrochloric acid, filtering, and determining the cupric reducing power of the filtrate) yields results which agree closely with those obtained by the official (French) method of estimating lactose in milk. The latter method is, however, to be preferred for the analysis of milks which have been preserved by the addition of dichromate, as the end-point of the titration with Fehling's solution is not obscured. W. P. S.

New Method for the Quantitative Estimation of Sucrose in the Presence of other Sugars. Adolf Jolles (*Zeitsch. Nahr. Genussm.*, 1910, 20, 631—638).—The method is based on the fact that sugars, such as arabinose, rhamnose, dextrose, lævulose, galactose, mannose, invert sugar, maltose, and lactose, are rendered optically inactive when heated in dilute alkaline solution, whilst sucrose remains unaffected. The reaction to some extent depends on the concentration of the sugar and alkali; for instance, a 1% dextrose solution containing sufficient sodium hydroxide to render the alkalinity of the whole approximately *N*/100 becomes optically inactive after being heated at a temperature of 37° for twenty-four hours. The solution, however, then becomes acid in reaction, and to avoid this, it is recommended that the solution have an alkalinity approximately *N*/10 and contain not more than 2% of the above-mentioned sugars; the quantity of sucrose present does not matter. Instead of heating at 37° for twenty-four hours, the mixture may be boiled in a reflux apparatus or heated in a closed flask in a boiling-water bath for thirty minutes, but the lower temperature is to be preferred, as the solution becomes less darkly coloured. As applied to the estimation of sucrose in wine, condensed milk, etc., the details of the process are as follows: A definite quantity of the sample is neutralised, clarified by the addition of lead acetate, filtered, and the excess of lead removed from the filtrate by means of sodium phosphate. After removing the lead phosphate by filtration, an aliquot portion of the filtrate is treated with a sufficient quantity of sodium hydroxide solution to render the alkalinity of the solution equivalent to *N*/10, and the mixture is then heated as described. After cooling, the solution is examined in the polariscope; any rotation observed is due solely to sucrose, and the quantity of the latter in the sample is then calculated. The results obtained by the process agree closely with those yielded by the ordinary polarimetric method of estimating sucrose. W. P. S.

A Modification of the Furfuraldehyde Method of Estimating Pentosans. K. H. BÖDDENER and BERNHARD TOLLENS (*J. Landw.*, 1910, **58**, 232—237).—It is usual to estimate pentosans by distilling with hydrochloric acid, collecting the furfuraldehyde formed, and then converting this into a weighable substance by precipitating with phloroglucinol in the cold, leaving the mixture for sixteen to twenty hours. The authors find that precipitation is practically complete in a much shorter time if the mixture is heated to 80—85°, and then allowed to cool for one and a-half to two hours; bluish-green flocks are thus formed, which are readily filtered and washed. The phloroglucide is not the same as is obtained in the cold, the reaction being $C_5H_4O_2 + C_6H_6O_3 = C_{11}H_4O_2 + 3H_2O$, whilst in the cold the products are $C_{11}H_6O_3 + 2H_2O$. The necessary tables are given for the conversion.

The modification is not suitable if it is desired to estimate the methylpentosans separately; further (this vol., ii, 63), it does not give identical results with the older method, but the differences are only small. Its great value is the considerable saving of time it effects. E. J. R.

Estimation of Starch. FRIEDRICH SCHUBERT (*Chem. Zentr.*, 1910, ii, 688—689; from *Österr.-ung Zeitsch. Zucker-Ind. Landw.*, 1910, **39**, 411—422).—The author discusses the more important processes which have been proposed for the estimation of starch, and describes the following modification of Lintner's process for the estimation of starch in barley (Abstr., 1907, ii, 823): A weighed quantity of the barley is rubbed down with 25 c.c. of a 1% phosphotungstic acid solution, 75 c.c. of hydrochloric acid are then added, and, after the lapse of thirty minutes, the solution is poured through a filter. As exactly 100 c.c. of reagents have been added to the barley, there is no need to dilute the mixture to any definite volume, but the optical rotation of the filtrate must be corrected for the quantity of water present in the barley and for the volume of the dissolved starch. One gram of pure starch occupies a volume of 0·49 c.c.

W. P. S.

Estimation of Acetaldehyde by means of Pyrrole and Application of this Method to the Estimation of Lactic Acid. W. Sobolewa and J. Zalewski (*Zeitsch. physiol. Chem.*, 1910, **69**, 441—451).—Into a number of test-tubes is placed the reagent, consisting of 5 c.c. of aqueous pyrrole and 10 c.c. of 2·2% hydrochloric acid. Into each of the tubes is introduced an increasing volume of acetaldehyde solution of known strength (about 0·25 gram per litre), and after half an hour the minimum quantity of acetaldehyde required to produce an opalescence is ascertained. This then serves as a measure for the estimation of the concentration of acetaldehyde solutions.

On boiling a lactate with dilute sulphuric acid in a current of air and cautiously adding potassium permanganate, 80—92% of the lactic acid is obtained as acetaldehyde, which may then be estimated by the pyrrole method.

L. de K.

Titanium Chloride in Volumetric Analysis. IV. Estimation of Quinones. Edmund Knecht and Eva Hibbert (*Ber.*, 1910, **43**, 3455—3457).—Quinones are reduced by titanium chloride in the cold. To the solution of the quinone in cold water is added an excess of the titanium trichloride, and the excess of the latter determined by titration with iron alum, using potassium thiocyanate as indicator. The titration of the quinone may also be carried out directly with the titanium chloride, using methylene-blue as an indicator; the quinone is quantitatively reduced before the methylene-blue enters into reaction and is decolorised.

Analytical results are given with *p*-benzoquinone, toluquinone, and β-naphthaquinone.

In a footnote it is pointed out that methylene-blue may be used as an indicator instead of potassium thiocyanate in the titration of ferric salts.

T. S. P.

Acids in Tan Liquors. Henry R. Procter and A. Seymour-Jones (*J. Soc. Chem. Ind.*, 1910, **29**, 1354—1362).—The estimation of the acids present in tan liquors is of technical importance, since these substances act on hide in such a way as to facilitate the absorption of tannin. Such action is confined to the relatively strong acids, and is not exhibited by weak acids, such as the phenols, and for that reason the method of estimation must discriminate between the two classes. Many methods have been devised for this purpose, and in the present investigation the best known of them have been examined, and the results obtained are discussed and criticised.

Among the methods available, the discrimination referred to above is effected in one of two ways, (*a*) the tannins and other weak acids are removed by precipitation with gelatin, hide powder, or some similar agent, and the acids in the filtrate estimated by titration with standard alkali, using a suitable indicator, or (*b*) liquors are titrated directly with standard alkali in presence of an indicator, which will react with the stronger acids only. A special case of class (*a*) is the "lime-water" method, which depends on the fact that lime forms soluble salts with the stronger acids, and insoluble salts with the tannins, phenolic matters, etc., the formation of a definite faint turbidity being taken as the end-point. The general objections to methods of class (*a*) are (1) co-precipitation of stronger acids, and (2) undue dilution of the liquors. Methods of class (*b*) present as chief difficulty the selection of a suitable indicator. The authors think that the best results are obtainable with methods of group (*b*), and they are now engaged in the investigation of suitable indicators. The most promising results were obtained with Congo-red (10^{-4}), methyl-orange (10^{-4}), hæmatein (10^{-1} to 10^{-15}), and fluorescein (10^{-5} to 10^{-7}). The figures given in brackets after the name of each indicator represent the concentration of hydrogen ions at which colour change occurs.

T. A. H.

Separation of Saturated Fatty Acids (Palmitic and Stearic) from Oleic Acid. PIETRO FALCIOLA (*Gazzetta*, 1910, **40**, ii, 217—229).—See this vol., i, 5.

Estimation of Total Tartaric Acid by the Goldenberg Process. CHARLES ORDONNEAU (*Bull. Soc. chim.*, 1910, [iv], **7**, 1034—1041).—In order to ascertain the effects on the analytical results obtained by the Goldenberg method for the examination of factory and commercial tartaric products of impurities likely to occur in such materials, the author has applied the 1907 modification of that process (Abstr., 1908, ii, 237) to potassium hydrogen tartrate containing known amounts of various impurities.

With calcium tartrate alone the results are 3·53% too low when phenolphthalein is used as indicator, and 3·60% for litmus, whilst with potassium hydrogen tartrate containing 5 and 10% of calcium tartrate, the corresponding losses are 2·24 and 2·39% for litmus and 1·25 and 1·34% respectively for phenolphthalein, but these losses are somewhat reduced by the presence of alumina, although the loss due to the presence of 5% of the latter alone is 19·35% for litmus and 8·80% for phenolphthalein. Similar errors are caused by ferrous, ferric, and aluminium phosphates. The errors caused by these and other substances are tabulated in the original. In general, the losses are about twice as great for litmus as for phenolphthalein, and an approximation to the correct figure may be got as a rule by adding to the result obtained with phenolphthalein the difference between this result and that furnished by the use of litmus as an indicator, although a further correction is needed in some cases. Phenolphthalein may be used in all cases in place of litmus if the titration is carried out at 50°, after boiling and cooling the liquid. Certain of the changes suggested by the author have been made in the most recent form of the Goldenberg process, adopted by the London Congress of Applied Chemistry (Abstr., 1910, ii, 758). T. A. H.

Detection of Hydrocyanic Acid in an Exhumed Corpse and the Stability of Hydrocyanic Acid in Presence of Putrefying Matter.

WILHELM AUTENRIETH (*Ber. pharm. Ges.*, 1910, 20, 432—446).—It is generally assumed that hydrocyanic acid disappears rapidly in animal organisms by (1) combination with dextrose in the blood; (2) interaction with proteins; (3) hydrolysis to formic acid, or (4), according to Ganassini (Abstr., 1904, ii, 758), conversion into xanthine derivatives. The detection of the acid in a child's corpse which had been exhumed after forty-three days lead the author to investigate the stability of hydrocyanic acid in presence of decomposing matter of various kinds, when it was found that, although the acid disappears, it does so comparatively slowly.

In a mixture of pig's stomach, intestine, and pancreas (50 grams) with bitter almond water (50 grams) and water (200 c.c.), hydrocyanic acid could still be detected by the Prussian blue, guaiacum, or thiocyanate tests after forty-five days, and this was also the case when dilute potassium cyanide solution was substituted for bitter almond water. When the quantity of acid initially present was reduced to 1 in 15,000 it could still be detected after thirty-six days. One part of the acid in 10,000 of cow's blood could still be detected by the Prussian blue reaction after forty-eight days.

In a series of quantitative experiments, an aliquot part of the mixture was distilled after twenty and also after sixty days, and the acid estimated by Liebig's method. The percentages of the acid originally present, found after twenty days, varied from 47·7 to 87·5, and after sixty days from 41·4 to 63·3. No evidence of more rapid disappearance of the acid in presence of dextrose or proteins could be obtained, and in this respect the behaviour of the acid seems to be different in the dead and living organism, probably because active enzymes are present in the latter case. T. A. H.

Influence of the Alkalinity of the Wash-Water on the Percentage of Water in Butter.

W. MEYERINGH (*Chem. Weeklad*, 1910, 7, 951—953).—Butter washed with acidified water appears to have a lower percentage of fat than that washed with alkaline water. A. J. W.

Reactions of Cyclic Amines.

F. LAVILLA LLORENS (*Anal. Fis. Quim.*, 1910, 8, 127—132).—The following bases give characteristic colorations when oxidising agents, such as potassium permanganate, potassium ferricyanide, potassium or ammonium persulphate, are added to their solutions in dilute acid. Potassium permanganate is the best reagent to use, a few drops of a 0·2% solution developing a coloration rapidly.

Aniline: greyish colour, initially, then more or less reddish-violet tinge, which changes to a characteristic blue; this, after a long time, takes on a greenish hue.

Methylaniline gives the same indications as aniline.

o-*Toluidine*: in absence of much free acid, a characteristic blue coloration, distinct from that of aniline; in presence of an increasing proportion of hydrochloric acid, the colour changes to bluish-green or yellowish-grey. With acetic acid, even in concentrated solution, only the blue shade appears. The coloration given by aniline is nearly independent of the amount of free acid, but with the toluidines and the following bases it varies greatly according to the concentration of the acid.

m-*Toluidine* : initially reddish coloration, changing to blue.

p-*Toluidine* : final coloration, red.

o-4-*Xylidine* : red colour, slightly violet in shade.

m-4-*Xylidine* : red colour, more violet than with *o* 4-xylidine.

p-*Xylidine* : red colour.

a-*Naphthylamine*: blue coloration; *β-naphthylamine*: greenish-grey coloration, only faint. W. A. D.

Estimation of Urea. Stanley R. Benedict (*J. Biol. Chem.*, 1910, **8**, 405—421).—The Folin method yields traces of ammonia nitrogen from creatinine, rather more from uric acid, and allantoin yields all its nitrogen. The method recommended is to add to the urine, potassium hydrogen sulphate, zinc sulphate, a piece of paraffin, and a little powdered pumice. The mixture is boiled to dryness, and then placed in a sulphuric acid bath at 162—165° for an hour. The contents are then washed with water into a distilling flask, sodium hydroxide added, and distillation continued for forty minutes with standard acid. The residual acid is then titrated, and the urea nitrogen calculated. W. D. H.

New Reactions of Morphine. Georges Denigès (*Compt. rend.*, 1910, **151**, 1062—1063).—Ten c.c. of a solution of morphine or one of its salts (minimum concentration 0·03 gram per litre) are treated with 1 c.c. of hydrogen peroxide (5—12 vols.) and 1 c.c. of ammonia. After shaking, one drop of a solution of copper sulphate containing 1—4% of the crystallised salt is added. On shaking again, the liquid develops a colour, varying from rose-pink to intense red, according to the amount of morphine present.

Sparingly soluble morphine salts should be dissolved in a few drops of hydrochloric acid before dilution. The reaction gives positive results with certain morphine derivatives, such as *apo*morphine or heroine, but not with codeine, thebaine, papaverine, narceine, or narcotine. It has the advantage of being applicable to solutions containing organic matter, such as sugar, and to plant extracts. W. O. W.

Volumetric Estimation of Quinine in Drugs, etc. Julius Katz (*Ber. Deut. pharm. Ges.*, 1910, **20**, 316—329).—In the method described, the quinine (or cinchona alkaloids) is converted into its hydrogen salt by evaporating its alcoholic solution with an excess of hydrochloric acid; sodium chloride is added to aid the evaporation of the excess of the acid, and the quinine hydrochloride is then titrated with alcoholic potassium hydroxide solution, using Poirrier's Blue as indicator. The details of the process as applied to the estimation of quinine alkaloids in cinchona bark are as follows: 6 grams of the dry and powdered bark are shaken for thirty minutes with 15 grams of chloroform and 5 grams of 5% sodium hydroxide solution; 1 gram of magnesia and 45 grams of ether are then added, and the mixture is poured on a filter. Forty grams of the filtrate are evaporated to a volume of about 1 c.c., and the residue is rinsed into a porcelain basin with alcohol; after the addition of 10 drops of hydrochloric acid and 0·25 gram of sodium chloride, the mixture is evaporated to dryness. The residue, after being dried for fifteen minutes in the water-oven, is dissolved in alcohol, 5 drops of a 0·2% Poirrier's blue solution are added, and the solution is titrated with *N*/10-alcoholic potassium hydroxide solution. Each c.c. of the latter solution is equivalent to 0·0162 gram of quinine. W. P. S.

Caution as to Testing for "Saccharin" in Sweetened Foods and Beverages. EZIO COMANDUCCI (*Boll. chim. farm.*, 1910, **49**, 791).—When solutions of dextrose and sucrose were extracted with a mixture of equal volumes of light petroleum and ether, it was found that the residue after distilling off the ethereal liquid yielded, on heating with resorcinol and sulphuric acid and subsequently treating with alkali and water, a fluorescent solution, the production of which has been regarded as a test for "saccharin." If the ethereal extract is washed with water three or four times, however, the residue obtained no longer shows this reaction, whilst "saccharin" would not be removed by such treatment. R. V. S.

A Sensitive Reaction for Scatole. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1910, **29**, 395).—In the reaction already described (Abstr., 1910, ii, 166) the iron salt concentration should not be too great. A convenient reagent is obtained by adding one drop of a 1% ferric sulphate solution to 100 c.c. of iron-free concentrated sulphuric acid. The methyl alcohol employed must be perfectly free from aldehydes. S. B. S.

Iodometric Estimation of Antipyrine in Migrainine. C. SLEESWYK (*Pharm. Weekblad,* 1910, **47**, 1282).—"Migrainine" is prepared by dissolving 90 parts of antipyrine, 9 parts of caffeine, and 1 part of citric acid in water, and evaporating the solution to dryness on the water-bath. In order to test the commercial product, the author uses the iodometric method, originally proposed by Bougault, and since modified by Zernik, with a further modification.

1·351 Gram of iodine, 2·5 grams of mercuric chloride, and 1·1 gram of the sample are each dissolved in 200 c.c. of 95% alcohol; 20 c.c. of the migrainine are then mixed with 20 c.c. of the mercuric chloride, and the iodine is run in until the liquid turns yellow; 1 c.c. of iodine = 0·005 gram of antipyrine. It is as well to check the iodine by means of pure antipyrine. The migrainine may also be dissolved in water instead of alcohol. The titration should be repeated, the bulk of the iodine being added at once, and the last drops more carefully; the end-point is then very distinct. L. DE K.

General and Physical Chemistry.

Recalculation of Atomic Refractions. FRITZ EISENLOHR (*Zeitsch. physikal. Chem.*, 1910, **75**, 585—607).—As certain factors, for example, optical exaltation, were not sufficiently taken into account in the older tables of atomic refractivities, the author has recalculated the refraction for the H_α, D, H_β, and H_γ lines, and the dispersions, $H_\beta - H_\alpha$ and $H_\gamma - H_\alpha$, for a large number of non-aromatic compounds, and from the results the atomic refractions and dispersions given in the accompanying table have been calculated. The experimental data is due mainly to Bruhl and to Landolt, and has been amplified by the author. On the basis of the new data, benzene is found to show no optical anomaly.

Atomic Refractions.

	H_α.	D.	H_β.	H_γ.	$H_\beta—H_\alpha$	$H_\gamma—H_\alpha$.
CH_2 group	4·598	4·618	4·668	4·710	0·071	0·113
Carbon	2·413	2·418	2·438	2·466	0·025	0·056
Hydrogen	1·092	1·100	1·115	1·112	0·023	0·029
Oxygen (in CO group)	2·189	2·211	2·247	2·267	0·057	0·078
,, (in ethers)	1·639	1·643	1·649	1·662	0·012	0·019
,, (in OH group)	1·522	1·525	1·531	1·541	0 006	0·015
Chlorine	5·933	5·967	6·043	6·101	0·107	0·168
Bromine	8·803	8·865	8·999	9·152	0·211	0·340
Iodine	13·757	13·900	14·224	14·521	0·482	0·775
Ethylene linking	1·686	1·733	1·824	1·893	0·138	0·200
Acetylene ,,	2·328	2·398	2·506	2·538	0·139	0·171

G. S.

Refraction and Magnetic Double Refraction of Solutions of the Rare Earths. G. J. ELIAS (*Ber. Deut. physikal. Ges.*, 1910, **12**, 955—962. Compare Abstr., 1908, ii, 549).—The refractive index of an aqueous solution of neodymium nitrate has been measured for wavelengths in the neighbourhood of the yellow absorption band. The data indicate the occurrence of slightly anomalous dispersion in this region.

Preliminary observations of the double refraction produced by a solution of erbium nitrate in a transverse magnetic field are also recorded. The double refraction increases with the intensity of the magnetic field; it is greater for blue than for yellow light, and appears to be somewhat anomalous in the immediate neighbourhood of the absorption bands. No magnetic double refraction could be detected in solutions of neodymium nitrate, manganous nitrate, or ferric chloride.

The double refraction phenomena are examined theoretically.

H. M. D.

The Sequence of Chemical Forms in Stellar Spectra. SIR NORMAN LOCKYER (*Proc. Roy. Soc.*, 1910, *A*, **84**, 426—432).—A brief account is given of recent work on the classification of stars on the basis of spectroscopic observations and the influence of temperature on the spectra of "chemical forms" characterised by special molecular or corpuscular groupings. H. M. D.

The Emission and Absorption of Luminous Gases from Experiments with Continuous Currents of High Intensity. WILHELM JUNGJOHANN (*Zeitsch. wiss. Photochem.*, 1910, 9, 84—103, 105—129, 141—168).—The intensity of the emission spectra obtained from nitrogen, hydrogen, carbon monoxide, and oxygen when subjected to continuous currents in Wehnelt tubes has been measured for currents of varying intensity. In the case of nitrogen and hydrogen the absorption was also investigated.

The data for nitrogen show that the intensity of the first group of bands is proportional to the current density between 1·4 and 12·7 amperes per square cm.; on the other hand, that of the second group of bands increases more rapidly than the current density or the energy consumption.

In the case of hydrogen, the variations of intensity of the spectrum do not appear to be related in any simple way with the current density or the energy consumption, and the lines of the first subsidiary series behave differently according to the pressure of the gas in the discharge tube.

The intensity of the red and green bands of carbon monoxide increases in a linear manner with the current density, that of the blue bands more rapidly. With increasing current intensity the energy maximum is displaced in the direction of smaller wave-lengths.

The conclusion drawn from these observations is that the changes in the energy of the radiation from a luminous gas cannot be accounted for in a simple manner by the changes in the intensity of the current, or by the variations in the energy consumption, or yet by the corresponding changes in temperature. H. M. D.

The Resonance Spectra of Iodine. ROBERT W. WOOD (*Physikal. Zeitsch.*, 1910, 11, 1195—1196 *).—Resonance spectra, similar to those investigated previously in the case of sodium vapour, are obtained quite readily when a large evacuated bulb containing a small quantity of iodine is subjected to the influence of white or mono-chromatic light. When the fluorescence is excited by white light, its colour is yellowish-green, but a reddish-yellow fluorescence is obtained when the rays from a mercury lamp are used as the exciting agent. Spectroscopic examination of the fluorescent light of iodine acted on by the mercury rays has shown that the spectrum consists of a series of isolated lines separated from one another by intervals of about 65—70 Ångström units. The investigation of the resonance phenomena can be carried out much more easily in the case of iodine as compared with sodium, for the fluorescence effects are developed by iodine vapour at the ordinary temperature. H. M. D.

The Glow Discharge in Rubidium and Cæsium Vapours. GEORG GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1910, 12, 963—969).—The phenomena accompanying electrical discharge through rubidium and cæsium vapour have been examined in a similar way to that described previously in the case of sodium and potassium (Abstr., 1910, ii, 679). Discharge commences through rubidium vapour at about 120°, and through cæsium at 60—70°. In both cases the negative glow is at first yellowish-green in colour, but at a higher temperature rubidium exhibits a bluish-violet, and cæsium a sky-blue, colour. The nature of the emission spectra of the negative and positive glow, and the effect of the admission of small quantities of hydrogen, nitrogen, and air are described in detail (compare following abstract). H. M. D.

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* and *Phil. Mag.*, 1911, [vi], 21, 261—265.

The Emission of the Series and Fundamental Spectra in the Glow Discharge of the Alkali Metal Vapours. GEORG GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1910, 12, 970—974).—The author compares the glow discharge emission spectra of sodium, potassium, rubidium and cæsium. All four metals show the lines of the principal and subsidiary series in the spectrum of the anodic glow light, although it is probable that the principal lines in the spectra of potassium, rubidium, and cæsium are due to the surrounding positive sheath. In the case of sodium, the spectrum of this positive column of light contains only the principal series of lines; in the case of the three other metals, both principal and subsidiary series are observed, although the secondary series is very faint for potassium. The negative glow spectrum of sodium shows the principal and subsidiary series, whereas the corresponding spectra for the three other metals exhibit the secondary series lines and the fundamental spectrum.

These relationships indicate a close relationship between the spectral emission and the atomic weight of the metal. It is assumed that the principal series lines are due to impacts between the atoms and electrons of small velocity, those of the subsidiary series to impacts with electrons of intermediate velocity, whilst the fundamental spectra are caused by impact of the atoms with high speed electrons. By taking into account the varying electropositive character of the alkali metals, it is shown that various phenomena observed in connexion with the glow discharge can be satisfactorily accounted for.

When the discharge tube contains both sodium and potassium vapours, the positive glow and sheath exhibit the potassium spectrum. The negative glow shows the principal and subsidiary series of sodium lines, and, in addition, the subsidiary series and the fundamental spectrum of potassium. This effect is explained in terms of the above assumption as due to the less electropositive character of the sodium. H. M. D.

Absorption in Luminous Hydrogen. RUDOLF LADENBURG (*Ber. Deut. physikal. Ges.*, 1910, 12, 1018—1022).—Polemical against Pflüger (compare Abstr., 1910, ii, 811). H. M. D.

The Ultra-violet Absorption of Benzene. L. GREBE (*Zeitsch. wiss. Photochem.*, 1910, 9, 130—140).—The absorption of ultra-violet rays by benzene in liquid and vapour form has been investigated. The spark discharge between aluminium electrodes under water was used as a source of ultra-violet radiation, and absorption spectra were obtained by means of a quartz spectrograph. In the case of benzene vapour, observations were made at temperatures ranging from 17° to 185°, and the records show that this variation of temperature is practically without influence on the position of the absorption bands. The same result follows from the observations on liquid benzene at 20°, 43°, and 70°. On comparing the positions of the liquid and vapour bands, it is found that the former are displaced in the direction of the visible spectrum by a nearly constant amount, represented by 17 Ångström units.

From experiments in ethyl-alcoholic solutions containing 0·1 and 50% of benzene respectively, it is found that with diminishing concentration the bands are displaced in the direction of smaller wave-lengths. In a 50% solution in ethyl ether, the bands occupy the same position as in the corresponding alcoholic solution. H. M. D.

Molecular Vibrations of Solid Substances. A. STEIN (*Physikal. Zeitsch.*, 1910, **11**, 1209—1212).—On the assumption that the molecules of solid substances are in vibratory movement and that the amplitudes of the vibrations are proportional to the distance between the centres of the molecules in the case of substances which have the same melting point, the author deduces an expression for the relative frequencies of the molecular vibrations. This may be written in the form $n_1/n_2 = \sqrt{m_2}\sqrt[3]{v_2}/\sqrt{m_1}\sqrt[3]{v_1}$, in which m, n, and v denote respectively the frequency, the molecular weight, and the molecular volume of a solid substance.

According to the theory that the absorption of ultra-red rays is a consequence of molecular (or atomic) vibrations, the values of n_1/n_2 can be obtained from observations on the behaviour of solid substances towards ultra-red rays. From the mean frequencies of vibration of the residual rays obtained by Rubens by selective reflexion from plates of rock-salt, sylvine, potassium bromide, and potassium iodide, the values of n_1/n_2 are obtained for the different pairs. On comparison of these ratios with the corresponding $\sqrt{m_2}\sqrt[3]{v_2}/\sqrt{m_1}\sqrt[3]{v_1}$ ratios, it is found that the two series of numbers are approximately the same. A similar agreement is found by a comparison of the data for quartz and fluorspar.

The values of $\sqrt{m}\sqrt[3]{v}$ are also tabulated for various series of metals having approximately the same melting points. These values indicate the existence of simple relationships, for the relative magnitudes correspond very closely with simple integral ratios. H. M. D.

Influence of Substituent Groups on the Spectrum of Progressive Phosphorescence. JOSEPH DE KOWALSKI and J. DE DZIERZBICKI (*Compt. rend.*, 1911, **152**, 83—85. Compare this vol., ii, 3).—The progressive phosphorescence of the following substances has been examined at about −190° in alcoholic solution: benzoic acid, the toluic acids, the amino- and hydroxy-benzoic acids, benzonitrile, and the three toluonitriles. The wave-lengths of the principal bands are given. The substituent groups are found to have a marked influence on the spectrum of progressive phosphorescence; those, like the CO_2H and CN groups, which extend it towards the red are termed "bathophosphic," whilst those which prolong the spectrum towards the violet are called hypsophosphic. Examples of the latter are the hydroxy- and methoxy-groups; the methyl group occupies an intermediate position between these. W. O. W.

Ultra-microscopic Observations. J. AMANN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 11—15. Compare Abstr., 1910, ii, 844).—If strongly illuminated ultra-microscopic particles are examined by means of an ultra-microscope which is slightly out of focus, the image of a particle presents the appearance of a series of concentric light and dark rings showing interference colours. With this arrangement the sparkling of the ultra-microscopic particles is much more evident than when the ultra-microscope is in focus. The sparkling effect is attributed to a variation in the amount of light reflected from a particle at different times in consequence of the irregular shape of the particle and its rotational motion. These movements are termed krypto-kinetic, in order to distinguish them from Brownian motion. The phenomenon in question has also been observed in sections of quartz from different sources.

Solutions of potassium ferro- and ferri-cyanide under the ultra-microscope exhibit numerous large particles. When subjected to white light, a large number of small particles suddenly appear, and this so-called photo-phase is supposed to be the immediate cause of the evolution of oxygen from hydrogen peroxide when a solution of this substance is brought into contact with a previously insolated ferro- or ferri-cyanide solution (compare Weigert, Abstr., 1908, ii, 5).

Observations of the colour of fluorescein under different conditions are recorded. According to these it appears that a colloidal substance may exhibit four totally different colours according to the method of illumination. H. M. D.

Micro-polarisation. EMIL FISCHER (*Ber.*, 1911, 44, 129—132. Compare Donau, Abstr., 1908, ii, 647).—The following pieces of apparatus are described: 1. A small glass cylinder, 20 × 7 mm., provided with a glass stopper. This is used for the preparation of small amounts of solutions of known concentration. 2. A pyknometer of the usual form, but with very thick walls, so that it holds about 0·07 c.c. of liquid. 3. Observation tubes for the polarimeter. These are of white glass, 50 × 1·5 mm., and do not hold more than 1 c.c. 4. A narrow glass tube drawn out to a capillary for transferring the liquids from one vessel to another. The light must be strong; either incandescent gas light or the apparatus made by Schmidt and Haensch for obtaining homogeneous light from the Nernst lamp is recommended.

An accurate balance is essential, and very volatile solvents are to be avoided. With tubes narrower than those described, the sedimentation of the solutions does not take place. J. J. S.

Action of Ultraviolet Rays in Accelerating Chemical Reactions and in Modifying a State of False Equilibrium. JEAN POUGNET (*J. Pharm. Chim.*, 1910, [vii], 11, 540—543).—Ultra-violet light accelerates the rate of change of plastic into rhombic sulphur, of vitreous selenium into crystalline selenium, and of barley sugar into the crystalline form. It also increases the velocity (1) of the transformation of potassium manganate into potassium permanganate; (2) of the reaction between potassium permanganate and oxalic acid; (3) of the inversion of sucrose by acids, and (4) of the saponification of ethyl acetate by sodium hydroxide. T. S. P.

Principal Types of Photolysis of Organic Compounds by Ultra-violet Light. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1910, **151**, 1349—1352. Compare Abstr., 1910, i, 349, 814).—Hydrogen predominates in the gases formed when alcohols of the type $CH_2R \cdot OH$ undergo decomposition through exposure to ultra-violet light; the hydrocarbon R_2 is evolved with the lower terms of the series, with the higher members it remains dissolved in the alcohol. Hydrocarbons of the type R_2 or RR' are not formed in the case of alcohols with a branched chain, but, owing to the greater ease with which the lateral chain is broken, methane and ethane occur in considerable quantity. Photolysis occurs more readily with the lower members of the alcohols, aldehydes, and acids than with the higher ones. Hydrogen (2 vols.) and carbon monoxide (1 vol.) are evolved from allyl alcohol

Carbon monoxide is the principal gaseous product when aldehydes are decomposed, the proportion rising as the series is ascended; hydrocarbons are also formed. Acraldehyde undergoes rapid polymerisation under the action of the light; the gas evolved contains carbon monoxide (80 vols.), carbon dioxide (5 vols.), hydrogen (5 vols.), and an unsaturated hydrocarbon (10 vols.). Citral gives carbon monoxide and hydrogen. Camphor forms carbon monoxide (5 vols.) and methane (1 vol.).

Acids give chiefly carbon dioxide, accompanied by hydrogen and carbon monoxide, with hydrocarbons in the earlier members of the series, the latter diminishing as the series is ascended. W. O. W.

Action of Light on Chlorophyll. P. A. DANGEARD (*Compt. rend.*, 1910, **151**, 1386—1388).—A simple method of demonstrating the effect of light of different wave-lengths on chlorophyll or other substances is to mix an alcoholic solution of chlorophyll with collodion and coat a glass plate with the mixture. When dry, the plate is exposed to a good spectrum. After some hours, colourless bands appear where action has taken place; the first band to appear corresponds with the principal absorption band of chlorophyll. W. O. W.

Canal Rays. JOHANN KOENIGSBERGER and K. KILCHLING (*Ber., Deut. physikal. Ges.*, 1910, **12**, 995—1017).—Observations relating to the nature and properties of canal rays are described with reference to the phenomena of dissociation, neutralisation, diminution in velocity, and deflexion. H. M. D.

The Rate of Development of Heat by Pitchblende. HORACE H. POOLE (*Phil. Mag.*, 1911, [vi], **21**, 58—62. Compare Abstr., 1910, ii, 176).—New determinations of the rate of heat development from pitchblende, by the former method, gave as the results 8·15, 6·5, and 6·2 ($\times 10^{-5}$ cal. per hour per gram), the last experiment, which was the best, agreeing well with the former determination, 6·1. On the assumption that 1 gram of radium generates 110 cal. per hour, the theoretical development should be 4·4. F. S.

The Ratios which the Amounts of Substances in Radioactive Equilibrium Bear to One Another. HUGH MITCHELL (*Phil. Mag.*, 1911, [vi], 21, 40—42).—From the general solution of the equation giving the quantity of the *n*th substance in a disintegration series after any time *t*, the parent substance being initially free from products, the correct relation between the quantities of the members of a radioactive series in equilibrium is deduced. The ratio of the number of atoms of the *n*th substance to that of it and all the preceding substances in equilibrium with it, is the same as the ratio of the average life of the *n*th substance to that of the parent substance. The correct relation is thus: $\lambda_1/\lambda_n = x_n/(x_1 + x_2 + x_3 + \ldots . x_n)$, instead of $\lambda_1/\lambda_n = x_n/x_1$, as usually written. The correct relation makes no assumption as to the relative periods of the parent and its products beyond the requirement that the parent element should be the longest-lived of the series. F. S.

The Relation between Viscosity and Atomic Weight for the Inert Gases; with its Application to the Case of the Radium Emanation. ALEXANDER O. RANKINE (*Phil. Mag.*, 1911, [vi], 21, 45—53).—From the temperature-coefficient of the viscosity of the inert gases, Sutherland's constant *C* is calculated, and from it the viscosities at the critical temperatures are deduced, and found to be proportional to the square-root of the atomic weights for argon, krypton, and xenon. The value so found for helium is about sixteen times the value so calculated from its atomic weight, but direct experiments by Schmitt of the viscosities of argon and helium from −193° to +184° have shown that, whereas argon conforms to, helium departs from Sutherland's equation the more seriously the lower the temperature. It is probable the equation fails so near to the absolute zero. The unknown critical temperature of neon, calculated from the assumption that its viscosity at the critical temperature is proportional to the atomic weight and from Sutherland's equation, is 61·1°*A*. Calculated from the relation that Sutherland's constant is proportional to the critical temperature, it is 62·7°*A*.

The viscosity of radium emanation at 0°, calculated from its atomic weight, critical temperature, and the value of Sutherland's constant, which is taken as proportional to the latter, is $2{\cdot}13 \times 10^{-4}$. The molecular volume calculated from this is 16·97 times that of helium, and larger than that of any other gas in the group. The deduction that the critical temperature, and therefore Sutherland's constant, is proportional to the fourth power of the true atomic radius, is found to hold good strictly for all the gases except helium, for which a departure is to be expected. F. S.

Researches on Helium. IV. Absorption of Helium by Salts and Minerals. ARNALDO PIUTTI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], **16**, 253—255 *).—The author finds that helium is absorbed by certain fused salts and minerals, and points out the bearing which this has on the calculations of the age of rocks, which have been made on the assumption that the helium contained in them has all been derived from radioactive elements.

Crystals of potassium sulphate deposited in the course of a month from an aqueous solution in an atmosphere of pure helium did not absorb the gas. On the other hand, antimonite, borax, and boric anhydride, after fusion in an atmosphere of helium, show the spectrum of the gas when they have been powdered in the air. If air is passed through fused borax or boric anhydride, and the fused mass then suddenly cooled by means of liquid air, the solid obtained shows the spectrum of helium. No helium can be found when air has not been passed through the fused salt. R. V. S.

The γ-Rays of Thorium and Actinium. ALEXANDER S. RUSSELL and FREDERICK SODDY (*Phil. Mag.*, 1910, [vi], **21**, 130—154. Compare Abstr., 1909, ii, 460, 851; 1910, ii, 474).—The two types of thorium γ-rays, from mesothorium-2 and thorium-*D*, resemble that of radium-*C*, both in the ratio of the intensity of the γ- to that of the β-rays and in their penetrating power. Thorium-*D* gives the most penetrating γ-rays known, the absorption-coefficient λ being from 8 to 21% less than for radium-*C* γ-rays, whereas for the mesothorium γ-rays, λ is from 4 to 25% greater than for radium, according to the experimental disposition used for the measurements. The γ/β ratio for mesothorium is from 1·0 to 0·8, and for thorium-*D* 0·69 to 0·51, times that for radium-*C*. The proportion of γ-rays contributed by the two thorium products in equilibrium in minerals is very similar. The γ/β ratio of actinium is only from one-eighth to one-sixteenth of that of radium-*C*, so that actinium in this respect resembles uranium-*X*. The γ-rays of actinium are abnormally highly absorbed by lead, the absorption curve showing two sudden changes in the value of λ at 0·3 cm. and 0·85 cm., whereas for zinc and aluminium the curves are exponential, λ being about 1·9 times that for radium-*C*. For lead the ratio ranges from about 8 times to about 2·2 times, according to the part of the range examined and the disposition employed.

Admixture of mesothorium with radium can be detected by the departure of the γ-ray absorption curve in lead from the exponential form, the γ-rays of mesothorium being distinctly the less penetrating. Some generalisations with regard to γ-rays show that they are more allied in properties to the α-rays which precede and follow them in the series than to the β-rays which accompany them. The penetrabilities of the γ-rays from uranium-*X*, mesothorium-2, radium-*C*, and thorium-*D* increase as the period of the product diminishes, as for α-rays in general, whilst the α-rays preceding and following these types of γ-rays show the same increase in penetrating power as the γ-rays themselves. The greater the penetrating power of the γ-rays, the less abnormal the absorption by lead as compared with other metals, and the less is the hardening produced by passage through lead. F. S.

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* and *Le Radium*, 1911, **8**, 13—14.

The Ionisation of the Atmosphere Due to Radioactive Matter. A. S. EVE (*Phil. Mag.*, 1911, [vi], **21**, 26—40).—The radioactive theory of the ionisation of the atmosphere is generally satisfactory, but some results remain unexplained. Assuming the presence of the emanation in equilibrium with 80×10^{-12} gram of radium per cubic metre of the atmosphere on the average, the ionisation so caused by the α-rays is 1·63 ions (per c.c. per second), while thorium, possibly, contributes not more than one additional.

From Wright's values of the natural ionisation in an aluminium electroscope at Toronto, on land and on the frozen surface of Lake Ontario, the ionisation contributed by the γ-rays from the radium in the earth is estimated to be in the free air about 2·5, which is smaller than that found in many experiments with lead-screened electroscopes, and suggests that part of the penetrating radiation comes from the atmosphere. It is calculated, however, that the penetrating rays of the atmosphere from the emanation and its products must produce an ionisation negligible in comparison with that due to the α-rays, and are one twenty-third as intense as the penetrating rays from the earth. The total ionisation of the air from all sources, assuming the penetrating rays of the radium and thorium series in the earth to be equal, and neglecting those from uranium and actinium, is 4·35, which is somewhat greater than the value normally found in clear weather.

The fact that the ionisation over the ocean is scarcely less than over the land is the greatest objection to the radioactive theory of atmospheric ionisation, for the amount of radium in sea-water is extremely small. It is calculated that there should be a rapid diminution of the effect due to γ-rays from the earth with altitude, detectable at an elevation of 100 metres, while at 1000 metres the effect should be negligible. In an appendix, Wulf's results (*Physikal. Zeitsch.*, 1910, **11**, 811) on the Eiffel tower are referred to as establishing this rapid diminution. F. S.

The Radioactivity of the Leinster Granite. ARNOLD L. FLETCHER (*Phil. Mag.*, 1911, [vi], **20**, 102—111).—The whole mass of the Leinster granite, covering 600 square miles, contains radium, the mean content being 1·7($\times 10^{-12}$ gram per gram). Separate specimens showed quantities varying from 0·41 to 4·36, the specimens showing the highest and lowest amount coming from the same locality. Probably the distribution is fairly homogeneous throughout. The mica in the granite, constituting about 20% of the whole, contained about half the radium, but the small quantity of thorium present did not seem to be concentrated in any constituent. One crystal of biotite, showing countless pleochroic halos and considerable radioactive darkening, contained 11·87 units of radium, but no thorium, and in the three specimens of granite containing the most radium there was no thorium. In ten out of twenty-three specimens, the ratio between the radium and thorium was between 2·0 and $2{\cdot}6 \times 10^{-7}$, the mean ratio for the whole series being $2{\cdot}4 \times 10^{-7}$. Details are given of the methods employed, including the latest form assumed by Joly's arrangement for estimating thorium in minerals. F. S.

A Spectroscopic Investigation of the Nature of the Carriers of Positive Electricity from Heated Aluminium Phosphate. FRANK HORTON (*Proc. Roy. Soc.*, 1910, *A*, 84, 433—449).—The value found for *e/m* for the positive ions from heated aluminium phosphate indicates a molecular weight of the carrier of about 28, and the possibility that the molecules are either nitrogen or carbon monoxide. Two hours' heating of a platinum strip coated with aluminium phosphate generated sufficient ions to allow of a spectroscopic examination of their nature. The spectrum was found to be the same whether the strip was heated simply, or in an electric field under conditions such that the ions would be formed, and in the electrodeless ring discharge showed the lines of carbon and oxygen together with others due to mercury and hydrogen, whilst in an electrodeless spectrum tube the banded spectrum of carbon monoxide was obtained. The conclusion is arrived at that the positive ions are molecules of carbon monoxide. F. S.

Relationship between Chemical Affinity and the Photo-electric Effects of Potassium in its Compounds. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1910, 12, 1039—1048. Compare Abstr., 1910, ii, 922).—The photo-electric properties of potassium alloys have been investigated, and it is shown that these are connected with the electro-chemical properties of the metal with which the potassium is associated. A comparison of the results obtained for bismuth, antimony, and phosphorus alloys shows that the normal photo-electric effect of potassium is displaced in the direction of smaller wave-lengths as the metal in combination with the potassium becomes more electro-negative. The same behaviour is exhibited by the alloys of the series bismuth, lead, thallium, mercury, and gold. In those cases in which a selective photo-electric effect can be observed, this is also found to be displaced in the same direction as the electro-negative character of the second component of the alloy becomes more pronounced. At the same time the range of wave-lengths which give rise to photo-electric activity becomes more restricted.

Since the frequency of the active rays affords a measure of the velocity with which the electrons leave the molecule of the photo-electrically active substance, it appears that the affinity between a metal and its electrons can be determined from observations on the wave-lengths of the rays which give rise to the photo-electric effect.
H. M. D.

Transference Experiments with Thallous Sulphate and Lead Nitrate. K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1910, 32, 1555—1571).—A study of the change of the transference number of tri-ionic salts with the concentration was carried out by Noyes (Abstr., 1901, ii, 143) with the object of ascertaining whether intermediate ions, such as KSO_4' in the case of potassium sulphate and $NO_3Ba^{\cdot}$ in that of barium nitrate, exist in appreciable quantities in solutions of such salts, and the results were recorded for potassium sulphate, barium chloride, and barium nitrate.

Transference experiments have now been made with 0·03*N*- and 0·1*N* solutions of thallous sulphate and lead nitrate at 25° with the aid of special apparatus. The cation transference numbers found for the thallous salt are 0·479 at 0·03*N* and 0·476 at 0·1*N*, and those for the lead salt 0·487 at both concentrations. The limit of error in these results does not exceed ±0·003. The transference numbers at zero concentration, as calculated from Kohlrausch's extrapolated values of the equivalent conductivities of the separate ions, are 0·489 for thallous sulphate and 0·503 for lead nitrate, and are thus 2·5—3·2% higher than the values obtained by direct measurement at a concentration of 0·03—0·1*N*. It is not certain whether this change of the transference number with the concentration is real. If so, it might be due, in the case of thallous sulphate, to the presence of the intermediate ion $TlSO_4'$. In the case of lead nitrate, however, the presence of the intermediate ion $NO_3Pb^{\cdot}$ would probably cause a change in the opposite direction.

The results of these experiments and those of Noyes (*loc. cit.*) on the transference values of tri-ionic salts indicate that either the intermediate ion is not formed to any considerable extent by the dissociation of such salts up to concentrations of 0·1 or 0·2*N*, or that, if it is formed, its equivalent conductivity has a definite value of such magnitude as to render the transference number independent of its concentration. E. G.

Method for Making Two Substances React in the Electric Arc. Paul Sabatier (*Compt. rend.*, 1910, **151**, 1328).—An apparatus similar to that described by Salmon (this vol., ii, 15) was employed by the author in 1899 (Congrès Assoc. francaise, I, 229). W. O. W.

A New Property of the Magnetic Molecule. Pierre Weiss (*Compt. rend.*, 1911, **152**, 79—81).—The magnetic susceptibility of magnetite has been measured at different temperatures between 550° and 900°, and the results plotted in the form of a curve. The conclusion is drawn that at certain temperatures the magnetic moment of the molecule increases by a definite aliquot portion of the magnetic moment at low temperatures, and the supposition is advanced that this is due to a variation in the size of the molecule or in the distance between the poles. W. O. W.

Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. V. Paul Pascal (*Bull. Soc. chim.*, 1911, [iv], **9**, 6—12. Compare Abstr., 1910, ii, 100, 179).—Further evidence of the additive character of magnetic susceptibility in organic compounds is given (compare Abstr., 1910, ii, 580), and the values of *B* (the correction, which peculiarities of structure necessitate in calculating molecular susceptibility) are given for a number of compounds free from oxygen and chlorine. The atomic susceptibilities for the usual constituents of organic compounds are as follows: $H = -30·5 \times 10^{-7}$; $C = -62·5 \times 10^{-7}$; $F = -63·0 \times 10^{-7}$; $Cl = -209·5 \times 10^{-7}$; $Br = -319·2 \times 10^{-7}$; $I = -465·0 \times 10^{-7}$. Those for nitrogen, sulphur, and variously linked oxygen have been given already (Abstr., 1910, ii, 100). For saturated open chain hydrocarbons, the value of B is *nil*, and the molecular susceptibility is given by the formula $S_M = -10^{-7}[n62{\cdot}5+(2n+2)30{\cdot}5]$. For a single open chain ethylenic linking, $B = +57 \times 10^{-7}$, and for two or more such linkings, $+110 \times 10^{-7}$. For a double linking between two nitrogen atoms, $B = +19 \times 10^{-7}$, for one between a carbon and a nitrogen atom it becomes $+85 \times 10^{-7}$, and for two such linkings it is $+106 \times 10^{-7}$, but for a triple linking, as in ·CN, it falls to $+8 \times 10^{-7}$. The influence of the *cyclo*propane nucleus is $B = +75 \times 10^{-7}$, which is much greater than that, $+31 \times 10^{-7}$, due to the *cyclo*hexane nucleus. Similarly, for the piperidine nucleus, $B = +37 \times 10^{-7}$. In *cyclo*hexene derivatives, $B = +72 \times 10^{-7}$, and in *cyclo*hexadiene compounds it is $+110 \times 10^{-7}$. These cases illustrate the general rule that the diamagnetism of the molecule in closed chain compounds falls with increase in the number of certain kinds of double linkings present. T. A. H.

Solutions. III. and IV. F. Schwers (*Zeitsch. physikal. Chem.*, 1910, **75**, 615—620, 621—627; *Bull. Soc. chim.*, 1910, [iv], **7**, 1072—1077, 1077—1083.* Compare Abstr., 1910, ii, 1039).—III.—*Relationship between the Density and the Magnetic Rotation of the Plane of Polarisation of Binary Mixtures.*—It is shown from the data of Sir W. H. Perkin, that the ratio between the alterations of the density (difference between observed density and that calculated according to the mixture rule) and the alterations of the magnetic rotation (difference between observed and calculated rotation) is a constant for mixtures of the two components in any proportion. The constant, Z, has a definite value for each system, and when solutions of the same substance (water) in the different members of an organic series are examined, Z is found to increase with increasing molecular volume.

It is shown by reference to mixtures of sulphuric acid and water, and of nitric acid and water, that when electrolytic dissociation occurs, Z diminishes steadily with increasing dilution.

IV.—*Density, Refractivity, and Magnetic Rotation of Dissociating Mixtures.*—As in the case of sulphuric and nitric acids, the constants Z for hydrochloric, hydrobromic, and hydriodic acids in aqueous solution also diminish on dilution. When the molecular volume is increased by substitution of iodine or bromine for chlorine, the rotation constant diminishes and the refraction constant (calculated in a similar way) increases. When, however, the increase of molecular volume is due to an increase in the number of atoms in the molecule, the effect on the constants is the converse of that mentioned above. Electrolytic dissociation brings about an increase of the magnetic rotation of the plane of polarisation, and a diminution of the refractivity with reference to the density, if the latter is regarded as constant. G. S.

The Isolation of Long-waved Heat Rays by Quartz Lenses. Heinrich Rubens and Robert W. Wood (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 1122—1137).—A method is described by means of which heat rays of wave-lengths ranging from 80μ to 200μ

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* and *Bull. Acad. roy. Belg.*, 1910, 850—883.

can be isolated from the rays emitted by an incandescent mantle. The rays from the mantle are passed through two quartz lenses which are suitably placed with reference to the source of light, and the isolation of the long-waved rays is essentially dependent on the selective refraction of the quartz lenses. The bundle of rays obtained by this method is far from homogeneous, but the energy content is much greater than that of the homogeneous rays obtained by selective reflexion. By means of a radio-micrometer, the distribution of energy amongst the component rays of the bundle has been examined, and these measurements show a maximum intensity in the neighbourhood of $\lambda = 100\mu$.

Observations are also recorded which show the extent to which the long-waved rays are absorbed by various solid, liquid, and gaseous substances, and a comparison is made between the amounts of these rays and of those obtained by selective reflexion from potassium bromide ($\lambda = 82\mu$), which are reflected; by various substances. In the case of rock-salt, fluorspar, and glass, the proportion of the reflected quartz rays is in good agreement with that calculated from the dielectric constants of those substances. H. M. D.

A Simple Automatic Stirrer for Use with the Depressimeter. Lodewyk Th. Reicher (*Chem. Weekblad,* 1910, **7**, 1085—1087).—The author has devised an automatic stirrer for use with the depressimeter. A copper disk supported by a horizontal axle held by a clamp is connected with a jointed iron rod by means of an eccentric attachment. A horizontal arm connects the rod with the vertical stirrer. The bearing of the rod can be moved nearer to, or further from, the centre of the disk, thus diminishing or increasing its eccentricity. The motive power is supplied by a hot air engine through a belt to the copper disk. A. J. W.

Vapour Pressures of Binary Mixtures in the Light of van der Waals' Theory. II. Philipp Kohnstamm (*Zeitsch. physikal. Chem.*, 1910, **75**, 527—551. Compare Abstr., 1901, ii, 145).—Considerable light is thrown on the vapour-pressure curves of binary mixtures by a mathematical treatment based on the introduction by van der Waals of a new factor, the vapour pressure of an ideal binary mixture, the "mixture assumed as uniform," defined as follows. In the ordinary *pv*-diagram for a single substance, the part of the isothermal joining the points on the diagram representing the gas and liquid phases is a straight line, but in the case of a binary mixture the corresponding part of the diagram will be a sloping and not a horizontal line (as evaporation does not occur at constant pressure). The "uniform mixture" is an ideal mixture, such that the line in question is horizontal, as for a simple substance. By making use of the (hypothetical) critical pressures and temperatures of such mixtures, a number of deductions as to the possible types of binary vapour-pressure curves are made. For the method used and the forms of the curves on different assumptions as to the relative magnitude of the factors concerned, the original paper should be consulted. G. S.

Method for Determining the Molecular Weights of Dissolved Substances by Measurement of Lowering of Vapour Pressure. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, 32, 1615—1624).—Apparatus is described for the determination of molecular weights in cases in which great accuracy is not required. It consists of an outer tube, in which the solvent is boiled, attached to a small, reflux condenser, and an inner test-tube provided with a pressure gauge-tube and a glass stopper. The side-tube from the outer tube to the condenser is of 1 cm. diameter, so that the solvent may boil under the barometric pressure, and is connected to the condenser by means of rubber tubing, furnished with a screw-clip. When the stopper is removed and the clip closed, the vapour of the liquid boiling in the outer tube escapes through the gauge-tube, which is open at both ends, into the test-tube. A narrow U-shaped side-tube connects the condenser with the lower part of the outer tube, and the condensed liquid is thus returned to the outer tube without cooling the upper part of the test-tube. Both the test-tube and gauge-tube are graduated. The lower end of the gauge-tube is in the form of a bulb, which is perforated by a number of holes to distribute the vapour as it issues. The boiling solvent in the outer tube maintains at a constant temperature the test-tube which contains the solution, the vapour pressure of which is being determined. The pressure is measured by the difference in the level of the liquids in the gauge-tube and test-tube.

The values of $K_{760} = p\text{-}p'$ (where p is the vapour pressure of the solvent, and p' that of the solution), that is, the lowering of vapour pressure in mm. of boiling solvent that would be caused by the presence of 1 gram-mol. of a non-volatile solute in 1 litre of solution, have been calculated for various solvents. The molecular weight can be calculated from the formula $M = 1000WKB/LV \times 760$, where W is the weight of solute added, L the measured lowering of the vapour pressure in mm., V the volume of the solution in c.c., and B the height of the barometer.

A series of determinations, carried out with this apparatus, are quoted, and the method is compared with ebullioscopic methods.

It is shown that, within the limits of error of observation, the vapour pressures are identical whether determined by static or dynamic methods, and that if any difference at all exists between the vapour pressure at the b. p., as measured statically and dynamically, of water and alcohol, such difference does not exceed 0·01 mm. of mercury. E. G.

Convenient Form of Apparatus for the Measurement o. the Vapour Densities of Easily Volatile Substances. ALAN W. C. MENZIES (*J. Amer. Chem. Soc.*, 1910, 32, 1624—1628).—The apparatus described is a slight modification of that recommended by the author for the determination of molecular weights of dissolved substances (preceding abstract). The test-tube is closed at the lower end by the introduction of 6—8 c.c. of mercury, which also serves, by its rise in the gauge-tube, to indicate the increase of pressure in the test-tube. The substance, the vapour density of which is to be determined, is placed in small glass bulbs, each provided with a capillary which is sealed off before the final weighing. The bulb is attached to the lower end of the stopper of the test-tube by inserting the point of the capillary into a hole drilled in the stopper and wedging it in with a few shreds of dry asbestos. The hole is made in an oblique direction, so that the neck of the bulb may be broken by rotating the stopper in such a way as to force the bulb against the top of the gauge-tube.

In order to obtain a constant for the apparatus, a quantity of benzene sufficient to give a rise in the mercury level of about 100 mm., is weighed in a small bulb and the latter is attached to the stopper of the test-tube. A liquid of suitable b. p. is placed in the outer tube and caused to boil steadily, so that its vapour surrounds the whole of the closed portion of the test-tube. As soon as the mercury in the gauge-tube has attained a constant level, the stopper of the test-tube is rotated in order to break the neck of the small bulb, which falls on to the surface of the mercury. The mercury instantly rises in the gauge-tube and reaches a constant level in a few seconds. The rise in the mercury column is observed, and a correction made by adding the amount of the slight fall of the level of mercury in the test-tube. From the data (1) weight of benzene taken, (2) molecular weight of benzene, and (3) rise of mercury in mm., the required constant K is calculated, representing the rise in mm. which would be caused by the volatilisation of one gram-mol. of any substance in the apparatus at the particular temperature.

The molecular weight of a substance can be calculated by means of the formula $M = WK/R$, where R is the rise of the mercury in mm., and W the weight of substance taken.

The apparatus is compact and can be easily manipulated. It is not suitable for temperatures above 200°, but determinations are quoted which show that the method is both rapid and accurate at other temperatures. E. G.

Fall of Temperature in Vapours of High Molecular Complexity at Small Pressures. C. von Rechenberg (*Zeitsch. physikal. Chem.*, 1910, **75**, 628—636).—Polemical against Hansen (Abstr., 1910, ii, 827). No new facts are adduced. G. S.

Critical Phenomena in Solutions under the Kardioid Ultra-microscope. W. G. von Lepkowski (*Zeitsch. physikal. Chem.*, 1910, **75**, 608—614).—The ultramicroscope, in its latest improved form, has been employed to elucidate the nature of the opalescence in binary mixtures in the critical region. The results are, on the whole, in favour of Donnan's theory (Abstr., 1904, ii, 240) that the opalescence is due to minute drops.

A mixture of amylene and aniline, critical temperature 14·2—14·5°, was used for the experiments. On cooling progressively from room temperature, 20°, a grey field with a clear circle in the middle was observed; at a certain point the previously clear field appeared as a rapidly agitated mass, in which separate particles could not be distinguished. As the temperature is further lowered (but still above the critical temperature), the flickering becomes still more pronounced, the ultramicroscopic particles moving with enormous velocity. Suddenly, relatively large drops appear, and the critical temperature is reached. The phenomena appear in the converse order on warming. Particles from the small drops are projected into the bulk of the liquid with enormous velocity; the drops become smaller and smaller, and finally disappear. The remarkable observation was made that when a relatively large drop is warmed until it has disappeared, and even the flickering has stopped, it reappears on cooling at the same point and with the same contours. This phenomenon occurs repeatedly on warming and cooling. It may be taken as showing that the rate of diffusion in the critical region is very small. G. S.

Sublimation Apparatus. EMIL DIEPOLDER (*Chem. Zeit.*, 1911, **35**, 4).—The apparatus consists of a wide glass tube sealed at the lower end, and closed at the upper by a rubber cork carrying two tubes, one of which serves for the entrance of air or other gas, whilst the other is attached to a wider tube which fits accurately into the outer closed tube and acts as a receptacle for the sublimate.

The substance to be sublimed is contained in a small beaker placed at the bottom of the outer tube.

The apparatus may be used for sublimation either at the ordinary or under diminished pressure. F. B.

Thermochemical Studies of Some Binary Compounds of the Alkali and Alkali-earth Metals. ROBERT DE FORCRAND (*Compt. rend.*, 1911, **152**, 27—31).—The author has collated in tabular form the best existing data for the heats of dissolution and formation of the chlorides, bromides, iodides, fluorides, and oxides of calcium, strontium, barium, lithium, sodium, potassium, rubidium, and cæsium. Determinations of the heats of dissolution of the following anhydrous compounds were made to complete the series. The values are in Calories. $CaI_2 + 28{\cdot}12$, $LiF - 1{\cdot}04$, $RbCl - 4{\cdot}50$, $RbBr - 5{\cdot}96$, $RbI - 6{\cdot}50$, $RbF + 5{\cdot}80$, $CsCl - 4{\cdot}68$, $CsBr - 6{\cdot}73$, $CsI - 8{\cdot}25$, $CsF + 8{\cdot}37$. The data are discussed from the point of view of Berthelot's principle of maximum work. W. O. W.

Thermochemistry of the Silicates. EMIL DITTLER (*Zeitsch. anorg. Chem.*, 1911, **69**, 273—304. Compare Abstr., 1909, ii, 970).—The difficulties of obtaining correct cooling and heating curves in the case of silicates, owing to the suspended transformation effects, are fully discussed, and the precautions which must be taken are enumerated. Thermal and optical measurements on diopside from Zermatt, adularia from St. Gotthard, oligoclase-albite from Wilmington (Delaware), labradorite from Kiew, an artificial labradorite, artificial anorthite, and anorthite from Pizmeda are given.

Owing to the extremely small velocity of melting, the absorption of heat at the melting point is not the chief factor in the heating curve, so that with different velocities of heating the melting point will occur at different points in the curve. Melting point determinations on large fragments must be avoided, since they are more readily superheated than a fine powder and thus give higher results.

Geologically, freezing points are more important than melting points, and are generally lower than the latter, owing to undercooling. The temperatures at which crystallisation begins to take place in various minerals are as follows: artificial diopside, 1290—1250°; artificial labradorite, 1230°; labradorite from Kiew, 1200—1160°; artificial anorthite, 1310°; anorthite from Pizmeda, 1200°. The temperatures at which crystallisation is complete could not be determined.

T. S. P.

Determinations of the Law of Chemical Attractions between Atoms from Physical Data. Richard D. Kleeman (*Phil. Mag.*, 1911, [vi], **21**, 83—102).—From data of Ramsay and Young, and Mills relating to surface tension and latent heat of benzene, chlorobenzene, carbon tetrachloride, and methyl formate, and to the critical density of ethyl ether, $\beta\gamma$-dimethylbutane, $\beta\epsilon$-dimethylhexane, *iso*pentane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, benzene, *cyclo*hexane, fluorobenzene, chlorobenzene, bromobenzene, iodobenzene, carbon tetrachloride, and stannic chloride, various consequences of the mathematical expressions deduced in previous papers are tested. F. S.

Recovery of Hammered Materials. Léon Guillet (*Compt. rend.*, 1910, **151**, 1127—1128).—Experiments on hard and soft steel and on nickel show that complete recovery on annealing, characterised by attainment of maximum length, occurs in each case at 750—800°. The curves showing elasticity on traction exhibit two elastic limits, one constant and characteristic for the metal in the ordinary state, the other variable with the temperature of recovery. The metals in this respect behave as heterogeneous materials of which only one constituent shows the effects of hammering. W. O. W.

Some Abnormal Temperature-coefficients of the Molecular Surface Energy of Organic Substances. Paul Walden (*Zeitsch. physikal. Chem.*, 1910, **75**, 555—577).—According to the Eötvös-Ramsay-Shields rule, the temperature-coefficient of the molecular surface energy, $d[\gamma(Mv)^{\frac{2}{3}}]/dt$, is about 2·121 for unimolecular substances, for associated substances it is less, and for dissociated substances greater. The author now finds that the coefficient in question is 6·21—5·35 for tristearin and 5·57—4·92 for tripalmitin, between 60° and 120°, whereas the molecular weights, according to cryoscopic determinations with a number of organic solvents, are normal. The coefficient for the *iso*butyl ester of ricinoleic acid amounts to 3·24—3·30 between 23° and 85°, whilst its molecular weight is normal. The above rule therefore does not hold even approximately, and the deviations appear to be the greatest for complex substances of high boiling point. The surface-tension of solutions of tripalmitin and tristearin in benzene has also been measured. The average value of the coefficient for both solutions calculated according to the mixture rule is about 2·18; the solutions therefore behave as non-associated and non-dissociated liquid systems.

On the other hand, two hydroxyl-free solvents with abnormally small coefficients of molecular surface energy, succinonitrile and formamide, have been investigated. From the results of surface-tension measurements, the coefficient for the nitrile between 80° and 100° is 0·565, indicating a molecular complexity of 7·27, from 100—118° it is 0·601, the complexity being 6·63. For formamide, between 5° and 60°, the coefficient varies from 0·638 to 0·710, corresponding with a molecular complexity of 6·75—5·17. The conclusion that these two compounds are highly associated is confirmed by cryoscopic and ebullioscopic measurements. G. S.

The Viscosity of Dispersoids. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 34—39. Compare this vol., ii, 19).—On the basis of certain assumptions relating to the form and distribution of the disperse phase in the dispersive medium, the author has examined the changes which should result from the disturbance of the normal arrangement of the disperse phase as a consequence of the relative movement of juxtaposed layers of an emulsion, and has deduced a relationship between the viscosity of the emulsion and that of the dispersive medium.

The effect of this relative movement, such as is involved in the flow of the emulsion through capillary tubes, is dependent on the relative magnitudes of the surface tension and the viscosity of the disperse phase if the proportion of this is very large, and a decrease in the viscosity of the disperse phase is shown to be accompanied in certain circumstances by an increase in the viscosity of the emulsion.

For a disperse system of this type, there is a critical velocity of displacement of juxtaposed layers at which an abrupt change takes place in the viscosity, and this velocity is determined by the rate at which the particles of the disperse phase regain their original structural form when deformed as a result of the lateral displacement of these layers. For velocities of displacement greater than this critical value, the relationship between the viscosity of the emulsion and that of the dispersive medium is expressed by $\eta_1 = \eta \sqrt[3]{f}/(\sqrt[3]{f} - 1)$, in which η_1 and η are the viscosities of the emulsion and the dispersive medium, and f is the ratio of the volume of the emulsion to that of the disperse phase. For velocities of displacement smaller than the critical value, the mathematical treatment of the question presents difficulties, but it is shown that the viscosity of the system under these conditions must be greater than for greater velocities.

H. M. D.

The Phenomenon of Agglomeration in Finely Powdered Substances. M. C. SCHUYTEN (*Chem. Zeit.*, 1910, **34**, 1357).—A sample of pure iron powder, kept for fifteen years in a well stoppered bottle, which had not undergone oxidation, had formed a globular mass with a peculiar goose-neck shaped excrescence.

Barium sulphate, prepared by mixing equivalent proportions of solutions of barium chloride and ammonium sulphate, gradually formed conical excrescence, reaching a length of 6—7 cm. The author ascribes these phenomena to physical actions. L. DE K.

Globular Appearance of Certain Precipitates. FRIEDRICH BARDACH (*Chem. Zeit.*, 1911, **35**, 33).—The globular or flocculent appearance assumed by finely divided substances, such as precipitated barium sulphate, etc., has been fully discussed by Quincke (Abstr., 1902, ii, 200) and others, who attribute the phenomenon to the action of osmotic pressure, surface tension, etc. The outer surface of the flocks has a characteristic appearance, whilst the interior frequently exhibits a cell-like structure. W. P. S.

Parallelism between the Occurrence of Cohesion and the Conditions Necessary for Dyeing. Auguste Rosenstiehl (*Bull. Soc. chim.*, 1911, [iv], **9**, 12—18. Compare Abstr., 1909, ii, 796).—A number of cases are quoted showing that the conditions under which cohesion occurs between the same or different substances are exactly analogous to those under which the dyeing of fabrics takes place, and it is suggested that cohesion between dye and fabric plays the principal rôle in this operation, although chemical affinity between dye and fabric may also be operative. T. A. H.

Deduction of the General Phase Theorem for Adsorption Systems. P. N. Pawloff (*Zeitsch. physikal. Chem.*, 1910, **75**, 552—554).—The form of the phase rule for a system capable of adsorption is deduced mathematically; it is similar to that for a system in which adsorption does not occur. Condensed disperse systems capable of absorption have six kinds of variables, whereas colloidal adsorption systems are characterised by seven variables.
G. S.

A New Proof of the Existence of an Adsorption Equilibrium in Hydrosols. Alfred Lottermoser and P. Maffia (*Ber.*, 1910, **43**, 3613—3618).—Experimental results are recorded in support of the view that electrolytes are adsorbed by hydrosols in accordance with an exponential law. Freshly precipitated ferric hydroxide was dissolved in ferric chloride solution, and a portion of the electrolyte removed by filtration through collodion. The contents of the filter were then diluted with water, and the solution again filtered, this process being repeated until a hydrosol containing relatively little chlorine was obtained. From this hydrosol a series of others were prepared by addition of varying quantities of water, and each of these was then subjected to filtration through collodion. The chloride in the various filtrates was estimated, and by difference the adsorbed chloride was ascertained. Denoting by c the number of millimols. of chlorine per c.c. of the filtrate, and by x/m the millimols. of chlorine adsorbed by one gram of ferric oxide, it is found that the experimental data can be satisfactorily represented by the equation: $x/m = \beta . c^{1/p}$, in which $\beta = 2{\cdot}83$ and $1/p = 0{\cdot}163$ are constants. Similar results were obtained in the investigation of a ferric oxide hydrosol prepared by addition of ammonium carbonate to a solution of ferric chloride. H. M. D.

"Anomalous" Adsorption. William M. Bayliss (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 2—4).—The so-called "anomalous" adsorption recently observed by Biltz and Steiner (Abstr., 1910, ii, 830) can be accounted for on the basis of the author's observations on "electric adsorption" (Abstr., 1906, ii, 344). In these experiments filter-paper was the adsorbent, and this becomes negatively charged in contact with water. In consequence of this electric charge, electro-positive colloids are attracted by the paper, whilst electro-negative colloids are repelled. In presence of neutral salts, the negative charge is partly or completely neutralised by the cation, and as a result the adsorption of electro-negative colloids is facilitated, whilst that of electro-positive colloids is hindered. This neutral salt action explains the absence of "anomalous" adsorption in the experiments of Biltz and Steiner, when dialysed night-blue was used instead of the commercial substance. It also accounts for the approximately normal adsorption observed in the experiments in which dilute solutions of the dye were examined. H. M. D.

Capillary Analysis of Colloidal Solutions. Naima Sahlbom (*Koll. Chem. Beihefte*, 1910, 2, 79—141).—The behaviour of colloidal solutions of a number of inorganic substances has been investigated by observations of the capillary effects produced when long strips of filter paper are supported with the lower edges immersed in the solutions. It has been found that the positive colloids are precipitated at the surface of contact, whereas negative colloids rise through the capillary network without hindrance. The precipitation of the positive colloids is not due to chemical action, but to the setting up of an *E.M.F.* as a consequence of the streaming of the liquid through the capillaries; this potential difference brings about the discharge of the positively charged colloidal particles. If the capillaries are not sufficiently narrow, the resulting *E.M.F.* is not large enough to give rise to complete precipitation, and a rise of the positive colloid is observed.

A detailed examination of the phenomena observed in the case of colloidal ferric hydroxide has shown that the free acid present in an incompletely dialysed solution prevents complete precipitation. Addition of acid to a completely dialysed hydrosol has the same effect. The capillary phenomena exhibited by solutions of colouring matters are in many cases closely similar to those observed with inorganic colloids. H. M. D.

Capillary Electrical Precipitation of Positive Colloids. Fritz Fichter (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 1—2. Compare preceding abstract).—The precipitation of positive colloids as a result of the production of electrical forces by diffusion through capillary tubes has been further examined by experiments with parallel glass plates. When a drop of a dialysed colloidal solution of ferric hydroxide is placed on one of the plates, and the second plate is allowed to sink slowly on to the former, it is found that the thin layer of solution between the plates exhibits a sharply defined circular opalescent zone in consequence of the precipitation of the positive colloid. A similar phenomenon is observed with colloidal solutions of chromic oxide, zirconium dioxide, and thorium dioxide. With coloured solutions of basic dyes, such as night-blue and methylene-blue, the visible effect is still more pronounced.

From the dimensions of the circular zone of precipitation and the weight of the solution between the plates, the critical distance between the plates requisite for the production of the precipitation can be calculated. In the case of ferric hydroxide, this was found to be 0·0322, but this is very much smaller than the value (0·075 mm.) expected on the basis of experiments with capillary tubes. The much smaller value is probably due to mechanical displacement of the precipitation zone when the plates are brought together.

In similar experiments with solutions of negative inorganic colloids and acid dyes no precipitation effects are observed. H. M. D.

Origin of Internal Pressure in Solutions. V. Polowzoff (*Zeitsch. physikal. Chem.*, 1910, **75**, 513—526).—According to Tammann (*Innere Kräfte und Eigenschaften der Lösungen*, Leipzig, 1907), the greater internal pressure in a solution as compared with the pure solvent is due to attraction between solvent and solute, and is of the same nature in electrolytes and non-electrolytes. Drude and Nernst (*Zeitsch. physikal. Chem.*, 1894, **15**, 79), on the other hand, ascribe the increased pressure, at least in the case of electrolytes, to the effect of the electrostatic field of the ions (theory of electrostriction), and in accordance with this view, it has been found that the complete ionisation of a mol. of a binary salt is attended by a contraction (resulting from the increase of pressure) of 13—14 c.c. In the present paper, further evidence is advanced in favour of the electrostriction theory.

From observations on the density of solutions of monochloroacetic acid in different dilutions, the degree of dissociation of the salt being known, it is calculated that the complete ionisation of a mol. of the salt is attended by a contraction of about 10 c.c. On the other hand, the apparent molecular volume of ethyl alcohol in benzene only varies slightly from dilute to very concentrated solutions, although the molecular complexity greatly diminishes on dilution. This is difficult to reconcile with Tammann's theory, as an increase in the number of molecules should cause increased attraction between solvent and solute, and therefore increased internal pressure and consequent contraction. The data of Ritzel (Abstr., 1907, ii, 740) on the compressibility of solutions of ethyl alcohol in benzene are also in favour of the view that the internal pressure does not increase on dilution. Finally, it is shown by an indirect method that the dissociation of amyl acetate into amylene and acetic acid is attended by an increase and not by a diminution of volume. This is in agreement with Nernst's theory—as no ions are concerned there can be no electrostriction.

The electrostriction theory cannot of course account for the increased internal pressure caused by dissolution of non-electrolytes, such as the sugars and glycerol, in water; these solutions require further investigation. G. S.

Influence of Foreign Substances Dissolved in the Mother Liquor on the Faces of Crystals of Meconic Acid and on their Pseudopolychroism. Paul Gaubert (*Compt. rend.*, 1910, **151**, 1134—1136. Compare Abstr., 1906, ii, 152).—Meconic acid occurs in orthorhombic, hemimorphic crystals having curved faces and showing marked double refraction [$a:b:c=0{\cdot}613:1:0{\cdot}900$; $\alpha=63°$, $\beta=138°$]. Addition of different substances to the solution in which the crystals are growing may modify the crystalline form to a considerable degree; thus, picric acid produces elongation in the direction of the axis *a*, whilst methylene-blue elongates the axis *b*. The extent of elongation depends on the amount of foreign matter absorbed by the crystal. A large quantity of methylene-blue produces hemimorphism, the crystals being H-shaped. Addition of carbamide to the mother liquor causes the crystals to exhibit pseudopolychroism when viewed through a Nicols' prism. This appears to be due to the presence of microscopic bubbles which produce partial absorption through repeated reflexion. W. O. W.

Theory of the Phenomena of Transition between Colloidal and True Solutions. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 24—33).—A theoretical paper in which the author discusses the relationships between unsaturated, supersaturated, and colloidal solutions in reference to the action of the dispersive and coagulating forces. The hydrosols of slightly soluble substances are qualitatively differentiated from the corresponding unsaturated solutions by the fact that continuous condensation takes place in the former. In accordance with this view, the disperse particles are not amorphous, but are characterised by vectorial structure. The forces which determine the vectorical arrangement are peculiar to the molecules, and the play of these forces is not inhibited by the excessive development of the surface which is characteristic of colloidal systems.

Observations relating to the precipitation of supersaturated solutions of barium sulphate are cited in support of the author's views.

H. M. D.

The Micellary or "Colloidal" State. Giovanni Malfitano (*Koll. Chem. Beihefte*, 1910, **2**, 142—212).—A theoretical paper in which the relationships and differences between the colloidal and crystalloidal states and between the processes of coagulation (flocculation) and crystallisation are examined. In part, the theoretical considerations have reference to experimental observations published previously (Abstr., 1909, ii, 473) on the behaviour of solutions of ferric chloride. H. M. D.

The Saturation Capacity of Colloidal Compounds. Walthère Spring (*Bull. Soc. chim. Belg.*, 1910, **24**, 446—453; *Arch. Sci. phys. nat.*, 1910, [iv], **30**, 561—571).—Observations relating to the influence of saponin on suspensions of soot in water are described, which seem to show that the capacity of colloidal substances to form complex aggregates is limited, in a similar way to that observed in the case of chemical combination.

From preliminary experiments with solutions of saponin, it appears that this substance occupies a position intermediate to the colloids and crystalloids. Its solutions show the Tyndall effect, and under the influence of a current the saponin moves towards the anode; on the other hand, dialysis experiments show that it undergoes diffusion.

To ascertain the influence of saponin on the durability of soot suspensions, solutions containing from 7·5 to 0·0045% of saponin were shaken up with the same quantity of soot, carefully freed from fatty matter by extraction with benzene, and the times required for the clarification of the solutions were observed. From these data it appears that a solution containing between 2·5 and 3% of saponin is most favourable to the persistence of the suspension. If the solutions are made either slightly acid or alkaline, clarification takes place in all cases very quickly, and there is no optimum effect. When a current is passed through the most durable suspension, the soot migrates to the anode, although a pure aqueous soot suspension shows the opposite effect. This indicates the formation of colloidal aggregates as a result of the adsorption of saponin by the soot. The effect of saponin on the behaviour of suspensions of soot when subjected to filtration has been examined, and it appears that the adsorption of the soot by other substances, such as filter-paper, is to a large extent prevented by reason of the formation of soot-saponin aggregates. The view that the formation of colloidal aggregates or adsorption compounds is limited by a definite saturation capacity, is supported by this and a number of other observations of similar character which are described in detail. H. M. D.

Colloidal Chemistry and the Phase Rule. W. P. A. JONKER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 15—18).—The applicability of the phase rule to colloidal systems is discussed, and the conclusion drawn that the relatively large amount of surface exhibited by colloidal substances is without influence on the nature of the equilibrium relationships from the phase rule point of view. The coagulation of colloids is not comparable with the separation of a liquid into two layers, for the former process is not accompanied by by an increase in the number of phases. Objection is taken to the introduction of surface tension as a new independent variable in the consideration of colloidal systems, for surface tension is quite different in character from temperature and pressure, in that its magnitude cannot be varied at will.

In reference to the connexion between the amorphous and crystalline states, it is stated that realgar is a suitable substance for experimental investigation. This can be obtained in amorphous or crystalline form by melting together equivalent quantities of sulphur and arsenic. The crystalline variety melts at 320°, whereas the amorphous becomes liquid at about 130°, and when heated to 350° its properties change in a continuous manner. These observations are cited as evidence in support of the view that the amorphous and crystalline forms are to be regarded as distinct phases. H. M. D.

The Equilibrium between Potassium Hydrogen Carbonate and Trihydrated Magnesium Carbonate. NANTY (*Compt. rend.*, 1910, **151**, 1352—1354).—Polemical against Engel (Abstr., 1886,

121) and Buchner (*Zeitsch. Elektrochem.*, 1908, **14**, 63). The author has re-examined the conditions of equilibrium in the reaction

$$KHCO_3 + MgCO_3,3H_2O + H_2O \rightleftarrows MgCO_3,KHCO_3,4H_2O,$$

and is unable to confirm the existence of two distinct limits of formation and decomposition for the reverse reactions at 20—30°. For the same temperature, at constant pressure, the actions appear to converge towards a common limit. W. O. W.

Electron Conception of Valency. K. George Falk and John M. Nelson (*J. Amer. Chem. Soc.*, 1910, **32**, 1637—1654).—Thomson's hypothesis, that each linking between the atoms of a compound is due to the transference of a negatively-charged corpuscle from one atom to the other, is considered in its application to various classes of organic compounds, and references to its application to inorganic compounds are quoted from the papers of Noyes (Abstr., 1908, ii, 349) and Ramsay (Trans., 1908, **93**, 774). It is shown that all cases of isomerism, connected with the presence of a double bond, whether between like or unlike atoms, can be interpreted on the basis of the direction of the valencies (that is, the direction of transference of the corpuscles) without recourse to spatial configurations. The theory of directive valencies is also employed to account for the existence of certain isomerides, and to account for certain reactions which have not been explained previously. E. G.

Stokes's Formula. Max Reinganum (*Ber. Deut. physikal. Ges.*, 1910, **12**, 1025—1038).—In view of the frequent application of Stokes's formula in the calculation of the diameters of small particles from observations on their velocities of movement under the influence of a known force, the author has examined the conditions under which this formula holds good. For very small particles, such as the ions in gases, the formula is not valid, and it is shown that the determination of the dependence of the velocity of such particles on the pressure of the gas may be used as a means of ascertaining whether Stokes's equation is applicable or not. In the use of the small metallic particles investigated by Ehrenhaft (*Physikal. Zeitsch.*, 1910, **10**, 318, 940), the uncorrected equation is inapplicable, and the calculated diameters of the smallest particles are in consequence incorrect.

On the assumption that the small particles can be regarded as elastic spheres similar to gas molecules, the author deduces a new formula connecting the radii of the spheres and their velocity of movement. According to this, the radius of the particles is proportional to the velocity, whereas in Stokes's formula the radius is proportional to the square-root of the velocity. For a given radius the new formula shows that the velocity is inversely proportional to the density of the gaseous medium, but according to the older formula the density of the gas is without influence on the velocity of the particles.

From the data of Ehrenhaft, the dimensions of the particles calculated from the two formulæ are compared. In the case of gold and platinum the calculated values are nearly the same for the larger particles, but the author's formula gives much smaller values for the radii when the most slowly moving particles are considered.

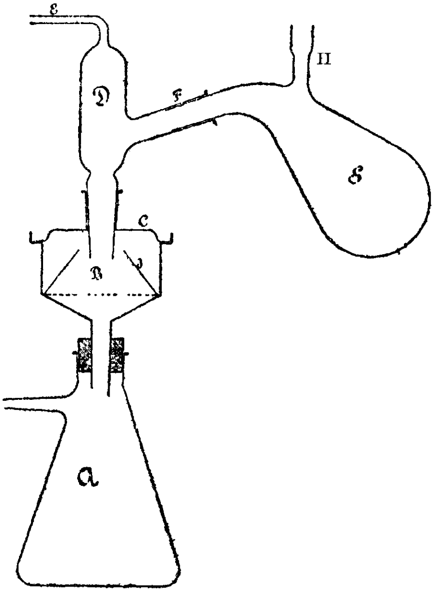
H. M. D.

Automatic Rapid Mercury Pump for High Vacua. A. BEUTELL (*Chem. Zeit.*, 1910, **34**, 1342—1343).—With one of the author's mercury pumps a vacuum of 0·0007 mm. can be obtained in ten minutes, and one of 0·0001 mm. in twenty minutes, whilst after twenty-five minutes it was impossible to measure the vacuum with a McLeod gauge. Only 0·29 kg. of mercury is necessary to work the pump.

A photograph of the pump, as mounted, is given, but no details.

T. S. P.

A Modified Separating Funnel and Washer for Heavy Liquids. HARFORD M. ATKINSON (*Chem. News*, 1910, **102**, 308).—The funnel consists of an ordinary tap funnel, with a second tap and short tube inserted about half-way up the side of the bulb. The washing liquid, etc., can be run off by this side tap, and further washings performed without running off the heavy liquid. The drying with calcium chloride can also be carried out in the funnel. N. C.



Filtering Apparatus for Substances which are Hygroscopic or Altered by Exposure to Air. WILHELM STEINKOPF (*Chem. Zeit.*, 1910, **34**, 1358).—On the suction flask, *A*, is placed a Büchner funnel, *B*, having a ground flange, the edge of which is turned upwards to prevent the lid from slipping; the funnel is closed by means of a ground-glass lid, *C*, furnished with a neck. Into this fits the adapter, *D*, which has a tube, *E*, bent at right angles, and a side tubulus, *F*, into which the neck of the reaction flask, *G*, is ground. This neck is bent at such an angle that when the bulb of the flask is turned upwards, the contents, liquid and precipitate, readily flow into *D*. The neck of the flask, *G*, also has a tubulus, *H*, which during the reaction proper may be connected with a reflux condenser or a gas-delivery tube, but during filtering is fitted with a separating funnel containing the washing liquid. *H* is placed not in the position shown in the diagram, but so much to one side that the contents will not run into it when the flask is rotated in *F*. To prevent moisture entering during the filtration, phosphoric oxide tubes are attached to *E* and to the side-tube of *A*, leading to the pump. As the solvents used are generally ether, benzene, light petroleum, and the like, it is advisable to place on the dry filter paper a cut and ground inverted funnel, *J*, which keeps the paper in position and also prevents any splashing of the precipitate on to the sides of the Büchner funnel. If desired, an inert gas can be transmitted through *E*. L. DE K.

Automatic Extraction of Aqueous Liquids by Organic Solvents of Lower Density. RICHARD KEMPF (*Chem. Zeit.*, 1910, **34**, 1365—1366).—The apparatus consists of a flask surmounted by two tubes placed concentrically to one another; the vapour from the boiling ether, etc., passes through the annular space between the tubes to a condenser. The condensed ether drops into a funnel tube which is placed concentrically in, and reaches to the bottom of, the inner tube, which is closed below and contains the liquid to be extracted. A flat glass spiral is twisted round the stem of the funnel, like an ascending stair, and so forces the ether into intimate contact with the liquid to be extracted as it ascends through it. The ether collects on the surface of the aqueous liquid, and flows through two openings in side of the inner tube back into the flask below. L. DE K.

Apparatus for Preserving and Measuring Poisonous, Hygroscopic, or Low-boiling Liquids. WILHELM STEINKOPF (*Chem. Zeit.*, 1910, **34**, 1319).—The liquid under investigation, for example, anhydrous hydrogen cyanide, is directly distilled into the cylindrical vessel in which it is to be preserved. Sealed into this vessel is a narrow tube reaching down to the bottom and connected with a measuring tube through a stopcock. Another tube containing a stopcock is also sealed into the top of the vessel, and by connecting this tube with a source of pressure, the liquid in the vessel may be forced over into the measuring tube, the various stopcocks being appropriately manipulated.

The whole apparatus in made of glass. T. S. P.

Aluminium Apparatus for Use in the Laboratory. HUGO MASTBAUM (*Chem. Zeit.*, 1910, **34**, 1319).—Condensing spirals made of aluminium tubing are very serviceable in distillations occuring in wine and brandy analyses. Boilers of the same material may also be used in the production of steam for distillations. T. S. P.

A New Apparatus for the Preparation of Liquid and Solid Air for Demonstrations. MAX BAMBERGER (*Oesterr. Chem. Zeit.*, 1910, [ii], **13**, 137—138).—The paper contains a sketch, with description of an apparatus suitable for the production of small quantities of liquid air. It consists of two series of copper tubes and a steel flask; the apparatus is cooled and the enclosed air subjected to a pressure of 120 atmospheres. F. M. G. M.

Inorganic Chemistry.

Reactions in the Presence of Nickel. (*a*) Inability of Nitrogen and Hydrogen to Combine in Presence of Nickel. (*b*) Reduction of Oxides of Nitrogen, Sulphur, and Phosphorus in Presence of Nickel. PAÑCHÁNAN NEOGI and BIRENDRA BHUSAN ADHICÁRY (*Zeitsch. anorg. Chem.*, 1910, **69**, 209—214).—A mixture of nitrogen and hydrogen (1 : 3 or 1 : 6 by volume) does not give rise to the formation of ammonia when passed over heated reduced iron, the temperature varying from dull to bright red heat. Similar negative results are obtained when the reduced iron is replaced by pure iron wire or by ferric oxide, no matter whether the gases are dried or not (compare Ramsay and Young, Trans., 1884, **45**, 93). No ammonia could be detected when the iron was replaced by reduced nickel, nickel wire, or electrolytic nickel.

When a mixture of nitric oxide and hydrogen (1 : 3 or better 1 : 4) is passed over reduced nickel, the nitric oxide is almost quantitatively converted into ammonia. The reaction begins at 300°, but once it has set in the temperature may be lowered to 120°.

Hydrogen sulphide is formed when a mixture of sulphur dioxide and hydrogen is passed over nickel heated to a dull red heat. The hydrogen sulphide is probably formed partly by direct reduction of the sulphur dioxide, and partly by reduction of nickel sulphide formed by the interaction of nickel and sulphur dioxide.

Hydrogen phosphide is produced when hydrogen is passed over a mixture of phosphoric oxide and reduced nickel at a dull red heat.

T. S. P.

Catalysis of Hydrogen Peroxide. ERNST H. RIESENFELD (*Ber.*, 1911, **44**, 147—150. Compare Abstr., 1908, ii, 951).—The reaction between chromic acid and excess of hydrogen peroxide can be represented by the equation: $4H_2Cr_2O_7 + 7H_2O_2 = Cr_2(Cr_2O_7)_3 + 11H_2O + 5O_2$. This agrees with Spitalsky's statement that only about 28% of the chromic acid is reduced, but this author did not notice that all the free acid is used up. The reaction is not a catalytic process (compare Spitalsky, this vol., ii, 36, 37). J. J. S.

Raschig's Nitrososulphonic Acid, "Blue Acid." WILHELM MANCHOT (*Zeitsch. angew. Chem.*, 1911, **24**, 13—14. Compare Abstr., 1910, ii, 956, 1055).—Mainly a reply to Raschig (*Zeitsch. angew. Chem.*, 1910, **23**, 2248). Raschig's ferric nitrososulphonate should have the ratio NO : Fe = 1·5 : 1, whereas the actual proportion is 2 : 1. It is pointed out that there is no trace of evidence for the existence of a blue compound formed by the union of nitric oxide with sulphuric acid. J. J. S.

Products Formed when Phosphoric Oxide Dissolves in Water. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1910, **69**, 215—216). —Phosphoric oxide was allowed to deliquesce over (1) 75% sulphuric acid, (2) 9% sulphuric acid; some was also thrown into water. In the first two cases the reaction was considered to be complete when the snow-like appearance of the phosphoric oxide has disappeared. In all cases metaphosphoric acid was the only product of reaction. After eighteen hours the metaphosphoric acid had completely changed into the ortho-acid in the last two cases.

The velocity of hydration of metaphosphoric acid produced by the deliquescence of phosphoric oxide is much greater than that of the metaphosphoric acid obtained by heating orthophosphoric acid.

T. S. P.

Rate of Hydration of Pyrophosphoric Acid. A Correction. G. A. ABBOTT (*J. Amer. Chem. Soc.*, 1910, **32**, 1576—1577).—In a paper on this subject (Abstr., 1909, ii, 661), it was stated that the specific conductivity of a mixture of pyro- and ortho-phosphoric acids is a linear function of its composition. It has been pointed out to the author that the experimental data quoted were not consistent with this statement, and it has been found that the wrong data were inadvertently given. The correct data are now recorded. Corrections are also given for certain typographical errors which occurred in Abbott and Bray's paper (Abstr., 1909, ii, 660) on the ionisation relations of ortho- and pyro-phosphoric acids and their sodium salts.

E. G.

New Determinations of Some Constants of the Inert Gases. CLIVE CUTHBERTSON (*Phil. Mag.*, 1911, [vi], **21**, 69—77).—Recent determinations of (1), the viscosity at different temperatures and (2) the refraction and dispersion of the argon gases, afford independent sets of measurements of the fraction of the volume containing the gas, which its molecules actually occupy. For argon, krypton, and xenon, the values in absolute measure so found by the two methods are of the same order, and there is a constant ratio between them; the volumes calculated from the viscosity being about 1·75 times that calculated from the refractivity. For helium and neon the ratios are 3·0 times and 2·53 respectively. For oxygen and nitrogen the ratios are similar to that found for argon, but hydrogen departs widely from it. For all the gases the numbers of "dispersion electrons" in the atoms, calculated from the refractivities and dispersions by means of Sellmeier's formula, bear a linear relation to the reciprocals of the radii of the spheres of action of the atoms as calculated from the viscosity. The squares of the numbers of "dispersion electrons" are for all the gases proportional to the radii of the spheres of action diminished by a constant equal to 0·95 of the radius of the sphere of action of helium at 0°. The squares of the relative numbers of "dispersion electrons" plotted against the critical temperatures of the gases fall on a straight line passing near the origin. From this relation the unknown critical temperature of neon is calculated to be about 46° *A*. The radii of the spheres of action also bear a linear relation to the critical temperatures. These results suggest that the electric charges which influence dispersion control also the critical temperature and the temperature-coefficient of viscosity, and show that

Sellmeier's formula, which is, in the manner of its derivation, tentative, can be safely employed to give results comparable with those obtained from the kinetic theory. F. S.

A General Method for the Preparation of Anhydrous Chlorides. ÉDOUARD CHAUVENET (*Compt. rend.*, 1911, **152**, 87—89. Compare Abstr., 1909, ii, 53).—The method consists in heating the oxide of the metal in a slow current of carbonyl chloride at a temperature varying from about 350° in the case of vanadium oxide to 650° in the case of thoria. Chlorides of the following elements have been prepared in this way: vanadium, tungsten, tantalum, titanium, zirconium, thorium, tin, barium, magnesium, zinc, glucinum, aluminium, iron, chromium, manganese, nickel, uranium, cerium, yttrium, lanthanum. An excellent yield of the anhydrous higher chloride was obtained in each instance, except with tungstic oxide, when the oxychloride was formed, and in the case of titanium, when a mixture of chloride and oxychloride was produced. The method is specially suitable for preparing the chlorides of the rare-earth metals. Silica is not attacked by carbonyl chloride. W. O. W.

The Causes of the Differences in the Action of Sodium and Potassium on Water. MANINDRANATH BANERJEE (*Chem. News*, 1910, **102**, 319—320).—When the metals are thrown on water, the hydrogen which is evolved is charged with the vapours of the metals, and so the motion is affected by their densities and molecular volumes, and those of their oxides and hydroxides. Thus in the case of potassium the high density and large molecular volume of its vapour counteract the motion of the hydrogen, its movement is retarded, the heat is not dissipated, and so the gas bursts into flame. In the case of sodium, the density and molecular volume being very low, the hydrogen keeps in a state of motion, and does not ignite, the heat being dissipated. N. C.

The Miscibility of Glaserite with Sodium Sulphate and its Dependence on the Temperature. RICHARD NACKEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1910, 1016—1026. Compare van't Hoff and Barschall, Abstr., 1903, ii, 434).—From a study of the solidification of fused mixtures of sodium and potassium sulphates, it has been found that the hexagonal modifications of the enantiotropic dimorphous components, which separate out first, form a complete series of mixed crystals. As the temperature falls, these primary mixed crystals undergo transformation, and the diagrammatic representation of the resulting relationships shows that the formation of the hexagonal mixed crystals, which crystallise from aqueous solutions at low temperatures, is confined to certain concentrations of the components. The limiting concentration on the one side is represented by glaserite, $Na_2SO_4,3K_2SO_4$ ($76\%K_2SO_4$). The other limiting concentration corresponds with about $49\%K_2SO_4$ at 180°, but with fall of temperature this proportion of potassium sulphate diminishes.

Crystalline forms corresponding with these limiting concentrations are obtained, together with potassium or sodium sulphate, when fused mixtures containing excess of potassium or sodium sulphate respectively are allowed to cool.

The relationships indicated by the concentration-temperature diagram have been supplemented by crystallisation experiments at 60° and 34°. When the aqueous solutions contain excess of potassium sulphate, glaserite and potassium sulphate are obtained. If excess of sodium sulphate is present, the crystals which separate consist of sodium sulphate together with mixed crystals containing glaserite and sodium sulphate, and the composition of these mixed crystals approximates towards glaserite as the temperature of crystallisation is lowered. H. M. D.

Fusions of Alkali Metaborates and Metaphosphates. H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1910, **69**, 122—134).—The freezing-point curve of mixtures of potassium metaborate and metaphosphate possesses two eutectics at 681° and 770° respectively, the former corresponding with 90% and the latter with 30% of potassium metaphosphate. The portions of the curve between the eutectics rises to a very flat maximum, extending between 50 and 60% of potassium metaphosphate. The eutectic arrest is only noticeable in the neighbourhood of the eutectics, so that it cannot be used to determine the position of the maximum. Investigation of the fusions showed that free borate could be detected by Tammann's reaction (characteristic red precipitate with mercuric chloride solution) up to 55% KPO_3, so that the composition of the compound lies between 55 and 60% KPO_3, and is probably 59% KPO_3, corresponding with KPO_3,KBO_3. Fusions of this composition give neutral solutions, whereas with higher and lower percentages of potassium metaphosphate they are respectively acid and alkaline. The presence of the compound KPO_3,KBO_3 is also indicated by the microscopic examination of thin sections. Between 65 and 85% potassium metaphosphate, the fusions would not crystallise, solidifying to a vitreous mass.

Potassium metaphosphate has m. p. 810°, and potassium metaborate melts at 947°.

The freezing-point curve of mixtures of sodium metaphosphate (m. p. 610°) and sodium metaborate (m. p. 966°) could only be followed between 0 and 30% and between 50 and 80% of sodium metaphosphate, the other mixtures solidifying to vitreous masses. The curve between 50 and 80% of sodium metaphosphate shows a flat maximum which is probably due to the existence of the compound, $NaPO_3,NaBO_2$, further evidence in support of the existence of which is given by chemical and optical investigations similar to those described for the potassium compounds. Conductivity measurements showed that this compound also exists in solution to some extent.

Sodium metaborate and potassium metaborate give a continuous series of mixed crystals, the freezing-point curve showing a flat minimum at 50% sodium metaborate. Indications of a decomposition of these mixed crystals at 522—553° were obtained in mixtures containing 40—60% of sodium metaborate.

Lithium metaborate (m. p. 843°) and sodium metaborate do not form a compound with each other, the freezing-point curve showing a eutectic at 650° with 52% of lithium metaborate. The miscibility in the crystalline condition is very limited, the lithium metaborate dissolving 2% of the sodium metaborate, and the latter dissolving 3% of the lithium metaborate. T. S. P.

Efflorescence of Washing Soda Crystals. ALEXANDER C. CUMMING (*Chem. News*, 1910, **102**, 311).—The author examined a specimen of large crystals of washing soda which had been for at least twenty years in a glass case with a wooden floor. The case fitted closely, but was not air-tight. It was at first thought that the crystals now consisted of the trihydrate, the existence of which had not been previously known. Further analysis, however, showed that the crystals consisted almost entirely of pure sesquicarbonate,

$$Na_2CO_3,NaHCO_3,2H_2O.$$

The loss of weight on the ignition of the sesquicarbonate, if calculated as due entirely to water, would lead to the formula for the trihydrate. N. C.

The Binary Systems: Li_2O–SiO_2, Li_2SiO_3–$ZnSiO_3$, $ZnSiO_3$–$CdSiO_3$, Li_2SiO_3–$LiBO_2$, Na_2SiO_3–$NaBO_2$, and Na_2SiO_3–Na_2WO_4. H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1910, **69**, 135—157).—The binary system Li_2O–SiO_2 forms two compounds, namely, lithium ortho- and meta-silicate, with m. p.'s 1243° and 1188° respectively; they are only slightly miscible in the crystalline state. Lithium metasilicate forms mixed crystals with silica up to 24·3% SiO_2. The existence of an acid silicate, $Li_2Si_5O_{11}$, has not been confirmed.

No compound is formed in the binary system Li_2SiO_3–$ZnSiO_3$. Mixed crystals exist from 0 to 7(?)% and 71(?) to 100% of lithium metasilicate. The eutectic temperature is approximately 990°, and the eutectic composition 52(?)% of lithium metasilicate. That portion of the freezing-point curve lying between 10 and 70% Li_2SiO_3 could not be determined thermally, and reliance had to be placed on the optical investigation. Zinc metasilicate has m. p. 1419°.

The system $ZnSiO_3$–$CdSiO_3$ gives an isomorphous series of mixed crystals, the minimum point of the curve being at 25% $ZnSiO_3$. The optical investigation did not completely verify the results obtained thermally. Cadmium metasilicate has m. p. 1155°.

In the system Li_2SiO_3–$LiBO_2$, mixed crystals exist from 0 to 24% and 91 to 100% of lithium metasilicate; no compound is formed. The eutectic temperature and composition are respectively 803° and 22% Li_2SiO_3.

No compound is formed in the system Na_2SiO_3–$NaBO_2$, but mixed crystals exist from 0 to 5% and 96 to 100% of sodium metasilicate. The eutectic temperature and composition are respectively 815° and 55% Na_2SiO_3. Sodium metasilicate has m. p. 1056°.

Below 1100° sodium tungstate is practically immiscible with sodium metasilicate. The two components are quite immiscible in the crystalline condition. Sodium tungstate has m. p. 700°, and transition temperatures at 589° and 572°.

Throughout this investigation optical methods were more trustworthy than the thermal ones for determining the compositions of the saturated mixed crystals. T. S. P.

Revision of the Atomic Weights of Silver and Iodine. II. Ratio of Silver to Iodine. GREGORY P. BAXTER (*J. Amer. Chem. Soc.*, 1910, **32**, 1591—1602).—From determinations of the value of the ratio $2Ag:I_2O_5$, Baxter and Tilley (Abstr., 1909, ii, 225) calculated the atomic weights of iodine and silver by the aid of the value 0·849943 for the ratio Ag : I (Baxter, Abstr., 1905, ii, 81, 579), and found them to be 126·891 and 107·850 respectively (O = 16). Richards and Willard (Abstr., 1910, ii, 292), however, have obtained a value of 107·871 for the atomic weight of silver. As it was thought possible that this discrepancy might have been due to an error in the ratio Ag : I, this ratio has now been re-determined.

Weighed quantities of iodine were reduced to hydriodic acid by means of a solution of hydrazine. The product was diluted, and treated with a slight excess of a very dilute solution of silver nitrate. The clear supernatant liquid was carefully filtered and concentrated by evaporation, and the excess of silver was estimated gravimetrically as silver iodide. Three samples of iodine and several specimens of silver were employed, each of which had been carefully purified. The results of thirteen experiments gave an average value for the ratio Ag : I 0·849906, and it is therefore considered probable that the silver iodide obtained in the earlier determinations was contaminated with occluded impurities. On combining this ratio with that of $2Ag:I_2O_5$, the atomic weights of silver and iodine are found to be 107·864 and 126·913 respectively (O = 16). E. G.

Revision of the Atomic Weight of Calcium. I. Analysis of Calcium Bromide. THEODORE W. RICHARDS and OTTO HÖNIGSCHMID (*J. Amer. Chem. Soc.*, 1910, **32**, 1577—1590; *Monatsh.*, 1910, **31**, 1203—1226).—Determinations of the atomic weight of calcium by the analysis of the pure chloride (Richards, Abstr., 1902, ii, 394) gave a value of 40·126 (O = 16; Cl = 35·455), which agrees fairly well with that obtained by Hinrichsen (Abstr., 1902, ii, 137). In the present paper, an account is given of a further study of this constant by the analysis of calcium bromide.

The calcium bromide was prepared in the following manner. Calcium nitrate was carefully purified by repeated crystallisation, and was converted into the carbonate by precipitation with ammonium carbonate. The carbonate was dissolved in hydrobromic acid, prepared by the action of hot platinum on a mixture of bromine vapour and hydrogen, and the solution was slightly acidified and afterwards concentrated. The bromide was repeatedly crystallised in quartz vessels, and was dried with special precautions and fused in a platinum boat, first in a current of hydrogen mixed with hydrogen bromide and afterwards in an atmosphere of nitrogen. The salt was then dissolved in water, and, when necessary, the solution was carefully neutralised, the deviations from exact neutrality being estimated by comparison with the pure crystallised salt with the aid of methyl-red. The analysis of the bromide was effected either by determining the amount of silver equivalent to the calcium present or by weighing the precipitated silver bromide. From the results of six experiments in each way, values for the two ratios $CaBr_2:2Ag$ and $CaBr_2:2AgBr$

were obtained, which gave essentially the same value for the atomic weight, 40·070 (Ag = 107·88) or 40·066 (Ag = 107·87). Two different specimens of the salt gave almost identical results.

The density of fused calcium bromide was found to be 3·353 at 25°.

E. G.

Electro-deposition of Lead from Perchlorate Solutions. FRANK C. MATHERS (*Chem. Zeit.*, 1910, **34**, 1316—1318, 1350—1351; *Trans. Amer. Elektrochem. Soc.*, 1910, **17**, 261—272).—Experiments with the lead perchlorate plating and refining bath are described. The properties of lead perchlorate which are of special value in plating or refining solutions are: (1) Great solubility. (2) Cathode deposits, which are smooth, dense, and free from "trees." (3) Approximately theoretical corrosion of the anode and deposition upon the cathode. (4) Absolute stability under all conditions to which it is subjected in a plating or refining bath. (5). No polarisation from the formation of lead peroxide on the anode. (6) Very high electrical conductivity.

The bath should contain about 5% of lead, 2—5% of free perchloric acid, and 0·25% of peptone. A current density of from 2—3 amperes per sq. dcm. (18—27 amperes per sq. ft.) may be used. The peptone is gradually used up, and after about four days a quantity equal to the original amount should be added. The free acid, which is very slowly neutralised by the chemical solution of the lead, must be restored by treatment of a suitable portion of the solution with the right amount of sulphuric acid, thus precipitating lead sulphate and leaving perchloric acid in solution. The filtrate is returned to the bath.

The bath gives excellent purification, the cathode being about 99·98% pure, and shows no deterioration with use, giving as good deposits after two months as at the beginning, if the concentration, acidity, and the required amount of peptone are maintained. Chlorides and barium salts must be absent. A bath that has been giving good deposits will form very bad "trees" if a quantity of hydrochloric acid or some barium perchlorate is added to it.

T. S. P.

Red Lead. IV. JAROSLAV MILBAUER (*Chem. Zeit.*, 1910, **34**, 1341—1342. Compare Abstr., 1910, ii, 294).—The oxidation of litharge to red lead in air at 460° follows a course similar to that already observed in the case of lead. Litharge obtained in the manufacture of nitrites is much better for this purpose than ordinary litharge; at 500° the former gave the same percentage of red lead after one hour as the latter after fifteen hours at 460°. Thus, although 460° is the optimum temperature for the formation of red lead, the increased velocity attained at 500° gives better results.

The rate at which red lead is formed is conditioned more by the origin or by the kind of lead oxide used than by the size of the particles. The percentage of red lead obtained depends on the partial pressure of the oxygen in the gas used, but even with pure oxygen at 450° it has hitherto been impossible to obtain 100% red lead.

T. S. P.

Studies in Vapour Pressure. VI. Quantitative Study of the Constitution of Calomel Vapour. ALEXANDER SMITH and ALAN W. C. MENZIES (*Proc. Roy. Soc. Edin.*, 1910, **31**, 183—185; *J. Amer. Chem. Soc.*, 1910, **32**, 1541—1555).—A review is given of previous work on the constitution of mercurous chloride vapour, and it is shown that there are no experimental data in existence from which the proportion of dissociated ($Hg+HgCl_2$) to non-dissociated molecules ($HgCl$) in the vapour can be deduced. An investigation has now been made, based on the principle of partial vapour pressures.

Determinations have been made of the vapour pressures of mercury, mercurous chloride, and a mixture of these substances, between 360° and 400°, by means of the static isoteniscope (Abstr., 1910, ii, 1036, 1037). The results show that mercurous chloride vapour, even when saturated, is completely dissociated into Hg and $HgCl_2$, and that molecules of the formula HgCl or Hg_2Cl_2 are not present. The b. p. of mercurous chloride is 382·5°, and its molecular weight, when dissolved in mercury, corresponds with the formula HgCl. E. G.

Double Nitrates of the Rare Earths. I. Double Nitrates of the Rare Earths with the Alkali Metals. GUSTAV JANTSCH and S. WIGDOROW (*Zeitsch. anorg. Chem.*, 1911, **69**, 221—231).—To prepare the double nitrates of the rare earths with the alkali metals, the procedure generally adopted was to dissolve the oxide of the rare earth, together with the necessary quantity of the nitrate of the alkali metal, in concentrated nitric acid and evaporate until crystals formed.

Wyrouboff's statements (Abstr., 1908, ii, 385) as to the hydration of the crystals of the double nitrates of sodium, potassium, and cæsium with lanthanum and cerium are not confirmed. The formulæ of the various compounds are written so as to indicate that the rare earths are tervalent in their stable forms of combination.

Lanthanum sodium nitrate, $[La(NO_3)_5]Na_2,H_2O$, forms slender, white needles; $D_4^0=2·63$, and molecular volume = 195·08; it is not completely dehydrated at 150°. Lanthanum potassium nitrate,

$$[La(NO_3)_5]K_2,2H_2O,$$

has $D_4^0=2·54$, and molecular volume = 221·76; hygroscopic, white shining crystals, which lose $2H_2O$ at 60°. *Acid lanthanum rubidium nitrate*, $[La(NO_3)_4]Rb,HNO_3,6H_2O$, obtained when lanthanum and rubidium nitrates are taken in the molecular proportion of 1 : 2; forms colourless plates, which lose $5H_2O$ and $1HNO_3$ at 120°; the resulting $[La(NO_3)_4]Rb,H_2O$ is not dehydrated at 200°; $D_4^0=2·377$, and molecular volume = 270·6.

When lanthanum and rubidium nitrates are taken in the molecular proportion of 1 : 4, lanthanum rubidium nitrate,

$$[La(NO_3)_5]Rb_2,4H_2O,$$

results; monoclinic crystals, m. p. 86°, $D_4^0=2·497$, and molecular volume = 277·1; it loses $4H_2O$ on prolonged heating at 60°. Lanthanum cæsium nitrate, $[La(NO_3)_5]Cs_2,2H_2O$, forms small, tabular crystals, $D_4^0=2·827$, and molecular volume = 265·5. *Lanthanum thallous nitrate*, $[La(NO_3)_5]Tl_2,4H_2O$, forms hygroscopic crystals, m. p. 72°; $D_4^0=3·318$, and molecular volume = 280·0; it loses $4H_2O$ at 100°. Cerous sodium nitrate, $[Ce(NO_3)_5]Na_2,H_2O$, consists of hygroscopic, slender needles, which are not completely dehydrated at 150°; $D_4^0 = 2·65$, and molecular volume = 194·0. Cerous rubidium nitrate, $[Ce(NO_3)_5]Rb_2,4H_2O$, has $D_4^0 = 2·497$, and molecular volume = 277·6; hygroscopic, monoclinic needles, m. p. 70°, which lose $4H_2O$ at 60°. *Cerous thallous nitrate*, $[Ce(NO_3)_5]Tl_2,4H_2O$, forms hygroscopic crystals, m. p. 64·5°; $D_4^0 = 3·326$, and molecular volume = 279·7; it loses $4H_2O$ at 60°.

Praseodymium rubidium nitrate, $[Pr(NO_3)_5]Rb_2,4H_2O$, green, hygroscopic, monoclinic crystals, m. p. 63·5°; $D_4^0 = 2·50$, and molecular volume = 277·4; it loses $4H_2O$ at 60°. *Neodymium rubidium nitrate*, $[Nd(NO_3)_5]Rb_2,4H_2O$, consists of hygroscopic, bright reddish-violet plates, m. p. 47°; $D_4^0 = 2·56$, and molecular volume = 272·3; it loses $4H_2O$ at 60°.

The temperature at which the above compounds melt in their water of crystallisation falls with increasing atomic weight of the rare-earth metal. T. S. P.

A New Element Accompanying Lutecium and Scandium in Gadolinite Earths: Celtium. GEORGES URBAIN (*Compt. rend.*, 1911, **152**, 141—143. Compare Abstr., 1907, ii, 956; 1908, ii, 283; 1909, ii, 735).—During repeated fractionation of the nitrates in the isolation of lutecium from gadolinite earths, a few drops of a mother liquor were obtained which did not crystallise. This contained a new oxide belonging to the rare earths and characterised by a magnetic susceptibility three or four times less than that of lutecia. The name celtium is given to the corresponding element, and the symbol Ct assigned to it.

Spectroscopic examination of the oxide showed the presence of lutecium, scandium, a trace of neoytterbium, and negligible traces of calcium and magnesium. The new element shows a large number of lines in the arc; the following are very intense: $\lambda = 2685·2$, 2765·8, 3080·7, 3118·6, 3197·9. The chloride is somewhat more volatile than that of lutecium, but less volatile than scandium chloride. The hydroxide is less basic than lutecium oxide and more basic than scandium oxide.

Celtium either appears to be entirely absent from xenotime, or else it occurs in very faint traces. W. O. W.

Electrical Properties of Aluminium-magnesium Alloys. WITOLD BRONIEWSKI (*Compt. rend.*, 1911, **152**, 85—87. Compare Abstr., 1910, ii, 128; Grube, Abstr., 1905, ii, 523).—From an examination of aluminium-magnesium alloys by the electrical method already described, the author comes to the conclusion that two definite compounds, AlMg and Al_2Mg_3, probably exist. These form a continuous series of solid solutions with one another, preventing their recognition by the thermal method. The existence of the compounds Al_4Mg and $AlMg_2$ could not be confirmed, and alloys of the metals in these proportions showed a heterogeneous structure under the microscope. W. O. W.

Formulæ of Aluminium Salts. GERRIT H. COOPS (*Chem. Weekblad*, 1910, 7, 1071—1076. Compare Coops, Abstr., 1910, ii, 506; and Olivier, *ibid.*, 507).—Polemical. A reply to Olivier.

A. J. W.

Colloidal Solubility of Metals in Distilled Water in Presence of Air and in a Vacuum. MARGHERITA TRAUBE-MENGARINI and ALBERTO SCALA (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 505—508. Compare Abstr., 1909, ii, 809).—Distilled water acts on aluminium in the warm and in the presence of air, and zinc and iron are attacked in the cold, colloidal solutions being formed in each case. Lead and iron, which alone were experimented with, yield colloidal solutions when treated with distilled water in a vacuum. The clear solutions become turbid in air, that of iron turning a greenish and finally a reddish colour, whilst the red solution becomes milky. The colloidal iron solution when kept in a vacuum forms black, green, and red deposits. Of these, the red and black ones are permanent in air, but the green deposit becomes red even in a vacuum. The bacteriform colloidal corpuscles of all these metals change (without passing into true solution) into the leaf-like crystals characteristic of colloidal solutions.

R. V. S.

Solid Solutions of Iron and Manganese Borides. JOSEF HOFFMANN (*Chem. Zeit.*, 1910, **34**, 1349—1350).—The heterogeneous nature of the borides prepared by the thermite process has already been shown by optical methods (Abstr., 1910, ii, 508), and is confirmed by the chemical behaviour of the various products. The composition of the saturated solutions obtained is 7 atoms of iron to 9 of boron for the iron boride, and 10 atoms of manganese to 28 atoms of boron for the manganese boride. Mineral acids extract compounds, such as Fe_5B_6, Fe_3B_4, and FeB, from the iron boride, leaving a residue consisting mainly of Fe_2B_3 with a little FeB_2. The soluble portions of manganese boride consist chiefly of MnB, together with some MnB_2, the undissolved residue being elementary boron mixed with some higher borides.

T. S. P.

Iso- and Hetero-poly-acids. I. Metatungstic Acid. ARTHUR ROSENHEIM and FRANZ KOHN (*Zeitsch. anorg. Chem.*, 1911, **69**, 247—260. Compare this vol., i, 109).—The authors distinguish between "isopoly-acids" and "hetero-poly-acids." The former are compounds containing the acid anhydride and the acid hydrate of one and the same element, for example, the polychromates, polytungstates, etc., whilst the latter are compounds in which acid anhydrides of one or more elements are combined with a hydrate or salt of the acid of another element, for example, the phosphomolybdates, etc., which have hitherto been called complex acids.

According to Copaux's views of the constitution of the metatungstates, boro- and silico-tungstates (Abstr., 1909, ii, 318), the metatungstates must contain water of constitution, so that they should belong to the hetero- and not to the iso-poly-acids. It order to find out how much water of constitution is contained in the metatungstates, the authors have prepared, by double decomposition, various insoluble salts, since these generally do not contain water of crystallisation. *Silver metatungstate*, $Ag_2W_4O_{13},3H_2O$, forms small, white crystals, which lose 1·1H_2O at 160° and 1·3H_2O at 200°; 2 molecules of water, and probably 3, are therefore firmly combined. In *thallium metatungstate*, $Tl_2W_4O_{13},3H_2O$, only 1 molecule of water is firmly combined. *Guanidine metatungstate*, $(CH_5N_3)_2H_2W_4O_{13},3H_2O$, was obtained from guanidine carbonate and metatungstic acid as a white, microcrystalline powder. Between 90° and 150° it loses $2H_2O$, so that probably only 1 molecule of water is firmly combined. The normal lead and mercury metatungstates, although frequently mentioned in the literature, could not be obtained. A solution of an alkali metatungstate gives with lead nitrate a precipitate of the *double* salt, $PbW_4O_{13},Pb(NO_3)_2,10H_2O$, which loses $7H_2O$ at 110°, so that 3 molecules of water are firmly combined.

From the above results, combined with Friedheim's statement (Inaug. Dissert.), that the metatungstates of sodium, barium, manganese, and cadmium still contain $3H_2O$ at 100°, and especially since insoluble salts are generally anhydrous, the authors draw the conclusion that the metatungstates contain 3 molecules of water of constitution, that is, they are aquo-salts, and must probably be formulated as

$$R_2\left[WO\begin{matrix}(WO_4)_3\\(H_2O)_3\end{matrix}\right],$$

although they may be $R_2\left[WO\begin{matrix}(WO_4)_3\\(H_2O)\end{matrix}\right]$. When heated at such a temperature that water of constitution is lost, they are decomposed.

Metatungstic acid was prepared by treating a concentrated aqueous solution of ammonium metatungstate with ether and concentrated hydrochloric (or sulphuric) acid. Of the three layers formed, the lower yellow one contains the free acid together with ether and the mineral acid, from which the free metatungstic acid is obtained by evaporation in a current of air. It readily effloresces; crystals were obtained corresponding with $H_2W_4O_{13},8H_2O$ and $H_2W_4O_{13},6H_2O$. It is quite insoluble in ether (compare Abstr., 1896, ii, 477), although in the presence of a mineral acid it is possible that a molecular compound of metatungstic acid and ether is formed. In aqueous solution it behaves as a normal electrolyte, and conductivity measurements after the addition of varying quantities of sodium hydroxide show it to be a dibasic acid. In absolute alcoholic solution it acts as a colloid.

Esters of metatungstic acid could not be obtained.

The above results cannot be brought into accordance with Copaux' formulation of metatungstic acid as $H_{12}W_{24}O_{78},3H_2O+aq.$ T. S. P.

Atomic Weight of Vanadium. D. J. McAdam, jun. (*J. Amer. Chem. Soc.*, 1910, **32**, 1603—1615).—The values previously obtained for the atomic weight of vanadium show considerable discrepancy, and a re-determination has therefore been made by a new method. This method is based on the observation of Smith and Hibbs (Abstr., 1894, ii, 455) that vanadium can be completely removed from sodium metavanadate by volatilisation in a current of dry hydrogen chloride.

Five samples of sodium metavanadate were used in the experiments. The apparatus employed is described with the aid of a diagram. A weighed quantity of the anhydrous salt was placed in a weighed quartz flask, and was heated in a current of hydrogen chloride containing a little chlorine. When as much as possible of the vanadium had been removed, a little water was introduced into the flask, and the mixture was again heated in the current of hydrogen chloride. The whole of the vanadium was thus expelled, and a residue of sodium chloride obtained. The flask and residue were weighed, and the weight of the sodium chloride obtained by subtracting that of the flask.

The results of five experiments gave an average value for the atomic weight of vanadium, $50·967 \pm 0·006$ ($Na = 23·00$; $Cl = 35·46$). This value agrees with that obtained by Prandtl and Bleyer (Abstr., 1910, ii, 135) by the analysis of vanadium oxychloride.

Anhydrous sodium metavanadate has D 2·79. E. G.

Bismuth. LUDWIG VANINO and EMILIE ZUMBUSCH (*Arch. Pharm.*, 1910, **248**, 665—669).—Trials with the various methods described for the preparation of bismuth hydroxide showed that it was difficult to prepare a product free from nitrate. Good results were obtained with Thibault's process (Abstr., 1901, ii, 106), but only when a very large excess of potassium hydroxide was employed. A satisfactory preparation was obtained eventually by dissolving bismuth nitrate (20 grams) in water (100 c.c.) containing mannitol (7·5 grams), adding 50 c.c. of ice-cold potassium hydroxide solution (22 grams in 100 c.c. of water), and finally dilute sulphuric acid until the mixture was only slightly alkaline (compare Abstr., 1902, i, 8).

Previous work by Vanino and Treubert (Abstr., 1898, ii, 435, 598; 1899, ii, 428; compare Herz and Guttmann, Abstr., 1907, ii, 274) has shown that bismuth suboxide probably does not exist, but the authors have made experiments with the process described by Jawarososki for the preparation of this substance (*Pharm. Zeit. Russ.*, 1896). This method consists in warming a mixture of ferrous sulphate, sodium potassium tartrate, and sodium hydroxide in water with basic bismuth nitrate. The brownish-black precipitate so obtained in the author's experience was never free from iron even when the reacting ingredients were used in calculated proportions for the production of the suboxide, so that they do not regard Jaworososki's preparation as a definite substance. T. A. H.

Brown Gold. MAURICE HANRIOT (*Compt. rend.*, 1910, **151**, 1355—1357).—This name is given to the residue obtained when nitric acid is allowed to act on an alloy of gold and silver containing about 20% of gold. It always contains a small quantity of silver and a considerable amount of nitric acid. The latter is lost at 175—200°; on further heating it changes colour and undergoes contraction; at 900° the substance evolves gas, and at 1040° it melts, changing into red gold.

The author has measured the contraction undergone by strips of alloy containing 1—3·5% of silver on treatment with nitric acid, and also the further contraction that ensues on heating. Results are also quoted showing the further contraction that occurs on a second and third heating. W. O. W.

Mineralogical Chemistry.

Mineral Oils from Potash-Salt Deposits. EDMUND GRAEFE (*Centr. Min.*, 1911, 1—4).—Two oils differing widely in their characters are compared. I, is from the potash-salt works "Desdemona" at Alfeld, on the Leine, and II, from the salt works "Glückauf" at Sondershausen.

	I.	II.
Colour, &c.	Yellow, transparent; thin liquid.	Dark brown; viscous.
Sp. gr.	0·802	0·935
Ignition point	16°	over 100°
Boiling point	115°	300°
Distillate up to 300°	54%	—
Sulphur	0·034%	0·95%
Iodine number	1·54	11·47
Paraffin	9·36%	4·30%
M. p. of paraffin	54·4°	56·2°
Heat of combustion	10,883	10,534
Asphalt	0%	35·5%

Suggestions are offered to explain as to how oils with these different characters may have originated. L. J. S.

Composition of Fahlerz. A. KRETSCHMER (*Zeitsch. Kryst. Min.*, 1910, 48, 484—513).—A historical review is given of the different formulæ that have at various times been proposed for fahlerz (tetrahedrite and tennantite), and one hundred and sixty-two published analyses are tabulated. Fifteen new analysis are given. Details of the method of analysis are given; the material was decomposed in bromine vapour in a current of carbon dioxide. The material analysed in some cases was massive, and not of ideal purity (and in others the fact that the fracture was uneven, rather than conchoidal, indicates that the material was not homogeneous).

I. Crystals from Horhausen, Rhenish Prussia. II. Massive from Hornachuelos, Cordoba, Spain. III. Massive from Huanchaca, Bolivia. IV. Crystals from Schemnitz, Hungary. V. Crystals from Aurora mine, Dillenburg, Nassau. VI. Crystals from Kapnik, Hungary. VII. Crystals from Botés, Transylvania. VIII. Massive from Schwaben mine, Müsen, Westphalia. IX. Massive from Kotterbach, Zips, Hungary. X. Crystals from Gross-Kogel, Brixlegg, Tyrol. XI. Massive from Mouzaïa, Algeria. XII. Crystals from San Lorenzo mine, Santiago, Chile. XIII. Crystals from Guanajuato, Mexico. XIV. Crystallised ("julianite") from Friederike Juliane mine, Kupferberg, Silesia. XV. Crystals (tennantite), mixed with erubescite, from Cook's Kitchen mine, Redruth, Cornwall.

	Cu.	Ag.	Zn.	Fe.	Pb.	Sb.	As.	S.	Total.	Sp. gr.
I.	37·75	0·11	6·51	1·10	0·71	28·66	—	24·61	99·98§§	5·079
II.	38·95	0·02	2·21	4·77	—	27·00	1·40	25·66	100·01	4·680
III.	29·99	12·74	2·49	3·29	0·25	26·42	0·58	23·71	99·47	4·769
IV.	37·93	0·45	7·57	0·60	—	26·12	1·84	25·21	99·72	4·780
V.	38·52	0·08	7·05	0·94	—	25·26	2·69	25·22	99·76	4·736
VI.	38·59	0·68	6·16	1·05	—	24·98	2·25	25·35	99·20*	4·794
VII.	36·10	1·51	6·44	0·78	2·72	24·00	2·75	24·99	100·13†	4·870
VIII.	33·30	1·70	5·32	2·66	0·83	23·44	4·48	23·83	99·06§	4·779
IX.	40·57	0·03	1·61	4·53	—	20·60	5·07	25·21	99·89‡	4·651
X.	40·91	0·23	4·85	2·57	—	15·77	9·03	26·34	100·50‖	4·738
XI.	42·35	0·09	1·48	4·31	—	14·51	10·24	26·38	99·36	4·740
XII.	42·05	0·04	6·09	1·48	—	10·87	12·57	27·12	100·22	4·597
XIII.	42·15	1·31	2·62	5·44	—	4·66	16·68	27·61	100·47	4·576
XIV.	48·50	0·23	—	2·77	—	2·44	18·82	27·04	100·24**	4·692
XV.	53·24	—	0 23	1·58	—	—	18·29	26·54	100·11††	4·746

§§ Including Bi, 0·53. * Including SiO_2, 0·14. † Including Mn, 0·26; SiO_2, 0·32. § Including Ni, 2·49; Hg, 0·75; SiO_2, 0·26: the nickel is present in an admixed nickel mineral. ‡ Including Hg, 1·52; $BaSO_4$, 0 75. ‖ Including Hg, 0·80. ** Including insoluble, 0·44. †† Including insoluble, 0·23.

The formula deduced from these analyses is $(R_x',R_y'')_3R'''S_{3+y/2}$, where $R'=Cu, Ag$; $R''=Zn, Fe$, etc.; $R'''=Sb, As, Bi$; $x+y=3$. This is identical with the formula proposed by Prior and Spencer, $3R_2'S,R_2'''S_3+x(6R''S,R_2S_3)$ (Abstr., 1900, ii, 21). In the latter formula, $R_6'S_3$ and $R_6''S_6$ are regarded as isomorphously replaceable, whilst the present author regards $R_9'R_3'''$ and $R_6''R_2'''$ as equivalent.

L. J. S.

Braunite from Minas Geraës, Brazil. B. JEŽEK (*Zeitsch. Kryst. Min.*, 1910, **48**, 543—544; from *Rozpravy böhm. Akad.*, 1908, **13**, II. Kl., No. 7).—A crystallographic description is given of small, brilliant crystals. The finely granular matrix of these crystals proved on analysis to be also braunite:

MnO.	O.	Fe_2O_3.	BaO.	SiO_2.	H_2O.	Total.	Sp. gr.
83·76	8·20	1·18	0·98	3·93	0·50	98·55	4·69—4·72

L. J. S.

Chromite from the Marjalahti Meteorite: Analcite from Brödtorp. LEONARD H. BORGSTRÖM (*Zeitsch. Kryst. Min.*, 1910, **48**, 540—541; from *Geol. För. Stockholm Förh.*, 1908, **30**, 331—337).—On the olivine and in contact with the nickel-iron of the Marjalahti meteorite (Abstr., 1905, ii, 537) are small crystals of chromite, some of which are rich in faces. Analysis gave:

Cr_2O_3.	Al_2O_3.	FeO.	MgO.	NiO.	Total.	Sp. gr.
65·63	3·78	25·84	4·27	0·73	100·25	4·93

Analcite occurs as crystals in cavities in granulite at Brödtorp. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	Na_2O.	K_2O.	H_2O.	Sp. gr.
54	22	trace	12	trace	8	2 241—2·246

L. J. S.

Calcium Carbonate. Józef Morozewicz (*Zeitsch. Kryst. Min.*. 1910, **48**, 522—523; from *Kosmos*, *Lemberg*, 1907, **32**, 487—495).—The name *lublinite* is applied to a variety of calcium carbonate occurring as felt-like masses in crevices in chalk-marl at Wysokie, govt. Lublin, Russian Poland. Analysis gave: CaO, 55·13; CO_2, 43·06; insol., 1·04; loss on ignition, 0·95. Under the microscope, the fibres are strongly birefringent with oblique extinction; they are, therefore, crystals of calcite greatly elongated in the direction of an edge of the primary rhombohedron.

Small crystals of aragonite, prepared artificially by precipitation with ammonium carbonate, were heated for several hours at a low red-heat; they thereby became transformed into calcite. When heated to bright redness, the crystals were converted into lime, although still preserving their external form. These isotropic crystal skeletons when moistened with ammonium carbonate solution are converted into calcite. The carbon dioxide can thus be removed and again replaced without destroying the external form of the crystals. L. J. S.

Natramblygonite, a New Mineral. Waldemar T. Schaller (*Amer. J. Sci.*, 1911, [iv], **31**, 48—50).—This was found in association with tourmaline, lepidolite, and albite in a pegmatite mass near Canon City, Colorado. It is a massive, cleavable, greyish-white mineral resembling amblygonite in appearance, from which it differs in containing sodium in place of lithium, being in fact a soda-amblygonite. The formula, $(Na,Li)Al(OH,F)PO_4$, is analogous to that of amblygonite. Analysis gave:

P_2O_5.	Al_2O_3.	Li_2O.	Na_2O.	K_2O.	H_2O.	F.	Total. (less O for F).	Sp. gr.
44·35	33·59	3·21	11·23	0·14	4·78	5·63	100·56	3·04

L. J. S.

Terminology of Alumosilicates. Józef Morozewicz (*Zeit. Kryst. Min.*, 1910, **48**, 523—524; from *Kosmos*, *Lemberg*, 1907, **32**, 496—499).—The decomposition of alumosilicates gives rise to alumosilicic acids, there being a greater affinity between silicon and aluminium than between aluminium and the metals of the alkalis and alkaline earths. Lemberg and Thugutt have obtained the well-crystallised compound $4(Na_2Al_2Si_2O_8),5H_2O$ by acting on kaolin $(H_2Al_2Si_2O_8,H_2O)$ with a 15% solution of sodium hydroxide. Kaolin is thus an alumosilicic acid of the following series with the general formula $H_2Al_2Si_nO_{2n+4}$.

$H_2Al_2Si_2O_8$, alumodisilicic acid: kaolin (without water of crystallisation); in sodalite, nosean, etc.

$H_2Al_2Si_3O_{10}$, alumotrisilicic acid: cimolite (without water of crystallisation); in natrolite.

$H_2Al_2Si_4O_{12}$, alumotetrasilicic acid: pyrophyllite; leucite is the potassium salt, $K_2Al_2Si_4O_{12}$.

$H_2Al_2Si_5O_{14}$, alumopentasilicic acid: in harmotone.

$H_2Al_2Si_6O_{16}$, alumohexasilicic acid: in albite, which is thus sodium alumohexasilicate, $Na_2Al_2Si_6O_{16}$. L. J. S.

Solid Solution in Minerals, with Special Reference to Nephelite. HARRY W. FOOTE and W. M. BRADLEY (*Amer. J. Sci.*, 1911, [iv], **31**, 25—32).—Even allowing for the presence of mechanically admixed impurities and isomorphous replacements, there are certain minerals for which a satisfactory and simple formula cannot be deduced. It is suggested that in such cases some other constituent may be present in the state of solid solution in the mineral, in much the same way as salt is dissolved in water, or as homogeneous crystals of ammonium chloride may contain ferric chloride (Roozeboom, 1892). Here we have homogeneous mixtures of different compounds (not of the same type, as in isomorphous mixtures) which cannot be separated by mechanical means, and between certain limits the composition of such mixtures may vary continuously.

This principle is held to apply in the case of nephelite, the formula of which approximates to, but never in the natural mineral quite agrees with, the simple formula $NaAlSiO_4$. This formula corresponds with those of the isomorphous minerals eucryptite, $LiAlSiO_4$, and kaliophilite, $KAlSiO_4$; and the artificial nephelites prepared by Doelter, in 1884, vary from $NaAlSiO_4$ to compounds containing potash and an excess of silica.

The following is the mean of four analyses made of carefully purified nephelite from Eikaholmen, Norway; the material contained a trace of intimately admixed albite (insoluble in hydrochloric acid), but under the microscope it appeared to be homogeneous.

SiO_2.	Al_2O_3.	Fe_2O_3.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
44·46	33·11	0 96	5·61	16·32	0·38	100·84	2·635.

The molecular ratios are $SiO_2 : Al_2O_3$, etc. : Na_2O, etc. = 2·23 : 1·00 : 0·98. In the nephelite analyses by Morozewicz (Abstr., 1908, ii, 201), $Al_2O_3 : Na_2O$ also = 1 : 1, whilst the ratio of $SiO_2 : Al_2O_3$ varies from 2 11 to 2·21, and the same relations hold with other published analyses. It is, therefore, assumed that the excess of silica over that required by the formula $NaAlSiO_4$ is present in solid solution in the sodium aluminium silicate. The "saturation ratio" of the silica is 2·21, since, when more silica is present, this has separated as albite ($NaAlSi_3O_8$), which occurs intimately intermixed with the nephelite.

L. J. S.

Chemical Distinction between Orthoclase and Microcline. WLADIMIR I. VERNADSKY and Mlle. E. RÉVOUTSKY (*Compt. rend.*, 1910, **151**, 1372—1374. Compare Barbier, Abstr., 1908, ii, 704).—Barbier has indicated as a general chemical distinction between orthoclase and microcline the existence of traces of lithium and rubidium in the former, and their absence from the latter. This being contrary to observations of one of the authors (*Bull. Acad. Sci. St. Petersburg*, 1909, **114**, 822), five new specimens of microcline from Russia, Colorado, Norway, and Finland have been examined spectroscopically, with the result that either lithium or rubidium or both were found to be present in each specimen.

W. O. W.

Remarkable Garnet from Fluminimaggiore [Sardinia]. AURELIO SERRA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], **16**, 222—224).—The garnet was found in association with galena. It has the following composition:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	Total.
34·53	6·05	25·10	0·84	trace	33·67	100·19

which indicates that it is andradite, in which the silicate $Ca_3Fe_2(SiO_4)_3$ is associated with $Ca_3Al_2(SiO_4)_3$. The colour of the mineral is honey-yellow, and in this and other respects it is similar to a garnet from Sala, in Isvezia (also found in association with galena), which was analysed by Bredberg. R. V. S.

Chemical Composition of the Gases Evolved from the Thermal Spring at Uriage (Isère). GUSTAVE MASSOL (*Compt. rend.*, 1910, **151**, 1124—1126. Compare Abstr., 1908, ii, 1004; Besson, *ibid.*, ii, 1005).—The spring at Uriage evolves a mixture of gases composed of nitrogen, 93·98%, carbon dioxide, 4·15%, rare gases, 1·87%, with traces of oxygen. The rare gases were passed over wood charcoal at the temperature of liquid oxygen, when about half the volume, consisting of argon, krypton and xenon, was absorbed. The remaining gas contained neon and helium, the latter constituting 0·932% of the original mixture. The spring probably emits not less than twenty litres of helium daily, and is one of the most considerable sources of this element hitherto discovered. W. O. W.

Ratio of the Cl-, SO_3-, and σ_0-Values of a Series of Sea-water Samples Examined in the Hydrographical Laboratories of Helsingfors, Kiel, Christiania, Monaco, and Nancy. ERNST RUPPIN (*Zeitsch. anorg. Chem.*, 1911, **69**, 232—246).—Analyses of sea-waters collected at different depths show that there is a fairly definite connexion between density, salt content, and percentages of SO_3 and Cl, although this has been disputed. A recalculation of Dittmar's results (*Reports of Voyage of H.M.S. Challenger*, 1873—76; Physics and Chemistry, Vol. I) shows that the salt content of the sea-waters examined can be determined from a knowledge of the chlorine content. T. S. P.

Physiological Chemistry.

Action of Asphyxia on the Spinal Animal. G. C. MATHISON (*J. Physiol.*, 1910, 41, 416—449).—Lack of oxygen is the main factor in asphyxia in the spinal animal, but the spinal vaso-motor centres are much less sensitive to various agencies than the medullary centres. Excess of carbon dioxide and injection of acids act on the spinal cord much in the same way as lack of oxygen. W. D. H.

Physiological Climatology. I. Relation of Loss of Water from the Skin and Lungs to the External Temperature in Actual Climatic Conditions. WILLIAM A. OSBORNE (*J. Physiol.*, 1910, **41**, 345—354).—The usual statement that heat loss by radiation and conduction makes up the greater portion of the total heat loss is only true under certain conditions; an air temperature equal to that of the body would reduce this loss to zero. If the metabolism of the body is constant during rest and the heat production fairly constant, it follows that if the air temperature is raised, and loss by radiation and conduction lessened, the heat loss due to evaporation must make up the balance, otherwise heat accumulation would occur. It would be expected therefore that the water loss would be a linear function of the air temperature. The linear relationship is, however, more perturbed; the cause is not clothing, but is more complex; one factor is the varying humidity and velocity of the air. If the air is dry and in movement it will tend to desiccate the skin, but if body temperature and skin imbibition are to be kept constant, then the metabolism must be augmented. What apparently occurs is a compromise; the skin loses some of its water of imbibition, and the metabolism undergoes a moderate rise. Hence the unpopularity of the East wind in N.W. Europe.

The lung ventilation is increased when the air temperature is high; this is a familiar fact with the lower animals. How the respiratory centre is affected by a high air temperature is a puzzle, for the body temperature does not rise; possibly the carotid blood may become heated in its passage up the neck.

It is also found that the carbon dioxide excreted varies directly, not inversely, as the external temperature; the increase in pulmonary ventilation will in part explain this; more carbon dioxide is produced from the additional work of the respiratory muscles, and more "washed out" from the tissues.

There is some indication that the respiratory quotient rises with rising shade temperature. Harvey Sutton found that this quotient approached unity when the wet bulb-temperature rose in a room which he could artificially make warm and moist, and made some suggestions regarding the relation of this reaction to the preponderance of carbohydrates in the diets of tropical aboriginals. W. D. H.

Influence of Lactic Acid on the Dissociation Curve of Blood. JOSEPH BARCROFT and L. ORBELI (*J. Physiol.*, 1910, **41**, 355—367).—Lactic acid is a valuable accessory to carbon dioxide in tissue respiration; both tend to turn out the oxygen from the blood. The method of determining the tensions of the blood gases is by a new tonometer, which is figured and described in detail; for this and for the discussion of certain difficulties which arise, the original paper must be consulted. W. D. H.

The Action of Choline on Blood-pressure. LEO POPIELSKI (*Zeitsch. physiol. Chem.*, 1910, **70**, 250—252).—The author reiterates the view expressed previously by Modrakowski and himself that choline produces a rise of arterial pressure, and that the opposite result obtained by others is due to their having used impure material.

W. D. H.

The Effect of Potassium Salts on the Circulation, with Special Reference to the Production of Heart-Block. G. C. MATHISON (*Proc. physiol. Soc.*, 1910, xix—xx; *J. Physiol.*, 41).—Potassium salts cause vaso-constriction when both brain and spinal cord are destroyed; they therefore act directly on the vessel walls. On the heart, large doses produce diastolic stoppage, but in some cases smaller doses produce heart-block, from which recovery occurs.

W. D. H.

The Influence of the Blood-corpuscle Lipoids on the Blood Formation. L. KEPINOW (*Biochem. Zeitsch*, 1910, **30**, 160—172).—The author shows that by the injection of blood-lipoids from ox-blood into rabbits rendered anæmic by bleeding, the rate of formation of new blood corpuscles is increased. The regeneration took about half the time to that required by control animals which had received no lipoid injection. The same result was not achieved by ovolecithin.

S. B. S.

Blood Sugar. VIII. The Sugar Content of the Corpuscles. PETER RONA and DENGO TAKAHASHI (*Biochem. Zeitsch.*, 1910, **30**, 99—106).—The authors confirm the observations of others as to the probable presence of dextrose in the corpuscles. The proteins were precipitated by the Michaelis-Rona dialysed iron method, sodium dihydrogen phosphate being the salt employed for precipitating the colloid, and the reducing power and polarisation were estimated in the filtrate before and after fermentation by yeast. In the latter case, the reducing power almost completely disappeared. The authors give a large number of estimations of the sugar in blood and serum, especially in the case of dogs after bleeding, where there is an increase of blood sugar, and call attention to the possible clinical importance of differentiating between the blood of the corpuscles and the serum.

S. B. S.

The Behaviour of the Red-blood Corpuscles in Chronic Oleic Acid Poisoning. ALEXANDER SCHMINCKE and FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1910, **64**, 126—140).—If the red corpuscles contain the normal amount of iron, they show an increased specific resistance towards the hæmolytic action of oleic acid in cases of chronic poisoning by that substance in dogs; this is attributed specially to an increase of the lipoid materials in the corpuscles; these consist of a mixture of saturated and unsaturated fatty acids united to cholesterol.

W. D. H.

Cocaine Hæmolysis. ERNST PŘIBRAM (*Pflüger's Archiv*, 1911, **137**, 350—358).—Koppe's hypothesis that the hæmolysis produced by cocaine is due to acid decomposing the alkaloid cannot be correct, for it occurs in neutral and increases in alkaline solutions, and the same is true for the hæmolysis produced by other members of the cocaine group, eucaine and novocaine; these produce an elevation of the surface tension of the solvent in an alkaline medium. The non-toxic members of the group (ecgonine, etc.) produce little or no such change. The physical and biological properties of the alkaloids run parallel with their pharmacodynamic properties, and probably there is a causal relationship between them; the anæsthetic and toxic properties rise with the changes they produce in surface tension and hæmolysis. Gros, moreover, has shown that their anæsthetic preperties are increased when in an alkaline medium. W. D. H.

Vegetable Agglutinins. FRITZ ASSMANN (*Pflüger's Archiv*, 1911, **137**, 489—510).—Previous work on vegetable agglutinins is referred to in relation to such toxic proteins as ricin and abrin. Previous writers manifest a good deal of difference of opinion on the mode of action of such poisons. A number of plants (beans, vetches, etc.) yield similar, relatively non-toxic, substances, for which the term *phasin* (from *Phaseolus*) is adopted. Details are given of the agglutinating action on various kinds of blood of both the toxic and non-toxic members of the group. The non-toxic compounds are believed to contain the same agglutinating component as is present in such toxic compounds as ricin, but to be destitute of the toxic element. W. D. H.

Calcium Metabolism. I. A New Method for the Quantitative Estimation of Small Variations of the Calcium Content of the Blood. N. VOORHOEVE (*Biochem. Zeitsch.*, 1910, **30**, 195—206).—The method depends on the determination of the amount of calcium necessary to add to the blood to produce clotting after the natural content has been removed by the addition of ammonium oxalate. A syringe of 5 c.c. capacity is so constructed that it can be automatically half-filled with physiological saline containing 229 mg. of ammonium oxalate in 100 c.c. The blood is then sucked into the syringe directly from the veins, and immediately mixed with the oxalate solution. After several hours, small measured portions are taken and mixed with varying quantities of calcium chloride, isotonic with the saline, and diluted with it to a definite bulk. In this way, the amount of calcium necessary to precipitate the excess of oxalate and thus produce clotting can be determined, from which the original calcium content of the blood can be calculated. Control experiments, where determinations were made by mixing the calcium solution with ascitic fluid, etc., show that the results obtained are independent of the amount of proferment present. S. B. S.

The Behaviour of Chlorine in the Serum. PETER RONA (*Biochem. Zeitsch.*, 1910, **30**, 332).—An admission that the "compensation-dialysis" method for estimating the chlorine in serum (this vol., ii, 50) was employed previously by Zunz and Loewy. S. B. S.

Trypsin Action. The Tryptic Digestion of Casein. MAX SIEGFRIED (*Pflüger's Archiv*, 1910, **136**, 185—202).—According to the old theory of Kühne, on hemi- and anti-products of digestion, casein (a hemi-protein) should not yield a peptone on tryptic digestion; it was, however, proved by the use of the iron method for isolating peptones that a peptone can be isolated from a tryptic digest of casein. This is regarded as a chemical unit, and a few incomplete details are given of its cleavage products; the large quantity of ammonia and the small amount of nitrogenous substances which are precipitable by phosphotungstic acid are noteworthy points. W. D. H.

The Formation of Carbohydrates from Fat in the Animal Organism. PETER JUNKERSDORF (*Pflüger's Archiv*, 1910, **137**, 269—328).—In dogs during inanition, during fat feeding, and when under the influence of phloridzin and free from glycogen, there is a genetic relationship between the excretion of nitrogen and sugar. In phloridzinised animals, the whole of the sugar, however, cannot originate from protein because of the high sugar:nitrogen quotient, and the conclusion is drawn that part of it comes from fat. In dogs fed on fat, there is at death abundance of body-fat present, and the nitrogen and sugar excretion sink. The highest excretion, both of nitrogen and sugar, is shown by those phloridzinised dogs which receive abundant protein and carbohydrate food. W. D. H.

The Influence of Muscular Work on the Decomposition of Subcutaneously-administered Sugar. HERMANN HOHLWEG (*Zeitsch. Biol.*, 1911, **55**, 396—408. Compare Abstr., 1909, ii, 162).—In continuation of previous work it is shown that after the subcutaneous injection of sugar, the amount which passes into the urine is diminished during muscular work in the dog. This amount (about 20%) is accounted for on the hypothesis that it is utilised as a source of energy by the muscles. Sugars also, which the cells are unaccustomed to, are similarly utilised, and details of experiments show the fact to be so for galactose, sucrose, and maltose. Lactose, however, passes quantitatively into the urine both during rest and muscular activity. W. D. H.

The Chemistry of Honey Formation. M. KÜSTENMACHER (*Biochem. Zeitsch.*, 1910, **30**, 237—254).—The author gives a detailed account of the morphology of the alimentary tract of the bee. In conversion into honey, the nectar undergoes the following changes: part of the water is evaporated, the sucrose undergoes almost complete inversion, the starch is converted into dextrin, the tannins are oxidised and partly deposited on the walls of the honey cells, the oxalic acid disappears and is resorbed by the body of the bee, and the odorous substances undergo a like fate; the mineral substances are partly resorbed and partly reappear in the honey. The invertase is derived, not from the bee itself, but from the spermatoplasma of the pollen. Diastase, however, could not be detected in the pollen, but arises probably from the saliva or gastric secretion of the animal. S. B. S.

Protein Metabolism. FRANZ FRANK and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1910, **70**, 98—128).—Experiments on dogs confirm Michaud's discovery that the kind of protein given influences the minimum amount capable of maintaining nitrogenous equilibrium after inanition. Much more is necessary of a foreign protein than if the protein of dog's muscle is given. W. D. H.

The Fate of Injected Foreign Proteins and Peptones. H. DE WAELE and ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1910, **30**, 227—236).—The experiments were carried out on rabbits with a known diet. The excretion of nitrogen and the protein in the urine were estimated, and the changes in the excretion noted after injection of various protein substances. When small quantities of Witte's peptone were injected there was a small addition of nitrogen to the body substances, and in the case of larger injections the animals kept approximately in nitrogen equilibrium. After injection of egg-white, a large amount of protein was excreted in the urine, which was greater than the amount injected, and came therefore partly from the animal's own body, as it underwent loss of weight. After a second injection the loss of weight is smaller. Part of the increased nitrogen output is in the form of urea. From the results obtained by themselves as well as those of other observers, the authors draw the conclusion that the animals gradually acquire the capacity of peptonising the injected proteins. S. B. S.

Chemical and Microscopical Investigation on Fat Transport through the Intestinal Wall during Absorption. ALFRED NOLL (*Pflüger's Archiv*, 1910, **136**, 208—247).—On the grounds mainly of microscopical and microchemical examination (with osmic acid), the conclusions are reached that the fat which is seen in the epithelial cells has the same composition as that in the chyle, that the fat in the epithelium cells is absorbed as fat, and not as its cleavage products, and that the fat the course of which can be followed in this way microscopically only accounts for a part of that which is actually absorbed. W. D. H.

The Carbamino-Reaction. WALTER SULZE (*Pflüger's Archiv*, 1910, **136**, 712—723).—If carbon dioxide is passed through a cooled solution of an amino-acid in lime water or baryta water, the amino-acid takes up carbon dioxide, and a carbamate of calcium or barium is formed. Other organic amino-compounds and hydroxyl compounds react in a corresponding way. This reaction, which has been particularly studied by Siegfried, is described at length for many such compounds, and is believed to have a physiological interest. Researches with serum, peptone, and crystallised serum albumin have shown that substances are present in the blood and lymph which give the reaction. The carbamates formed are readily decomposed, and possibly come into action in such physiological occurrences as the production of carbon dioxide in muscles, or in the liberation of hydrochloric acid in the gastric juice. W. D. H.

Physiology of Cell-Division. III. Action of Calcium Salts in Preventing the Initiation of Cell-Division in Unfertilised Eggs through Isotonic Solutions of Sodium Salts. RALPH S. LILLIE (*Amer. J. Physiol.*, 1911, **27**, 289—307. Compare Abstr., 1910, ii, 522).—The addition of small quantities of calcium chloride to isotonic solutions of sodium salts (1) prevents the rapid increase in permeability produced in the unfertilised eggs of *Asterias* and *Arbacia* by the pure solution; (2) lessens the toxicity of the solution, and (3) prevents the membrane formation and initiation of cell-division which are induced by the pure solution. The toxic action of the pure salt solution and its action in initiating cell-division are due primarily to a condition of increased surface permeability. This increase is, however, temporary in normal favourable parthenogenetic fertilisation. Treatment with hypertonic sea-water, after the formation of fertilisation membranes by salt solution, leads to an increase in the proportion of successfully developing eggs. W. D. H.

The Dextrose of the Egg and its Biological Significance. VINCENZO DIAMARE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1910, [iii], **16**, 242—244. Compare Abstr., 1910, ii, 320).—From experiments with eggs of the domestic fowl and of *Testudo graeca*, it appears that those nearing maturity (in the ovary) contain dextrose, of which about equal amounts are removed by dialysis and hydrolysis respectively. In the younger eggs the proportion of dialysable sugar is less, and in the very smallest no reducing sugar is present. R. V. S.

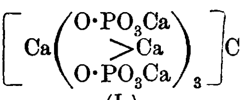
Lipoid Nature of an Active Substance Secreted by the Corpus Luteum of Mammals. P. BOUIN and P. ANCEL (*Compt. rend.*, 1910, **151**, 1391—1393),—When the corpus luteum of a sow is extracted with physiological salt solution, a turbid extract is obtained. After centrifugation, the clear liquid is found to show no characteristic physiological properties, the substance in suspension, however, when injected into rabbits produces sneezing, nystagmus, convulsions, and finally death from respiratory arrest. The active substance does not occur in any other part of the ovary. Its behaviour towards solvents, acids, and alkalis, and its stability to heat when dry, suggest that the substance is of a lipoid nature. W. O. W.

The Alkaline Odour. MAX VON FREY (*Pflüger's Archiv*, 1910, **136**, 275—281).—The so-called alkaline taste is really due to the sense of smell; it depends on the development of volatile bases (methylamines) which are decomposition products of epithelial cells. Freshly secreted saliva does not contain these bases. W. D. H.

Sulphur Compounds of the Nervous System. II. A Sulphatide from Nerve Substance. WALDEMAR KOCH (*Zeitsch. physiol. Chem.*, 1910, **70**, 94—97).—The sulphatide was prepared from human brain; the analytical figures given of various preparations do not appear very concordant; the S : N ratio is given as 1 : 3·03. The preparation regarded as the purest contained 3·1% of potassium. The sulphur is considered to act as a link in connecting phosphatides and cerebrosides. W. D. H.

Chemical Investigations of Healthy and Rachitic Bones. TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1910, **70**, 161—170).—Normal

bones contain about 1% more water than those in rickets; calcium, phosphoric acid, and carbon dioxide are less in rachitic than in normal bones. The relationship Ca : PO_4 : CO_3 is the same in both; and the complex in which they are contained is suggested to be (I). Other details given refer to magnesium (increased in rickets), potassium, sodium, chlorine, etc.
W. D. H.



$$\left[\mathrm{Ca}\left(\begin{matrix}\mathrm{O{\cdot}PO_3Ca}\\ >\mathrm{Ca}\\ \mathrm{O{\cdot}PO_3Ca}\end{matrix}\right)_3\right]\mathrm{CO_3}$$

(I.)

Action of Tervalent Ions on the Heart and on Certain Colloidal Systems. George R. Mines (*Proc. physiol. Soc.*, 1910, xvii–xviii; *J. Physiol.*, 41).

—Eight simple tervalent positive ions which were examined agree in producing diastolic arrest of the frog's heart when perfused at a concentration of 0·00001M. They also all confer a positive charge on gelatin and on agar-agar, and precipitate, in very low concentration, a variety of colloidal solutions with negative particles. The complex tervalent positive ion, $Co(NH_3)_6$, scarcely affects the heart in concentrations one hundred times greater, but it precipitates negative colloidal solutions, and confers a positive charge on agar-agar. It differs from the simple ions in its inability to precipitate unboiled diluted egg-white or dialysed hæmoglobin, or to confer a positive charge on gelatin or frog's red corpuscles.

The tervalent negative ions of the citrate and phosphate arrest the heart in diastole in concentration 0·01M. They powerfully antagonise the effects of acid or of tervalent positive ions on the heart. These actions are not shared by the tervalent negative ion of the ferricyanide; the latter also differs from the other two by being inactive in conferring a negative charge on a gelatin membrane. In the action of tervalent ions on certain colloidal systems there exists an unexplored factor qualifying the familiar valency law of precipitation and Perrin's law. This factor is also of physiological importance. W. D. H.

The Relationship of Kidney Function and the Glycogen of the Liver. Hermann Friedrich Grünwald (*Arch. exp. Path. Pharm.*, 1910, 64, 147—160).

—Any severe bilateral kidney injury (extirpation, ligature of renal arteries or veins, or ureters) leads to a disappearance of the hepatic glycogen in spite of feeding on dextrose. The action is attributed to the lack of a chemical stimulus from kidney to liver; extirpation of the right kidney produces no such effect; but extirpation of the left kidney (except when it has previously been denervated), and injuries which involve the left kidney nerves, lead to a great diminution of the glycogen in the liver. There is, therefore, in addition to the hormone, a nervous stimulus, which without passing through the central nervous system runs in the path of the nerves on the left side. The experiments were performed on rabbits.
W. D. H.

Formation of Sugar in the Liver. M. Loewit (*Pflüger's Archiv*, 1910, 136, 572—594).

—Numerous researches have shown that the liver can produce sugar from substances which are not carbohydrate, and in the present research it is shown that the liver free from

glycogen will produce sugar after death. What the parent substance or substances of the sugar are is a question discussed at length, but left still open. Tissues other than the liver yield under similar conditions either no sugar after death, or only mere traces.
W. D. H.

The Isolation of a Uricoclastic Ferment. GINO GALEOTTI (*Biochem. Zeitsch.*, 1911, **30**, 374—383).—Solutions containing this ferment in an active condition were obtained from the livers of the dog and the dog-fish in the following manner: The organ was ground with sand, and the juice expressed at 300 atmospheres. The juice was diluted with water, the fat separated, and an equal volume of acetone added. The precipitate was then filtered off as rapidly as possible, and the last traces of acetone removed by spreading on filter paper. The ferment was extracted from the precipitate by means of a very dilute solution of sodium chloride.
W. J. Y.

Chemical Factors of Fatigue. W. BURRIDGE (*J. Physiol.*, 1910, **41**, 285—307).—In a muscle nerve preparation very small quantities of sarcolactic acid produce fatigue phenomena, by acting specially on the end-plates. If more than the merest trace is present free, fatigue occurs; therefore in muscle the lactic acid formed even in rest must be neutralised, and creatine is credited with a power to perform this neutralisation. Another chemical factor in fatigue is believed to be the liberation of potassium salts from the active muscles; these also affect primarily the nerve-endings.
W. D. H.

The Replacement of Calcium in so-called Physiological Fluids. (Experiments on the Excitability of Striated Muscles of Warm-blooded Animals, and the Variations of Tonus of the Atrium in Emys europea.) GIUSEPPE BUGLIA (*Zeitsch. Biol.*, 1911, **55**, 343—359. Compare Abstr., 1910, ii, 630).—The excitability direct and indirect of striated muscles soon disappears in Ringer's solution if the calcium in it is omitted, and is restored on the restoration of that element. The place of calcium cannot here be taken by cæsium. In the variations of tonus in the atrium of the tortoise, cæsium also has not the same action, and cannot replace calcium. In both varieties of striped muscle, the action of cæsium is different from what occurs in smooth muscle.
W. D. H.

Investigations on Smooth Muscle. IV. The Replacement of Calcium in so-called Physiological Fluids. (Experiments on Smooth Muscle; Dog's Oesophagus.) GIUSEPPE BUGLIA (*Zeitsch. Biol.*, 1911, **55**, 360—376. Compare Abstr., 1910, ii, 630).—In maintaining the rhythmical contractions of the smooth muscle of the dog's œsophagus, it has been previously shown that cæsium chloride can replace calcium chloride in Ringer's solution. Cæsium nitrate or iodide can also be used; the sulphate is not so efficacious, the anion appearing to have a harmful effect. A large number of other metallic salts were employed with negative results; the only one found to act like cæsium chloride was rubidium chloride.
W. D. H.

Some Changes in Normal Tissues Produced by Radium. Albert S. Grünbaum and Helen G. Grünbaum (*Proc. physiol. Soc.*, 1910, xviii; *J. Physiol.*, 41).—Radium destroys liver cells, but only to a short distance; in the gall bladder no obvious changes occur; in the stomach an atrophic fibrosis of the mucous membrane and destruction of the submucosa take place. The effect on incubating eggs is, like that of *X*-rays, to destroy the embryo. In the skin the inflammation produced is characterised by a relative absence of polynuclear leucocytes and the presence of many plasma cells. W. D. H.

A Microchemical Method for Demonstrating the Presence of Guanine in Tissues. Amatore de Giacomo (*Zeitsch. wiss. Mikroscop.*, 1910, **27**, 257—258).—A method was required for demonstrating the presence of guanine in the renal system of birds. The animal tissue (after the usual preparation) is treated with a solution of diazobenzenesulphonic acid (which has been previously tested and found sensitive to guanine); after about ten minutes, sodium hydroxide is carefully added, when the presence of guanine is shown by a red coloration; in its absence the tissues remain pale yellow F. M. G. M.

The Oxidation of Succinic Acid by Animal Tissues. Fr. Battelli and Lina Stern (*Biochem. Zeitsch.*, 1910, **30**, 172—194).—All tissues of higher animals possess the capacity of oxidising succinic acid. This oxidation does not cause an increased output of carbon dioxide, as inactive malic acid is the product produced. The most active tissues are the heart, muscle, and liver, with the exception of rabbit's muscles. The oxidative power of the blood is not very marked. The substance causing the oxidation cannot be extracted from the tissues by water, and the tissues also lose their oxidative capacity after extraction with alcohol or acetone. The reaction takes place best in neutral or slightly alkaline media at the optimum temperature of 40°. The reaction rate is greater in pure oxygen than in air. Hydrocyanic acid acts toxically on the reaction, but other substances, such as arsenious acid and sodium fluoride, have but a relatively small effect. S. B. S.

The Biological Significance of Inositolphosphoric Acid (Phytin). Emil Starkenstein (*Biochem. Zeitsch.*, 1910, **30**, 56—98). —It was found that inositolphosphoric acid gives a precipitate with uranium, magnesium, and lead salts, but not with ammonium molybdate in nitric acid solution. For this reason, only the latter reagent is available for estimation of free phosphoric acid in the presence of phytin. The commercial preparation of the latter substance contains free inositol and phosphoric acid. To prepare pure phytin from the commercial product, the latter is dissolved in dilute acetic acid, and lead acetate is added; only the inositolphosphoric acid lead salt is precipitated. This, after washing and decomposition, is decomposed by hydrogen sulphide, and the filtrate is treated with glacial acetic acid and calcium acetate until a precipitate is formed. The pure phytin (inositolphosphoric acid) is then obtained in the form of an insoluble calcium salt. The conclusion is drawn from the analysis of the salts that phytin is a complex derivative of pyrophosphoric acid (for which a formula is suggested). The author gives an exhaustive review of the literature, from which is drawn various conclusions, the chief being that the free inositol in the body has no particular physiological significance. In view of the fact that inositolphosphoric acid is also precipitated by various reagents for phosphates, he draws attention to various possible errors in phosphate estimation in urine, etc. S. B. S.

Tetrodon Poison. YOSHISUMI TAHARA (*Biochem. Zeitsch.*, 1910, **30**, 255—275).—The toxin was extracted from the ovaries of the fish, and from the aqueous extract the proteins were separated by heating the solution after acidification with acetic acid. From the solution thus obtained, the phosphates, etc., were precipitated by lead acetate. From the filtrate, on addition of ammonia (not more than 0·34%), the toxin is precipitated with lead acetate. This is then decomposed with hydrogen sulphide. On evaporating under low pressure to a syrup and adding alcohol, a precipitate is formed, whilst the greater part of the toxin remains in solution and can be precipitated therefrom by the addition of ether. From the precipitate, by redissolving in water and treating as before with alcohol and with ether, a further amount of toxin can be obtained. The tetrodotoxin obtained in this way is not pure, but contains a sugar, *tetrodopentose*, which is deposited in stout, colourless prisms on keeping the solution, and a crystalline base, which does not melt even at 280°, has the formula $C_{11}H_{11}O_2N_9$, and can be precipitated as an aurichloride from a solution of the crude tetrodotoxin. The tetrodotoxin, freed as completely as possible from these two substances, has the approximate formula $C_{16}H_{13}O_{16}N$. It is very soluble in water, but is insoluble in most organic solvents, although soluble in aqueous alcohol. It reduces Fehling's solution, and its toxic dose was found to be 0·0041 mg. per gram of body-weight for mice, and 2·5 to 4 mg. per kilo. for rabbits. The toxicity is readily destroyed by mineral acids, alkalis, and strong ammonia. Tetrodotoxin is neither acid nor base, and yields on hydrolysis a base and a crystalline substance. The author considers that tetrodotoxin is not a protamine. S. B. S.

Occurrence of Hæmatoporphyrin in the Meconium. V. BORRIEN (*J. Pharm. Chim.*, 1911, [vii], **3**, 59—63).—Hæmatoporphyrin has been detected spectroscopically in a purified acetone extract of the meconium. The author suggests, therefore, that the passage from blood pigment to biliary pigment takes place in the following stages: hæmoglobin ⟶ hæmatoporphyrin ⟶ bilirubin. T. A. H.

The Catalase of Milk. FRANZ SPINDLER (*Biochem. Zeitsch.*, 1911, **30**, 384—412).—The activity of the catalase was compared in a number of samples of milk from healthy and diseased cows, and also in preparations from cow's milk and in milk from other animals. A measure of the activity was obtained by determining the total volume of oxygen liberated at 37° by 15 c.c. of milk from 5 c.c. of 1% hydrogen peroxide by means of Lobeck's "catalase glass."

It was found that the activity was greater in sour than in fresh milk, and increased with the age of the milk. This was, however, partly due to the growth of moulds in the milk. Sour milk products, like Bulgarian "Yoghurt" and "Kephir," also contained more active catalases than fresh milk. Diseases of the udder and other complaints were accompanied by a markedly increased activity in this ferment, and this activity decreased to the average for normal milk as the animal regained its health. The method is suggested as a means of detecting disease in cows. W. J. Y.

The Excretion of Subcutaneous Injections of Sodium Chloride, and their Effect on Nitrogen Metabolism. G. Trosianz (*Zeitsch. Biol.*, 1910, **55**, 241—266).—Dogs were kept on a constant diet containing known quantities of sodium chloride, phosphoric acid and nitrogen, and the daily excretion of these three substances determined in the urine and fæces. In each case, after a period of from two to four days, solution of sodium chloride was injected, and the effect produced on these excretions observed. The effect was tried of varying the concentration of the salt (1) when the diet employed was rich in sodium chloride; (2) when the food contained only small quantities of this salt, and (3) during starvation. The injections varied from 116 c.c. of 0·3% NaCl to 20 c.c. of 10% NaCl. Similar experiments were also carried out, in which 100 c.c. of a solution of urea (5 or 10%), containing in some cases 1% NaCl, were injected into the animals. It was found that when equal amounts of sodium chloride were injected, the time required for the whole to reappear in the excretions was less the more concentrated the solutions employed. With a diet rich in sodium chloride, injections of hypo- and iso-tonic solutions of sodium chloride caused no perceptible increase in the nitrogen output, hypertonic solutions produced a slight increase, whilst urea was almost quantitatively recovered in the excretions, and had no effect on the nitrogen metabolism.

With food poor in sodium chloride, even hypotonic solutions of salt produced a marked increase in the nitrogen excreted.

The effect was still further marked in the case of starving animals, both salt and urea causing an increased nitrogen metabolism.

Practically no changes were observed in the phosphoric acid excreted. W. J. Y.

The Excretion of Phosphates Ingested per os, Especially of Calcium Phosphate. Ragnar Berg (*Biochem. Zeitsch.*, 1910, **30**, 107—142).—The author carried out a series of experiments on his own person, taking over long periods of time diets with small calcium content, in which the caloric value and the protein, fat, carbohydrate, calcium, magnesium, and phosphoric acid contents were known. This was done with the object of diminishing the calcium store in the body. During the period of this diet, he rapidly lost weight. At certain intervals during the experiment he added to his diet the following sources of calcium and phosphorus :—Calcium phosphate (neutral) and calcium hydrogen phosphate, calcium hypophosphite, lecithin, lecithin and calcium lactate, and calcium lactate alone. The phosphate, magnesium, and calcium were estimated both in the urine and fæces. He draws the conclusion, from a long series of experiments, that these substances are of little therapeutic value in increasing the calcium and phosphate stores in the body. Tricalcium phosphate is excreted mostly in the fæces, and the acid calcium phosphate is positively harmful, in that it is also excreted in the fæces as neutral salt, and actually draws on the phosphoric acid store in the body. The effect of these preparations on diuresis and acidosis is also discussed.

S. B. S.

The Influence of the Fat of the Food on the Excretion of the Acetone Substances. GUNNAR FORSSNER (*Skand. Arch. Physiol.*, 1910, 23, 305—325).—The experiments were made with the object of determining the influence of the amount of fat ingested on the excretion of β-hydroxybutyric acid and acetone, and were performed on the person of the author. The constant diet taken contained only a small amount of carbohydrate, and relatively large amounts of fat. To eliminate the influence of stored glycogen, a definite amount of hard exercise was taken each evening, and during the investigation the conditions of living were kept as constant as possible. On certain days, definite additional amounts of fat (olive oil) were ingested after the period of exercise and before retiring to rest, and the influence of this added fat was determined by estimating the amount of acetone substances excreted in the urine in different periods during the course of the investigation. From the results, the author draws the conclusion, amongst other things, that the addition of fat to the food causes an increased output in the acetone substances, which is approximately proportional to the amount of added fat. S. B. S.

Studies on Water Drinking. III. Uric Acid Elimination following Copious Water Drinking between Meals. S. A. RULON and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1910, 32, 1686—1691. Compare Abstr., 1910, ii, 625).—It has been stated by some authors that the ingestion of large quantities of water has the effect of decreasing the amount of uric acid excreted, whilst others have stated that it has the opposite effect. Experiments have now been made to ascertain the influence of copious water drinking between meals on the elimination of uric acid. The subjects were two men, aged twenty-four and twenty-nine, and a uniform diet was maintained throughout the experiments. In one case, the data showed that the amount of uric acid excreted was not affected, whilst in the other case they indicated that there was a marked decrease in the quantity. It is considered, however, that the latter result was probably due to the fact that the Folin-Shaffer method of estimation which was employed does not give a sufficiently high result with urines of very low sp. gr. The urines in the other case were of such a character as to admit of accurate estimation, and it is therefore considered probable that the ingestion of large quantities of water does not have any influence on the amount of uric acid excreted.

E. G.

The Relation of the Precursors of the Normal Yellow Pigment of Urine to the Diazo-reaction, and a Colorimetric Estimation of Urochrome and Urochromogen. MORIZ WEISZ (*Biochem. Zeitsch.*, 1911, **30**, 333—356).—The proteic acid fraction of urine, which is precipitated by baryta and alcohol, yields a precipitate with basic lead acetate containing the normal yellow pigment (the urochrome of Thudichum and Garrod) and the urochrome obtained by Dombrowski by means of copper acetate. These two pigments are not identical, and may be separated from each other by means of the greater solubility of the lead salt of the normal yellow urochrome in dilute acetic acid.

The substance in pathological urine which brings about Ehrlich's diazo-reaction (red coloration with a mixture of aniline-*p*-sulphonic and nitrous acids) is precipitated from the proteic acid fraction by mercury acetate. The nature of this substance is not known, but it is termed urochromogen on account of its properties. Another urochromogen is found in urine; this does not give the diazo-reaction, but on digesting the urine for some time, it changes into a urochromogen which does give the reaction; it is therefore termed urochromogen-α, and the other urochromogen-β. Both these substances yield on oxidation a urochrome identical with the normal yellow pigment of urine.

Urochrome and its precursors are probably produced from the protein of the cell, and the presence of urochromogens in pathological urine points to a change in the metabolisms of the organism brought about by toxic substances.

Estimations of the urochrome in different urines were made by precipitating the other pigments with ammonium sulphate, and comparing the filtrate in a Dubosq colorimeter with a standard solution of a yellow dye, the quantity of urochrome being expressed in terms of the standard. The urochromes were estimated in the same manner after oxidation to urochrome. W. J. Y.

Narcotics and Local Anæsthetics. OSCAR GROS and C. HARTUNG (*Arch. exp. Path. Pharm.*, 1910, **64**, 67—71. Compare Abstr., 1910, ii, 793).—Details are given of the limits of concentration which produce narcosis in tadpoles, etc., of cocaine, eucaine, novocaine, and alypine. W. D. H.

The Significance of the Active Constituent of the Suprarenal Capsules in Conjunction with Local Anæsthetics. P. ESCH (*Arch. exp. Path. Pharm.*, 1910, **64**, 84—104).—The addition of adrenaline to novocaine, alypine, and especially cocaine intensifies their local narcotic action. This is a specific influence on nerves. The addition of adrenaline to tropococaine does not increase its action. W. D. H.

The Influence of the Presence and Position of the various Radicles of Adrenaline on its Physiological Activity. C. H. H. HAROLD, MAXIMILIAN NIERENSTEIN, and HERBERT E. ROAF (*J. Physiol.*, 1910, **41**, 308—317).—The activity of adrenaline is largely dependent on the presence of an amine (or substituted amine)

group separated from the benzene nucleus by some other group. Two hydroxyls attached to the benzene ring in the 3 : 4-position increase the action, and when these are present, the placing of a secondary alcohol group between the benzene ring and the amine-containing group intensifies the activity. In the latter case it is the lævorotatory compound that is mainly responsible for the "sympathomimetic action."
W. D. H.

The Production of Glycosuria by Adrenaline in Thyroidectomised Dogs. Frank P. Underhill (*Amer. J. Physiol.*, 1911, **27**, 331—339).—Renewed investigation concerning the efficiency of adrenaline in provoking glycosuria in thyroidectomised dogs confirms the author's previous conclusion that doses of 1 mg. per kilo. of body-weight causes glycosuria in dogs deprived of both thyroids, but retaining at least two parathyroids ; these dogs thus resemble normal dogs. Falta and Rudinger's criticisms in no way invalidate this conclusion.
W. D. H.

The Fate of Cineol (Eucalyptol) in the Organism. Juho Hämäläinen (*Skand. Arch. Physiol.*, 1910, **24**, 1—12).—After oxidation of the metabolism product (a glycuronate) with permanganate, the author succeeded in isolating cineolic acid, from which he draws the conclusion that the cineol, before conjugation, is oxidised, yielding one of two possible products of which he gives the formulæ. It was also noticed that the toxic action of the cineol was greatly diminished in animals which had been immunised with emulsin, and the urine of such animals after cineol ingestion is much more strongly lævorotatory than in non-immunised animals. The author gives reasons for deducing from these facts that the glycuronate formed after cineol ingestion has the β-glucoside structure. S. B. S.

Physiological Action of Organic Bases. A. Brissemoret and A. Joanin (*Compt. rend.*, 1910, **151**, 1151—1153).—The physiological effect of an organic base is regarded as the resultant of the effects of the hydrocarbon residue and the basic nitrogen-containing group. It has been found by experiments on dogs that in the case of coniceine the secondary narcotic effects are similar to those induced by *n*-octane. In the same way, the narcosis produced by morphine can be imitated by intraperitoneal injection of hexahydrophenanthrene, the parent hydrocarbon of the alkaloid. W. O. W.

Physiological Action of β-Iminoazolylethylamine [4-β-aminoethylglyoxaline]. Henry H. Dale and Patrick P. Laidlaw (*J. Physiol.*, 1910, **41**, 318—344).—This amine is produced when carbon dioxide is split off from histidine. It is identical with one of the ergot bases (compare Barger and Dale, Trans., 1910, **97**, 2592). It has a direct stimulating effect on plain muscle, especially of the uterus and the bronchioles; cardiac muscle is mildly stimulated, and skeletal muscle not affected. In rodents it produces a rise of blood pressure unless this is masked by embarrassed respiration; in carnivora the direct action on plain muscle in the systemic arterioles is overcome by an antagonistic peripheral action, the mechanism of which is not clear. The result is general vaso-dilatation (in which the kidney vessels do not participate), and a fall of arterial pressure; the pulmonary pressure rises. The drug also produces narcosis, and is a mild direct stimulant to the salivary glands and pancreas. The general effect is not unlike that of the injection of Witte's peptone and of certain agar extracts, and of Popielski's "vasodilatin." The base has in fact been separated from intestinal extract. It has no effect on blood coagulability. It is further pointed out that the general effect is not unlike that seen in anaphylaxis. W. D. H.

Pharmacology of the Rue (Peganum harmala). FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1910, **64**, 105—125).—The physiological action of some of the derivatives was investigated, namely, harmine ($C_{13}H_{12}ON_2$), harmaline ($C_{13}H_{14}ON_2$), dihydroharmaline ($C_{13}H_{16}ON_2$), and *apo*harmine ($C_8H_8N_2$). The first three have a paralysing action on frogs, whilst *apo*harmine causes increased reflex irritability and tetanus. Harmine and harmaline paralyse the skeletal and cardiac muscle of the frog. Harmaline has an anthelmintic action, probably by paralysing the musculature of the parasites. In warm-blooded animals, harmine and harmaline cause convulsions, increase of saliva, interference with respiration, and depression of temperature. In the East the seeds are used as a substitute for hashish, and in dogs it is evident that psychic disturbances occur. The drugs are partly destroyed in the body (blood, liver, and nervous system), and partly excreted by the kidneys and intestine. W. D. H.

Comparative Effects of Yohimbine, Protoveratrine, and Veratrine on Isolated Muscle and Nerve. AUGUSTUS D. WALLER (*Proc. physiol. Soc.*, 1910, xi—xiv; *J. Physiol.*, **41**).—The results described confirm the author's previous conclusion, that veratrine especially affects muscle, and protoveratrine, nerve. The characteristic effect on nerve produced by protoveratrine is not produced by yohimbine, although Tait regards the two drugs as pharmacologically identical. W. D. H.

The Toxic Action of the Free Fatty Acids in Animal and Vegetable Fats and Oils. J. HERTKORN (*Chem. Zeit.*, 1911, **35**, 29—30).—The decompositions taking place when a fat or oil becomes rancid result in the formation of lower and higher fatty acids and aldehydic substances, etc. It may happen that higher aldehydes are formed, and these, together with the acids (crotonic, acrylic, etc.) into which they are readily converted, may cause the injurious effects noted when rancid fats and oils are consumed. W. P. S.

The Sensitising Action of Hæmatoporphyrin. WALTHER HAUSSMANN (*Biochem. Zeitsch.*, 1910, **30**, 276—316).—If paramæcia are exposed to light in solutions containing small quantities of hæmatoporphyrin, which in the dark is harmless, they rapidly die. This is a case of photosensitisation, as if they are treated with the same solution in the dark after the solution has been exposed to light, the paramæcia remain alive. The toxic action is not due therefore to a decomposition product of the hæmatoporphyrin after exposure to light. The most active rays, as determined by light filters, are those of about $\cdot 500\mu\mu$. Hæmatoporphyrin solutions under the same conditions can also act hæmolytically. Furthermore, if hæmatoporphyrin is injected into mice, and the animals are exposed to light, toxic effects are produced which can ultimately end in death. Control animals kept in the dark remain healthy. According to the degree of light to which the animals are exposed, or the time which has elapsed since injection, various stages of intoxication can be distinguished, namely, acute, sub-acute, or chronic. The various symptoms characterising these stages are described in detail by the author. The injury to the peripheral vessels seems to be the primary effect of the toxins. When toxic action took place, no hæmatoporphyrin could be found in the blood (tested by the hæmolysis method). White mice are much more sensitive to the hæmatoporphyrin action than grey or black mice. In the case of the latter, no lethal effects were ever experienced. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Oxidation of Phenol by Certain Bacteria in Pure Cultures. GILBERT J. FOWLER, EDWARD ARDERN, and WILLIAM T. LOCKETT (*Proc. Roy. Soc.*, 1910, 83, *B*, 149—156).—It was noticed that phenol was oxidised on bacterial sewage filters from which three or four different organisms could be afterwards isolated. The chief were *Bacillus liquefaciens fluorescens*, a liquefying organism, and another organism which Sidebotham has identified with *B. Helvolus* (Zimmermann). The experiments, made with cultures on various media, show that the oxidation of phenol is due to the latter organism, which can grow on media in which the phenol is the only source of carbon. S. B. S.

Production of Acid and Alkali by Diphtheria Bacilli. K. A. JACOBSEN (*Centr. Bakt. Par.*, 1910, i, 16—27).—The results both of Madsen (*Zeitsch. Hyg.*, 26) and of Lubenau (*Arch. Hyg.*, 66) are confirmed, their divergence being due to different experimental conditions. N. H. J. M.

Production of Nitrite by Bacteria. ERICH PELZ (*Centr. Bakt. Par.*, 1910, i, 59, 1—16).—In addition to cholera vibrios a number of bacteria have the power of reducing nitrates to nitrites. These are divided into three groups, according to the vigour with which they act on nitrates. The most active are the cholera vibrios, *Paratyphus* B., mouse typhus, *Aerogenes*, *Vibrio Nordhafen*, *Vibrio Metschnikoff*, swine cholera, and some varieties of type Flexner.

The following bacteria show less activity in producing nitrites: Typhus, Paratyphus A., *Enteritis* Gärtner, *Bacterium coli*, Yersin, and *Proteus Dysenteriae*. The production of nitrites by this group never exceeded 18—20 mg. in 50 c.c. It is, however, possible that some of the nitrite produced underwent further decomposition, with liberation of free nitrogen. No ammonia could be detected except in a culture of *Staphylococcus aurens*, which produced nearly 5 mg. in four days.

Dysentery bacteria of type Kruse and streptococci produce only small amounts of nitrite. N. H. J. M.

The Chemical Reactions of Kumiss and Kephir Fermentation. I. The Kumiss of the Steppes. ALEXANDER GINZBERG (*Biochem. Zeitsch.*, 1910, **30**, 1—24).—The course of the reactions occurring during the souring and fermenting of mare's milk to form kumiss was followed by mixing fresh mare's milk with an equal volume of kumiss, incubating at 25°, and determining the lactic acid, sugar, and alcohol present at intervals during the "ripening" of the mixture. The results show that the lactic and alcoholic fermentations proceed concurrently, beginning slowly and gradually increasing in intensity. At the same time the casein and albumin of the milk are acted on by the ferments, the former losing its mineral constituents, and both being partly hydrolysed.

W. J. Y.

The Chemical Reactions of Kumiss and Kephir Fermentation. II. Artificial Kumiss and Kephir. ALEXANDER GINZBERG (*Biochem. Zeitsch.*, 1910, **30**, 25—38).—Kephir is produced from cow's milk by lactic and alcoholic fermentations of the sugar, which take place side by side in a manner similar to that observed during the preparation of kumiss (preceding abstract). The fermentations are not, however, carried so far as in the case of kumiss; thus kephir contains only 1% alcohol, kumiss 2 to 3%, whilst the proteins are not hydrolysed to the same extent in kephir. Artificial kephir and kumiss may be prepared from cow's and mare's milk respectively by means of a mixture of *Bacillus bulgaricus* and beer yeast. In these cases, also, the course of the reactions is similar to that described above.

A number of photomicrographs are given of the micro-organisms found in these fermentations. W. J. Y.

Action of the Bulgarian Ferment on Proteins. GABRIEL BERTRAND (*Compt. rend.*, 1910, **151**, 1161—1162; *Bull. Soc. chim.*, [iv], **9**, 103—104).—The observations of Effront (this vol., ii, 61) are not in agreement with results published by the present author (Abstr., 1907, ii, 120; 1909, i, 623; Margaillan, Abstr., 1910, ii, 163). The production of lactic acid in milk by the action of the Bulgarian ferment is mainly due, in the author's opinion, to transformation of the lactose,

and not to degradation of casein. Effront's results may be due to the presence of foreign bacteria in the Bulgarian ferment employed.
W. O. W.

The Influence of Alkalis and Acids on the Autolysis of Yeast. E. NAVASSART (*Zeitsch. physiol. Chem.*, 1910, **70**, 189—197).—Alkali lessens the autolysis of yeast, as it does that of animal tissues; the action is proportional to the alkali added, that is, the more alkali the less is the autolysis noted. The action of acid (hydrochloric) does not increase autolysis as it does in animal tissues, but it diminishes it. Nuclease is more affected by change in reaction than proteolytic enzymes.
W. D. H.

The Action of Rubber on Mercurial Antiseptic Solutions. A. T. GLENNY and GEORGE S. WALPOLE (*J. Hygiene*, 1910, **10**, 586—588).—Mercurial solutions in which rubber articles (tubing, catheters, stoppers, etc.) are placed lose mercuric salt and the rubber is attacked, especially on prolonged immersion. The knowledge of this fact is important in view of the extensive use of mercurial solutions for sterilisation and sterile storage. The loss of mercury means that the solution is no longer of the same antiseptic strength.
W. D. H.

Conservation of Salts during the Course of Vegetation of an Annual Plant. GUSTAVE ANDRÉ (*Compt. rend.*, 1910, **151**, 1378—1382).—The view has been held that loss of mineral matter may occur from osmosis through the roots and dead leaves of plants. This is not supported by the observations described in the present communication, which contains an account of experiments on beans, lupins, and pinks. No appreciable loss of salts was detected up to complete development of the plants, even when some of the leaves had partly withered, and were only acting imperfectly as organs of assimilation and elaboration.
W. O. W.

The Action of Salts on the Respiration of Plants. A. REINHARD (*Ber. Deut. Bot. Ges.*, 1910, **28**, 451—455).—The author confirms a result he has previously obtained, that phosphates increase the evolution of carbon dioxide from powdered seeds, whilst other salts do not. He now works with more dilute solutions, and finds as before that nitrates tend to depress respiration and phosphates increase it.
E. J. R.

Induced Maturation of Grains. Antigerminative Action of Acetaldehyde. PIERRE MAZÉ (*Compt. rend.*, 1910, **151**, 1383—1386).—Seeds of maize or peas collected from the plant when they contain 50—60% of water do not germinate when placed in a sterile atmosphere. If previously dried, however, in a vacuum, in the air, or in a current of carbon dioxide, germination is enabled to take place. This appears to be due to the removal in the latter case of volatile substances which inhibit germination. Acetaldehyde is effective in this way, and has been shown to occur in the freshly collected seeds. It may be removed by desiccation, or by the destructive action of moulds, such as *Aspergillus*, *Mucor*, etc., which have been shown to act in this way. The juice of the young plant also contains aldehyde, and this may play an important part in regulating maturation. The oxygen absorbed by the juice of the living plant is partly employed in oxidising this to alcohol. W. O. W.

Tolerance of Maize to Boron. HENRI AGULHON (*Compt. rend.*, 1910, **151**, 1382—1383).—Plants which have been grown in a medium containing somewhat less than the fatal amount of boric acid produce seeds, the plants from which have acquired a certain measure of immunity against the poison. They benefit by the administration of small doses to a greater extent than the parent crop, and support a toxic dose more easily. W. O. W.

Occurrence of *d*-Galactose. EDMUND O. VON LIPPMANN (*Ber.*, 1910, **43**, 3611—3612).—Following a sudden frost, the first after a late, dry, warm autumn, the berries of an ivy were observed to be covered with a colourless, crystalline efflorescence, resembling hoar frost, which proved to be galactose. No other carbohydrate was found accompanying it, and the berries themselves did not contain galactose or any substance yielding mucic acid on oxidation. E. F. A.

Microchemical Examination of Tannins and Natural Colouring Matters. LUIGI ERMANNO CAVAZZA (*Zeitsch. wiss. Mikroscop.*, 1910, **27**, 34—40).—An account of experiments on the natural colouring matters contained in plants, which the author tabulates in a list containing fifteen groups. The colour reactions given with these by various reagents are also appended. F. M. G. M.

Intravital Caffeine Reactions. THOMAS BOKORNY (*Pflüger's Archiv.* 1911, **137**, 470—488).—Caffeine is a reagent for active albumin first introduced by O. Loew and the author. Details are given in the present paper of the reactions (mainly microchemical) produced by caffeine in various vegetable structures; the most characteristic of them is the formation of *proteosomes*, and evidence is adduced that these are not a simple precipitate of tannic acid compounds of caffeine, or of protein. W. D. H.

Relative Proportions of Arsenic Present in Marine Algæ and their Preparations. EUGÈNE TASSILLY and J. LEROIDE (*Bull. Soc. chim.*, 1911, [iv], **9**, 63—66. Compare Gautier, Abstr., 1903, ii, 92).—The estimation of the arsenic was made by Gautier's method as modified by Bertrand (Abstr., 1904, ii, 85). The following quantities, expressed in mg. per 100 grams of seaweed, were found. *Chondrus crispus* ("Irish moss"), 0·07; *Fucus vesiculosus* ("Bladder wrack"), 0·01; "Corsican moss," 0·025; *Laminaria digitata*, 0·05; *L. saccharina*, 0·01, and *L. flexicaulis*, 0·01. "Norgin" prepared from *Laminaria* spp. contained 0·03, and "gelose," prepared from Japanese seaweed, gave 0·20 to 0·25. The amounts in Irish moss, norgin, and gelose may be due, in part, to the use of impure chemicals in preparing them for the market. "Kelp" made from *L. digitata* contained the whole of the arsenic naturally present in the seaweed. T. A. H.

Alkaloids of Datura Metel Seed. ERNST SCHMIDT (*Arch. Pharm.*, 1910, **248**, 641—643).—de Plato has stated recently (Abstr., 1910, ii, 742) that *Datura Metel* seed contains allantoin, but neither alkaloids nor cyanogenetic glucosides. The author has therefore repeated Kircher's work on this seed (Abstr., 1905, i, 717), and confirmed his observation that the chief alkaloid present is scopolamine (hyoscine). Small quantities of hyoscyamine and of a third alkaloid, giving an *aurichloride*, m. p. 140°, crystallising in dark yellow needles, are also present. T. A. H.

Constituents of Iris versicolor Rhizome. FREDERICK B. POWER and ARTHUR H. SALWAY (*Amer. J. Pharm.*, 1911, **83**, 1—14).—Authenticated rhizomes and rootlets of *Iris versicolor* ("blue flag root") furnished the following constituents on extraction with alcohol and separation of the alcoholic extract into (*a*) matter volatile in steam, (*b*) matter soluble in water, and (*c*) matter insoluble in water. Fraction (*a*) consisted of volatile oil, D_{20}^{20} 0·9410, possessing a yellow colour and a strong, rather unpleasant odour. From portion (*b*), *iso*phthalic acid, a trace of salicylic acid, tannin, and a reducing sugar, which gave *d*-phenylglucosazone, were isolated. The first of these substances has not been recorded from a natural product previously.

Fraction (*c*) was composed chiefly of a dark-coloured soft resin, forming 8·7% by weight of the crude drug. This resin contained, apart from amorphous matter, (1) a *phytosterol*, $C_{27}H_{46}O,H_2O$, m. p. 133° (148° when anhydrous), $[\alpha]_D$ $-35{\cdot}6°$ in chloroform, which crystallised in colourless needles from alcohol; (2) myricyl alcohol; (3) ipuranol (compare Abstr., 1910, ii, 338); (4) heptacosane; (5) a mixture of lauric, palmitic, stearic, cerotic, oleic, and linolic acids; and (6) possibly some ceryl alcohol.

Physiological tests made with the crude alcoholic extract, an aqueous extract of the drug, and fractions (*b*) and (*c*) referred to above, proved that these were all inactive. Since the physiological activity of *fresh* "blue flag root" is apparently well established, it would seem that the drug may lose its activity entirely on keeping. T. A. H.

The Cyanogen Compounds of Tobacco Smoke. JULIUS TÓTH (*Chem. Zeit.*, 1910, **34**, 1357. Compare Abstr., 1910, ii, 443).—The amount of cyanide compounds (calculated as C_2N_2) in tobacco smoke is not influenced by the amount of nicotine present in the samples. The cyanide found in tobacco smoke is not due to a reaction between dicyanogen and the ammonia which is always present in the smoke, for a direct experiment showed that, contrary to Wöhler's idea, no hydrogen cyanide or other cyanides are formed when these products interact. L. DE K.

The Glucoside of Pear Leaves [Arbutin], and its Function in Producing Autumn Tints. ÉMILE BOURQUELOT and [Mlle.] A. FICHTENHOLZ (*J. Pharm. Chim.*, 1911, [vii], **3**, 5—13. Compare Abstr., 1910, ii, 742).—The authors have examined leaves from a number of trees that were formerly classified as *Pyrus*, but are now regarded by most botanists as distinct. They find that *Pyrus communis* alone contains arbutin, while none of the other trees do; none could be detected in *Cydonia vulgaris, Malus communis, Sorbus aucuparia*, or *S. torminalis*, all of which were at one time classed with *Pyrus*. There are therefore recognisable chemical characters correlated with the botanical characters, and the modern classification is justified on biochemical, as well as on morphological, grounds.

The leaves of certain varieties of *Pyrus* turn black when they fall; in other cases a golden-yellow tint first appears, but then gives place to black. The authors support Wewers' hypothesis that the black colour is due to the oxidation of quinol by an oxydase, but, as the quinol arises from arbutin, this latter substance must first undergo hydrolysis by the emulsin in the leaf before the blackening can appear. Methylarbutin does not at once produce a black oxidation product, but a yellow one, and evidence is adduced that those leaves that first turn yellow contain methylarbutin [compare H. E. and E. F. Armstrong, Proc., 1910, **26**, 334]. E. J. R.

The Behaviour of Penicillium in the Presence of Acetic Acid and its Salts. JOHANNES REICHEL (*Biochem. Zeitsch.*, 1910, **30**, 152).—Free acetic acid was found to have an inhibitory action on the growth of *Penicillium glaucum*. The presence in an otherwise favourable medium of a very small concentration of acetic acid (0·0123 to 0·0420*N*) considerably delayed the production of spores, whilst greater concentrations (0·0940 and 0·2996*N*) completely prevented growth. This action was not due to the hydrogen ions of the acid, since the mould grew quite well on the same medium in the presence of either sulphuric, hydrochloric, tartaric, or oxalic acid of much greater normality. It was also not caused by the acetyl ions, since acetates did not exhibit this property, which was therefore ascribed to the undissociated acetic acid.

When *Penicillium* was grown in the presence of acetates, it was observed that the acidity of the medium was decreased. It is suggested that the mould regulates the acidity of the medium by utilising the acetate as a source of carbon, thereby preventing the liberation of sufficient acetic acid to inhibit its growth. W. J. Y.

The Alkaloids in Strychnos Nux Vomica During Germination. O. TUNMANN (*Arch. Pharm.*, 1910, **248**, 644—657. Compare Feldhaus, Abstr., 1905, ii, 648; Kerbosch, Abstr., 1910, ii, 1101).—The author has investigated the distribution of alkaloids in nux vomica seeds before and after germination, and finds that there is no justification for Heckel's view that the alkaloids are wholly transformed into more assimilable substances, as one result of germination. A portion of the alkaloids is passed into the soil, another is thrown off in the seed shell, whilst a small part is used in forming a protective layer for the embryonic leaves. The following are the chief conclusions arrived at. The two alkaloids, brucine and strychnine, occur only in the oil-plasma of the endosperm cell contents. The embryo of the resting seed contains brucine only. The alkaloids of the endosperm

are not absorbed by the embryo on germination. Nearly one-third of the total alkaloids is excreted into the surrounding soil and remains there in a form insoluble in water, and probably forms a protecting layer for the rootlets. About one-fifth, together with the residue of unabsorbed endosperm, is thrown off with the seed shell. Brucine is to some extent converted into strychnine during germination, but there is no evidence of the formation of nitrates from the alkaloids. Brucine is formed first in all parts of the embryo during germination, and both alkaloids are formed before the formation of chlorophyll takes place in the leaves. The following quantities in grams of total alkaloids were found in the various parts of one seed: whole seed, 0·0556; seed shell thrown off in germination, 0·0156; young embryonic root, 0·018; older embryonic root, 0·021; hypocotyl axis, 0·003; young embryonic leaf, 0·0072; older embryonic leaf, 0·0078.
T. A. H.

Non-protein Nitrogenous Substances in the Sugar-Beet. K. SMOLENSKI (*Zeitsch. Ver. deut. Zuckerind*, 1910, 1215—1261).—The diffusion liquors of a Russian sugar factory were found to contain the following non-protein nitrogenous substances: vernine, allantoin, asparagine, glutamine (?) and betaine. Tyrosine and choline were absent. A summary of the literature available as to the rotatory power of these compounds shows that glutamine will have but little effect on the polarisation of beet juice; asparagine will slightly increase the polarisation in aqueous solution. In alcoholic solution with lead acetate, the foreign substances have no influence on the polarisation. Polarisation after inversion in presence of glutamine or asparagine will indicate an excess of dextrorotatory carbohydrate. E. F. A.

Manurial Experiments with Sugar-Beet. E. SAILLARD (*Bied. Zentr.*, 1910, **39**, 859—860; from *J. Agric. prat.*, 1910, i, 267).—Sodium nitrate and cyanamide produced about the same amounts of roots and sugar, whilst calcium nitrate gave rather higher results.

Kainite produced more roots and more sugar than the same amount of potassium as chloride. This is attributed to the magnesium present in the kainite. N. H. J. M.

Relationship between the Fertility of the Soil and the Contained Phosphoric Acid Soluble in Water. ISIDORE POUGET and D. CHOUCHAK (*Rev. gen. Chim. pure Appl.*, 1910, **13**, 157—178, 219—222).—A detailed account of numerous experiments on the relationship between the fertility of soils and the contained phosphoric acid soluble in water, or in 1% citric acid solution.

The methods of culture are described, with photographs showing the relative growths of the plants experimented on; the mechanical, mineralogical, and chemical conditions of the soils are noted, and the amount and composition of the produce tabulated.

The second paper contains the results of varying the concentration of the solution of phosphoric acid supplied; when the concentration was greater than 1 mg. of P_4O_{10} per litre, the quantity absorbed was in direct proportion to the concentration; at a lower concentration the absorption decreased more rapidly than the concentration, and at 0·1 mg. per litre assimilation practically ceased. F. M. G. M.

Barium in Soils. G. H. FAILYER (*U.S. Dept. Agric. Bur. Soils Bull.* 72, 1910).—Barium occurs in most soils in the United States, the greatest amounts being found in soils derived from the neighbourhood of barite deposits, and in soils derived from the rocks of the Rocky Mountains.

Analyses of about a hundred Colorado and Kansas soils and subsoils showed that they contained from 0·01 to 0·11% of barium. Other soils were examined spectroscopically.

Barium was also found in various plants collected in different parts of Nebraska, Colorado, and Kansas (compare *Bureau of Plants, Ind. Bull.* 129). N. H. J. M.

Studies in Soil Oxidation. OSWALD SCHREINER, MICHAEL X. SULLIVAN and F. R. REID (*U.S. Dept. Agric. Bur. Soils Bull.* 73, 1910).—Oxidation in soils is, in part, due to the action of roots and partly to processes, mainly non-enzymatic, in the soil itself. Oxidation in soils is increased by the presence of salts of manganese; iron, aluminium, calcium, and magnesium, especially in conjunction with hydroxy-acids (citric, tartaric, malic, and glycollic acids) and their salts, the greatest effect being obtained with manganese, and the stimulating effect of manganese is attributed to this increased oxidation rather than to any direct action on the plant. Manurial salts increase the oxidising power of roots, whilst their action on the oxidising processes in the soil itself is variable. Excessive oxidation is injurious to vegetation. N. H. J. M.

Pentosans in Soils. EDMUND C. SHOREY and ELBERT C. LATHROP (*J. Amer. Chem. Soc.*, 1910, 32, 1680—1683).—Estimations of the pentosans in ten soils of widely different character have been made by boiling the soils with hydrochloric acid and weighing the furfuraldehyde produced in the form of its phloroglucinol compound. The results show that the amounts of pentosans in these soils ranged from 0·027 to 2·750%, whilst the proportion of carbon in the form of pentosans to the total carbon in the soils varied between 1·30 and 28·53%. The soil which contained the largest quantity of pentosan (2·75%) was a Marshall loam taken from a field in North Dakota on which flax had been grown for several years. From this soil, a crude pentosan was obtained which, when heated with hydrochloric acid, yielded furfuraldehyde, and on digestion with sulphuric acid furnished a pentose which was identified as xylose. Tests for other pentoses gave negative results.

It is pointed out that the method employed for estimating pentosans is merely an estimation of the furfuraldehyde which may originate from a pentosan, a pentose, or a pentose-yielding material other than a pentosan. The pentosans or pentose-yielding material in soils must be regarded either as plant residues, such as a portion of the lignocellulose which has resisted decomposition, or as products of the decomposition of complex compounds, such as nucleoproteins.

E. G.

Some Acid Constituents of Soil Humus. OSWALD SCHREINER and EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1910, **32**, 1674—1680). —The authors have already isolated certain acid substances from the soil, namely, dihydroxystearic, 2-picoline-4-carboxylic, and agroceric acids (Abstr., 1908, ii, 421, 889, 1067; *Bull.* **53**, *Bureau of Soils, U.S. Dept. Agric.*, 1909).

The study of the acid constituents of soil humus has been continued, and α-hydroxystearic, paraffinic, and lignoceric acids have now been isolated. The so-called α-hydroxystearic acid,

$$CH_3\cdot[CH_2]_6\cdot CH(OH)\cdot[CH_2]_9\cdot CO_2H,$$

m. p. 84—85°, and the dihydroxystearic acid described previously are probably produced in the soil by the action of micro-organisms on organic matter of vegetable or animal origin. The paraffinic acid, $C_{24}H_{48}O_2$, is identical with that obtained by Pouchet (Abstr., 1875, 50), by the action of fuming nitric acid on paraffin. The manner in which this substance is formed in the soil is not clear, but it is probably produced by the oxidation of solid hydrocarbons, such as are known to occur in plant tissues. Lignoceric acid, $C_{24}H_{48}O_2$ (Hell and Hermanns, Abstr., 1881, 249), occurs as a glyceride in ground-nut oil, and may possibly be a constituent of other vegetable oils; its production in the soil may be due to the decomposition of such glycerides. This acid is also obtained by the distillation of wood, and it is therefore possible that its occurrence in the soil may be the result of the decomposition of woody tissues by the agency of micro-organisms. E. G.

Chemical Nature of Soil Organic Matter. OSWALD SCHREINER and EDMUND C. SHOREY (*U.S. Dept. Agric. Bur. Soils Bull.* **74**, 1910). —In addition to the four substances previously obtained from soils (dihydroxystearic acid, picolinecarboxylic acid, agroceric acid, and agrosterol), the following compounds have now been isolated: hentriacontane, α-hydroxystearic acid, paraffinic acid, lignoceric acid, phytosterol, pentosan, histidine, arginine, cytosine, xanthine, hypoxanthine, fatty glycerides, and several resin acids. N. H. J. M.

Manurial Value of Manganese Sulphate. A. CARLIER (*Bied. Zentr.*, 1910, **39**, 859; from *Ann. Gembloux*, 1910, 423).—Manganese sulphate applied to grass at the rate of 50 and 100 kilos. per hectare increased the yield of hay 0·9 and 9·5% respectively.

The same amounts of manganese sulphate reduced the yield of potatoes by 9 and 0·6%. The yield of mangolds (roots) was reduced by 2·5 and 1%, and the leaf of mangolds by 25 and 20%.

N. H. J. M.

Analytical Chemistry.

Preparation of a Sensitive and Stable Litmus Solution. A. PÜSCHEL (*Oesterr. Chem. Zeit.*, 1910, [ii], **13**, 185—186).—The sensitive violet-coloured constituent of litmus can be separated from the other colouring matters and gums present in the commercial product by heating with dilute sulphuric acid (about 4%), when it is precipitated presumably in the form of a sulphonic acid; this, after collection and washing, is redissolved in hot water and neutralised with sodium hydroxide, when an exceedingly sensitive violet solution is obtained. F. M. G. M.

The Colouring Matter of Red Radishes. JULIUS F. SACHER (*Chem. Zeit.*, 1910, **34**, 1333).—Further particulars as to the colouring matter of red radishes and its applications in titrations (Abstr., 1910, ii, 1106).

In aqueous solutions alkali carbonates behave like hydroxides. In dilute alcoholic solutions, however, the case is different. If, for instance, to 1 c.c. of the alcoholic solution of the indicator is added a small crystal of sodium carbonate and then water drop by drop, a solution is at first obtained which in incident light is of an emerald-green, and in transmitted light of a red, colour. On shaking, the liquid looks bluish-green. With gas light, it is wine-red in any direction. On adding more water, the liquid turns violet, then blue, and after about half an hour the colour changes to green and finally to yellow. It has been remarked that the indicator is too unstable to be of use in practice, but the author states that it keeps unchanged in alcoholic solution; moreover, it may be prepared fresh in a few minutes. L. DE K.

Use of Sulphur Dioxide in Checking Strengths of Volumetic Solutions of Iodine, Alkali, and Silver. ELIAS ELVOVE (*Amer. J. Pharm.*, 1911, **83**, 19—23).—A scheme is outlined for basing the determination of the strengths of volumetric solutions on pure silver as a standard. The solutions would be prepared in the following order, each serving as a standard for the succeeding one: ammonium thiocyanate (standardised against pure silver), silver nitrate, hydrochloric acid, sodium hydroxide, oxalic acid, potassium permanganate, sodium thiosulphate, iodine. To control the standardisation, 25 c.c. of the standard iodine solution should be just decolorised by freshly prepared sulphur dioxide solution and the acid formed titrated with the standard sodium hydroxide solution. The total iodide in this neutralised solution could then be determined by adding excess of silver nitrate and titrating the excess of silver with standard ammonium thiocyanate, allowance being made for the pure potassium iodide used in preparing the iodine solution. T. A. H.

Rapid Estimations and Separations by means of a Mercury Cathode and Stationary Anode. RAYMOND C. BENNER and M. L. HARTMANN (*J. Amer. Chem. Soc.*, 1910, **32**, 1628—1636).—It has been shown (Stoddard, Abstr., 1909, ii, 347; Benner, Abstr., 1910, ii, 999) that electro-analysis can be carried out with a mercury cathode and stationary platinum gauze anode, sufficient agitation being produced by the evolution of gas to enable the metal to be deposited in an adherent form.

Comparisons have now been made of the rates of precipitation, under similar conditions, which show that although the rate is greater with the rotating anode than with the stationary anode, it is not sufficiently so to justify the use of the much more complicated apparatus. The results obtained with the stationary anode are as accurate as those obtained by other mercury cathode methods, and it has been found that the estimation and separation of various metals can be effected under the same conditions as are employed with the rotating anode.

E. G.

A New Apparatus for Effecting Slow and Certain Incineration. EDMOND J. APS (*Chem. Zeit.*, 1910, **34**, 1374).—The vessel in which the ignition is carried out is supported on three prongs attached to a vertical axis, which is slowly rotated by means of a motor.

By this means, it is claimed that uniform heating is obtained and spurting prevented. F. B.

Gas-Volumetric Estimation of Hydrogen. OTTO BRUNCK (*Chem. Zeit.*, 1910, **34**, 1313—1314; 1331—1332).—After a short reference to the various methods for estimating hydrogen, the remainder of the paper is occupied by a description of Paal and Hartmann's method, which makes use of colloidal palladium (compare Abstr., 1910, ii, 237). T. S. P.

Gas Analysis by Toepler's Pressure Balance. ERNST MOHR (*J. pr. Chem.*, 1910, [ii], 540—546. Compare Toepler, Abstr., 1896, ii, 235).—An apparatus is described for the measurement of the small amount of hydrogen in technical electrolytic oxygen. Two similar vertical glass tubes of the same height and open at the upper ends are connected by their lower ends to a bent tube, containing a thread of petroleum, the two limbs of which are very slightly inclined to the horizontal plane. One tube is filled with the gas under examination, the other with pure dry oxygen; in consequence of the small difference in density of the two gases, the thread of petroleum is shifted from its null position, the amount of the displacement being read by an optical micrometer. An equation is given by which the desired percentage of hydrogen can be calculated. The constant of the apparatus is determined by using gaseous mixtures of known composition. About 0·02% of hydrogen can be estimated rapidly and with sufficient accuracy. C. S.

Estimation of the Acidity of Hydrogen Peroxide. LOTHAR WÖHLER and W. FREY (*Zeitsch. angew. Chem.*, 1910, **23**, 2353—2354).—The acidity of hydrogen peroxide can be accurately determined by direct titration with *N*/10-alkali. Methyl-orange should be used as indicator when the acid present allows of it, since its indications are quite sharp, even with a 30% solution of hydrogen peroxide. When the acid present necessitates the use of phenolphthalein as indicator, it is best to destroy the hydrogen peroxide with platinum-black or by warming with excess of alkali, before the acidity is determined, taking great care to exclude carbon dioxide. Endemann's results (Abstr., 1909, ii, 432) are due to the fact that carbon dioxide was not excluded, so that correct results could not be obtained with phenolphthalein as indicator. T. S. P.

Estimation of Chlorides in Blood. BERTHOLD OPPLER (*Zeitsch physiol. Chem.*, 1910, **70**, 198—204).—The removal of protein by phosphotungstic acid gives good results in the estimation of sugar, but not of chlorides in such fluids as blood. Metaphosphoric acid is for chlorides the best substance to use for getting rid of the protein. The chlorine may be estimated gravimetrically as silver chloride, or electrolytically. W. D. H.

Estimation of Iodine in Alcoholic Solutions. G. FAVREL (*Ann. Chim. anal.*, 1911, **16**, 12—13).—The author has tried the gravimetric process recommended by Desvignes (weighing as silver iodide after conversion into potassium iodide) and the volumetric process recommended by Lebeau for aqueous solutions (titration with silver nitrate after treatment with zinc powder), and finds both processes to give the same result as the titration with thiosulphate.

When applying Lebeau's process to tinctures, it is advisable to neutralise any free acid present by means of a little zinc carbonate. Both processes have the advantage over the thiosulphate method that they are applicable to alcoholic solutions which have been kept for a long time, and in which hydriodic acid may be present. L. DE K.

Estimation of Sulphur in Brass and Bronze.—GUSTAV THURNAUER (*J. Ind. Engin. Chem.*, 1910, **2**, 293).—The author recommends the following process adapted from organic analytical procedure for estimating sulphur in brass and bronze; it gives excellent results, and avoids the tedious operations of oxidising with aqua regia and subsequently removing metals.

One gram of bronze filings is thorougly mixed with six grams of a mixture consisting of potassium chlorate (2 parts) and sodium carbonate (1 part), transferred to a wrought-iron crucible (lined with a layer of sodium carbonate), and covered with a further quantity of the mixture. The crucible is gradually heated until the mass is completely fused; after cooling, the fusion is digested with hot water and the metallic oxides are removed by filtration, the solution acidified with hydrochloric acid, and the sulphur estimated in the usual manner as barium sulphate. If great accuracy is required, a silver crucible should be employed, but the amount of sulphur abstracted from the iron does not usually introduce an error exceeding 0·01 per cent.

F. M. G. M.

Red Coloration given by Esbach's Reagent [with Urine]. C. GAZZETTI and C. SARTI (*Arch. farm. sperim. Sci.*, 1910, **9**, 319—325). —A pathological urine was found to give a ruby-red coloration with Esbach's reagent. The colour was due to picramic acid, formed from the picric acid by ammonia and ammonium sulphide present in the urine. It was also produced on addition of picric acid alone, and, in fact, is destroyed by excess of citric acid. Since the amount of ammonium sulphide present was scarcely to be detected with lead test-papers, it appears that this reaction is very delicate. R. V. S.

A New Apparatus for the Quantitative Estimation of Sulphur Trioxide in Sulphuric Acid. GEORGE FINCH (*Zeitsch. Schiess und. Sprengstoffwesen*, 1910, **5**, 167—168.)—The apparatus consists of a flask, to the lower bulb portion of which is attached a narrow tube bent at a convenient angle, through which the liquid to be analysed is introduced by suction ; this can be closed by an accurately fitting capsule. The neck of the flask may be closed with a stopper, or by a dropping funnel which is connected below its tap with a U-tube, the other arm of which is open to the atmosphere.

The required amount of fuming acid is drawn into the tared flask and weighed, the neck stopper is then replaced by the dropping funnel, and the U-tube at its side half filled with water ; the acid is then diluted with distilled water by means of the dropping funnel (the stem of which is drawn out into a capillary), made up to a convenient volume, and titrated with sodium hydroxide. F. M. G. M.

Gravimetric Estimation of Tellurium and Alkalimetric Estimation of Telluric Acid. ARTHUR ROSENHEIM and M. WEINHEBER (*Zeitsch. anorg. Chem.*, 1911, **69**, 266—269).—When the estimation of tellurium by reduction with hydrazine in weakly alkaline solutions is carried out according to Gutbier's instructions (Abstr., 1901, ii, 687), the results are not trustworthy, some tellurium often remaining unprecipitated, or else some of it is oxidised in the drying. The authors recommend that the tellurium solution be reduced with a 10% hydrazine sulphate solution while contained in a covered beaker in an autoclave heated to 130° under 3—4 atmospheres' pressure. The tellurium is then deposited completely in half-an-hour, and in such a form that it does not oxidise during the subsequent treatment.

Telluric acid, when mixed with glycerol in aqueous solution, behaves as a monobasic acid towards phenolphthalein, but the results are somewhat variable. Better volumetric results are obtained as follows: To the solution of telluric acid is added a large excess of *N*/10-barium hydroxide or of *N*/10-sodium hydroxide containing barium chloride. In consequence of the excess of barium ions, the precipitation of the telluric acid as barium tellurate, $BaTeO_4$, is complete. The excess of hydroxide can then be determined by titration with oxalic acid, using phenolphthalein as indicator, without it being necessary to first collect the precipitate. In this process telluric acid acts as a dibasic acid. T. S. P.

Estimation of Free Ammonia and Ammonium Carbonate by Titration. JOHN C. THOMLINSON (*Chem. News*, 1911, **103**, 13).—The author states that this may be effected as follows : The liquid is titrated into *N*-sulphuric acid, using phenolphthalein as indicator, until the liquid assumes a transient pink colour through its entire bulk ; this gives the normal ammonium carbonate. Methyl orange is then added, and the titration is continued ; this gives the total ammonia. L. DE K.

Detection and Estimation of Nitric Acid in Milk by means of the Diphenylamine-Sulphuric Acid Test. J. TILLMANS (*Zeitsch. Nahr. Genussm.*, 1910, **20**, 676—707).—The results of an investigation of this test are given, the chief object being to ascertain the conditions under which the test is capable of detecting very small amounts of nitric acid in milk, as the presence of nitric acid indicates that water containing nitrates has been added to the milk. The milk is first treated with calcium chloride, and the serum thus obtained is shaken with ether and calcium hydroxide in order to remove certain proteins and lactose. A portion, 0·5 c c, of the clear solution obtained is then mixed with 2 c c. of the reagent, cooled, and placed aside for a hour; the blue coloration produced if nitric acid is present reaches its full intensity after this lapse of time. The reagent is prepared by mixing 0·085 gram of diphenylamine with 190 c.c. of dilute sulphuric acid (1 : 3), and adding a quantity of concentrated sulphuric acid; the mixture becomes heated, and the diphenylamine dissolves. Concentrated sulphuric acid is now added to make the volume of the whole nearly 500 c.c., the mixture is cooled, and finally made up to a volume of 500 c.c. by the addition of concentrated acid. It is essential that chlorides be present in the solution to be tested; water containing a large amount of nitrates, but free from chlorides, does not yield a coloration with the reagent. Water containing 0·1 mg. of nitric acid (N_2O_5) per litre, and milk serum with 0·25 mg. per litre, yield distinct colorations. In the absence of nitric acid, milk serum gives a yellow or pink coloration. By comparing the coloration obtained with those yielded, under similar conditions, by portions of milk serum containing known quantities of nitric acid, it is possible to estimate the amount of nitric acid in the milk from which the serum was prepared. Nitrous acid also yields a blue coloration with the reagent; in this case the presence of chlorides is not essential, and the coloration develops almost at once. Milk containing an abnormal quantity of dirt may give a reaction for nitric acid, but the small amounts of foreign matters usually present in milk do not cause the production of a coloration.

W. P. S.

Estimation of Phosphoric Acid in Soils and Crops.

HERMANN KASERER and IGNAZ K. GREISENEGGER (*Zeitsch. landw. Vers.-wesen Oesterr.*, 1910, **13**, 795).—The methods advocated for the analysis of organic material by Neumann (*Hoppe-Seyler's Handbuch der Physiologischen und pathologisch-chemischen Analyse*) are discussed, and some modifications suggested. For the estimation of phosphoric acid, the author advises that a measured portion of the liquid from the "Kjeldahl" flask be treated with excess of ammonium nitrate, ammonium molybdate added, the mixture thoroughly agitated, and rapidly cooled. The precipitate is collected in an asbestos-lined Gooch crucible, washed with water and alcohol, and the whole transferred into a beaker and titrated with $N/4$-sodium hydroxide (employing phenolphthalein as indicator) until the precipitate is completely dissolved:

$$2(NH_4)_3PO_4,24MoO_3,4HNO_3 + 56NaOH = 2Na_2HPO_4 + 24Na_2MoO_4 + 4NaNO_3 + 32H_2O + 6NH_3.$$

The red liquid is then boiled until all ammonia is evolved (more sodium hydroxide being added as required), excess of standard sulphuric acid added and any carbon dioxide removed by boiling, and the hot solution then finally titrated back with alkali. A table of comparative results with those obtained by Neumann's method is given in the paper.

F. M. G. M.

Easy Detection of Arsenic; Rapid Separation of Arsenic and Some Other Metals from Liquids. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1910, **70**, 186—188. Compare Carlson, Abstr., 1910, ii, 998).—Attention is drawn to the fact that it has been known for a long time that the addition of ether or chloroform to an aqueous colloidal solution produces a precipitation of the colloid. Arsenious sulphide is not dissolved by either ether or chloroform, but the use of ether for precipitating is preferable, as the separation of the sulphide can be effected more readily than when chloroform is used.

J. J. S.

Convenient Potash Bulb. C. E. WATERS (*J. Amer. Chem. Soc.*, 1910, **32**, 1691—1693).—The apparatus consists of an inner tube terminating in either a bulb or disc, pierced by a number of small holes to break the gas up into small bubbles, and an outer, larger tube or bulb, which is sealed to the inner tube at the top. From the shoulder of the large bulb pass two tubes, one for the exit of the gas and the other for the admission of the potassium hydroxide solution; the latter is furnished with a ground glass stopper. Between the inner and outer tubes are a number of annular glass discs which fit so loosely that they can move freely up and down between projections blown on the wall of the inner tube. The gas, after passing through the inner tube, rises in the outer tube, and is trapped successively by the discs, which alternately rise and fall, thereby wetting the wall of the outer tube with fresh solution. The free spaces between the discs and the walls of the tubes should not be less than 1 mm. wide. The volume of solution in the bulb is usually sufficient if it just reaches the second disc.

This apparatus is less fragile and much lighter than Geissler's bulb, and by means of the special stoppered tube for filling, all danger of contact between the solution and the rubber connexions is obviated.

E. G.

Detection and Estimation of Potassium Perchlorate in Potassium Chlorate. K. SCHERINGA (*Pharm. Weekblad*, 1911, **48**, 15).—The new method is based on the fact that potassium perchlorate is not reduced by sulphur dioxide. One gram of a sample of potassium chlorate is dissolved in 130 c.c. of water in an Erlenmeyer flask plugged with cotton wool. A current of sulphur dioxide, generated by heating a solution of 15 grams of sodium sulphite with 3 c.c. of sulphuric acid, is passed just above the solution; the sulphur dioxide is rapidly absorbed, and causes reduction of the chlorate to chloride. After boiling for some time, a solution of 1·5 gram of silver nitrate is added, and the silver chloride is collected and weighed as usual.

The filtrate, which contains the perchlorate, is made alkaline with sodium carbonate, and, after filtering off from the silver oxide, it is evaporated to a very small bulk, introduced into a test-tube, boiled until solidification sets in, and then dried completely in an air-bath. After plugging the tube with asbestos, the mass is heated to redness for some time, and the asbestos layer is then also heated for a while.

The chlorine in the mass, which represents the perchlorate, is then estimated as usual.

Potassium perchlorate free from chlorate does not reduce indigo solution. L. DE K.

Character of Silver Deposits from Various Electrolytes.

JOSIAH SIMPSON HUGHES and JAMES R. WITHROW (*J. Amer. Chem. Soc.*, 1910, **32**, 1571—1576).—Experiments are described which include the repetition of some of the earlier work on the electrolytic estimation of silver, and a series of trials with electrolytes which have not been used previously.

In the case of the nitric acid electrolyte, it was found that dense deposits could not be obtained if the *E.M.F.* was high, but that, with a low *E.M.F.*, good crystalline deposits were produced; this is in accord with the statement of Küster and von Steinwehr (Abstr., 1899, ii, 125). With an electrolyte of ammonium sulphate and ammonium hydroxide, bright deposits were often obtained at first, but became more velvet-like as their weight increased, and darkened when the *E.M.F.* was over 1·4 volts; in all cases, the weights of the deposits were too high unless the *E.M.F.* was kept below 1·4 volts. When ammonium sulphate was used in the absence of ammonium hydroxide, a heavy, black, graphite-like deposit was formed on the anode, but disappeared on the addition of a few drops of ammonium hydroxide. With electrolytes consisting of ammoniacal solutions of ammonium phosphate and pyrophosphate, crystalline deposits were produced, but were spongy if the *E.M.F.* was too high. Potassium cyanide gave good, white deposits, especially at a temperature of 60—70°.

The other electrolytes studied were sulphuric acid, sulphuric acid and glycerol, ammonium thiocyanate, sodium hydroxide and ammonium hydroxide, ammonium perchlorate, potassium fluoride, and hydrofluosilicic acid. The deposits from sulphuric acid and glycerol were coarsely crystalline and non-adherent. Hydrofluosilicic acid gave satisfactory results.

In the case of each of these electrolytes, except potassium cyanide, there is a point at about 1·4 volts above which spongy deposits are produced; with potassium cyanide, the point is much higher.

E. G.

Estimation of Minimum Quantities of Calcium in Presence of a Large Excess of Magnesium.

CH. LIESSE (*Ann. Chim. anal.*, 1911, **16**, 7—8).—The sample is dissolved in twenty-five parts of hydrochloric acid, one hundred parts of water are added, and the solution is neutralised with ammonia, using phenolphthalein as indicator. The precipitate (silica, alumina, iron oxide) is removed by filtration, and water is added up to 1500 c.c. for each gram of sample. Four grams (or more) of solid ammonium oxalate are introduced, and the solution is acidified with acetic acid. After waiting for two hours with occasional stirring, the calcium oxalate is collected and treated as usual. Owing to the large dilution, it is free from magnesium oxalate. L. DE K.

New Test Paper for the Volumetric Estimation of Zinc [with Sodium Sulphide]. R. Kopenhague (*Ann. Chim. anal.*, 1911, **16**, 10—12).—As external indicator is used a strip of filter-paper impregnated with a 10% solution of cadmium nitrate and dried at 80—90°.

A small drop of the solution deposited on the paper will, in a few seconds, turn yellow if sufficient sodium sulphide has been added.

L. de K.

Rapid Estimation of Lead in Ores by Electrolysis with Stationary Electrodes. R. C. Benner (*J. Ind. Engin. Chem.*, 1910, **2**, 348—349).—The work of Sand was repeated and his results confirmed, showing that it is possible to deposit all the lead which can occur in a 0·5 gram sample of ore in five to ten minutes; for the electrolysis, 75 c.c. of the solution, in the presence of 20 c.c. of nitric acid (D 1·4), are used with a current of 4·8 amperes and 2·5 volts; the electrolyte is warmed during the deposition so as to maintain the cell just below boiling point.

About 0·5—1 gram of pulverised ore was freed from sulphide by boiling with hydrochloric acid, but not concentrated to the point where lead chloride would crystallise out; the hydrochloric acid was then expelled with concentrated nitric acid, and the volume of the solution reduced to about 10 c.c., diluted to 75 c.c., and electrolysed as above.

In ores where this method was impossible, aqua regia was employed, and the solution evaporated until fumes of sulphur trioxide became apparent, water added, and the basic iron sulphates dissolved by boiling; the lead sulphate was then collected, and converted into lead carbonate by treatment with hot ammonium carbonate; this was collected, washed, redissolved in nitric acid, and the lead finally deposited by electrolysis.

F. M. G. M.

Quantitative Analysis of German Silver and Similar Alloys. Reinhold Korte (*Zeitsch. angew. Chem.*, 1910, **23**, 2354—2356).—The author recommends the following methods of analysis: To determine the copper, nickel, and zinc, about 0·8 gram of the alloy is dissolved in aqua regia, the solution evaporated to dryness, and the residue taken up with hydrochloric acid and water. The copper is precipitated with hydrogen sulphide, the copper sulphide collected, dissolved in nitric acid, and the copper determined electrolytically. The filtrate from the copper sulphide is concentrated to about 50 c.c., a hot solution of 2 grams of dicyanodiamidine sulphate in 20 c.c. of water added, cooled, and then made alkaline with ammonia. A 30% solution of potassium hydroxide is then added until the blue colour changes to yellow; on remaining overnight, the nickel dicyanodiamidine sulphate has completely precipitated. It is washed by decantation with ammonia water, dissolved in dilute sulphuric acid, and the nickel determined electrolytically after the addition of ammonium sulphate and ammonium hydroxide; or the precipitate may be collected in a Gooch crucible, dried at 115°, and weighed directly, but in this case it is necessary to add a little tartaric acid to the solution before precipitating, in order to retain the iron in solution.

The filtrate from the nickel precipitate is acidified with hydrochloric acid, made up to 500 c.c., and the zinc in 100 c.c. determined by direct titration with potassium ferrocyanide, using ammonium molybdate as indicator.

To determine iron and manganese, the latter is precipitated as peroxide from a nitric acid solution of 2 grams of the alloy by heating with potassium chlorate. The collected and washed manganese peroxide is dissolved in hot concentrated hydrochloric acid, the diluted solution made ammoniacal, and the manganese again precipitated as peroxide by boiling with ammonium persulphate; it is weighed as Mn_3O_4.

The iron in the filtrate is precipitated by ammonium hydroxide, after the addition of solid ammonium chloride, the ferric hydroxide collected, and dissolved in hydrochloric acid. After the addition of 150 c.c. of warm water and a few drops of a 5% solution of copper chloride in hydrochloric acid, together with 15—20 c.c. of a 10% solution of sodium salicylate, the deep violet solution is titrated with a standard solution of sodium thiosulphate until colourless; this gives the percentage of iron.

The author recommends this method for estimating iron as being quite as trustworthy as titration with permanganate; it is only necessary to exclude nitric acid, or a large excess of hydrochloric acid.

T. S. P.

Separation of Iron, Chromium, and Aluminium. TCHARVIANI and WUNDER (*Ann. Chim. anal.*, 1911, **16**, 1—7).—*Separation of Iron and Chromium.*—About 0·5 gram of the mixed oxides is fused in a platinum crucible with 6 grams of sodium carbonate over a Téclu burner for three hours with free access of air. The fused mass is boiled with water, and the residual iron oxide subjected to a second fusion to remove the last traces of chromium. As iron oxide always retains alkali, it must be purified by solution in hot dilute hydrochloric acid and reprecipitation with ammonia. The chromium is recovered as oxide from the alkali chromate solution in the usual manner; it should be purified by solution in hydrochloric acid and reprecipitation with ammonia.

Separation of Chromium and Aluminium.—The fusion should be continued for about six hours. The aqueous solution is then heated with excess of ammonium nitrate until the free ammonia has been expelled. The alumina is thus obtained in a pure condition. The filtrate is acidified with nitric acid, reduced by addition of alcohol, and the chromic oxide is precipitated with ammonia.

Separation of Iron and Aluminium.—A double fusion is required, and both iron and aluminium are then estimated as just directed.

Separation of Iron, Chromium, and Aluminium.—A seven hours' fusion is required; although this suffices for a complete disintegration, a second fusion is perhaps advisable. The fused mass is then treated as previously directed.

L. DE K.

Analysis of Chromium Tungsten-Steel. F. WILLY HINRICHSEN and TH. DIECKMANN (*Mitt. K. Materialprufungsamt Gross-Lichterfelde West.*, 1910, **28**, 229—246. Compare Abstr., 1908, ii, 900).—A comparative discussion on the different methods employed by the author and others for the estimation of chromium, tungsten, and phosphoric acid in steels. Knorre's method of precipitating tungsten with benzidine (Abstr., 1905, ii, 286; 1908, ii, 231, 779) is considered fairly satisfactory, the employment of tartaric and tannic acids and hydroxylamine is likewise discussed. F. M. G. M.

Estimation of Chromium in Chrome-Tungsten Steel. HENRIK WDOWISZEWSKI [with P. BOGOLUBOFF] (*Chem. Zeit.*, 1910, **34**, 1365).—A modification of von Knorre's method (Abstr., 1908, ii, 779). One to two grams of steel borings are placed into a 500 c.c. Erlenmeyer flask, 10—15 c.c. of 15% solution of sodium hydrogen phosphate are added, and then 8—16 c.c. of sulphuric acid (D 1·65) and 5 c.c. of water. The metal dissolves with the aid of a gentle heat in about fifteen minutes, and, after heating a little more strongly, 2 c.c. of nitric acid (D 1·4) are added, which converts the tungsten into soluble phosphotungstic acid. The clear liquid is then diluted with 300—500 c.c. of hot water, 3—5 grams of ammonium persulphate are added to oxidise the chromium to chromic acid, and the excess of the reagent is then destroyed by boiling. After adding a few more c.c. of sulphuric acid, the chromic acid is titrated with standard ferrous ammonium sulphate, the excess of which is titrated with standard permanganate. L. DE K.

The Analysis of Ferro-Uranium. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 61—62).—The powdered alloy (0·4 to 0·6 gram) is dissolved in warm aqua regia, three hours' warming being sufficient even when much carbon and silicon are present. After diluting with water and cooling, an excess of solid ammonium carbonate is added, and the solution is repeatedly stirred. After twenty-four hours, the precipitate, containing the whole of the iron and aluminium, and the silica, is collected. The filtrate is boiled, precipitating most of the uranium. The addition of a few drops of ammonia precipitates the remainder, and the precipitate is then collected, washed with ammonium nitrate, and weighed as U_3O_8.

Carbon is estimated by direct combustion in oxygen, and silicon by the usual method. Aluminium may be estimated by fusion with sodium peroxide, precipitation of alumina and silica by ammonia, and separation by means of hydrofluoric acid, or by fusion with potassium hydrogen sulphate. C. H. D.

The Analysis of Ferro-Zirconium. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 62).—The alloys, which contain less than 20% of zirconium, may be roasted in a platinum crucible, fused with sodium carbonate and a little nitrate, dissolved in water with the aid of a little hydrochloric acid, and repeatedly evaporated to dryness with hydrochloric acid. The silica is estimated in the usual way, and is then tested for purity by fusion with potassium hydrogen sulphate. It retains from 1·2 to 2·9% of the zirconium present. The zirconium is best estimated by boiling the approximately neutral filtrate with sodium thiosulphate, fusing the ignited precipitate with potassium hydrogen sulphate, and repeating the precipitation. If aluminium is present in the alloy, it passes into the zirconia, and must be removed by fusion with sodium peroxide.

The alloy may also be dissolved, after roasting, in hydrofluoric acid, the zirconium being estimated by any of the usual methods. Carbon is estimated by combustion in oxygen. C. H. D.

A New Reagent for Nickel and Cobalt and its Use for Distinguishing between these Metals. H. Weil (*Bull. Soc. chim.*, 1911, [iv], 9, 20—22).—The process depends essentially on the difference in solubility of the basic chromates of the two metals in water.

Potassium chromate gives with cold neutral aqueous solutions of cobalt salts, containing not less than 2 grams per litre, a reddish-brown precipitate of the basic chromate, $CoCrO_4,CoO,x$aq. With very dilute solutions the precipitate only appears on boiling, and in this way 0·000032 gram of cobalt may be detected. The precipitate is soluble in acids or ammonia, and is decomposed by alkali hydroxides.

Nickel gives under the same conditions a chocolate-brown precipitate, $NiCrO_4,2NiO$, which forms very slowly in the cold, even in concentrated solutions, but rapidly on boiling. A precipitate is formed with 0·000028 gram of nickel.

For use in distinguishing between the two metals when present in nearly equal quantities, the cobalt is precipitated in the cold, and the nickel on boiling the filtrate, both being recognised by the colour of the respective precipitates. If nickel is present in small amount relatively to cobalt, the precipitate obtained on boiling the filtrate, which may contain some cobalt, is washed, dissolved in dilute ammonia solution, and the liquid freed from ammonia by evaporation, when chocolate-brown basic nickel chromate is precipitated, whilst cobalt under these conditions gives a green precipitate. If nickel is present in great excess, cobalt is no longer precipitated in the cold, and the deposit obtained on boiling must then be treated with ammonia as described, when the formation of a green precipitate indicates the presence of cobalt. T. A. H.

Analysis of Tin Alloys. Franz Kietreiber (*Oesterr. Chem. Zeit.*, 1910, [ii], **13**, 185—186).—Alloys containing tin, antimony, lead, and copper (such as Britannia metal and type metal) can be conveniently analysed as follows. About 1 gram of the alloy after heating with moderately concentrated nitric acid (10—15 c.c.) until all action has ceased is tranferred to a basin and evaporated down with about 25 grams of pure crystalline sodium sulphide ($Na_2S,9H_2O$), and the temperature subsequently raised until the melt begins to harden; it is then digested with hot water, whereby the tin and antimony are dissolved and the lead and copper remain insoluble; the former are then separated as described by Panatojow (Abstr., 1909, ii, 523). F. M. G. M.

A New Method of Analysing White Metal. E Schürmann (*Mitt. K. Materialprufungsamt Gross-Lichterfelde West.*, 1910, **28**, 349—350).—Alloys containing possibly tin, antimony, copper, arsenic, lead, and mercury, and can be conveniently analysed by converting the metals into their bromides. The alloy is carefully treated with a solution of bromine in chloroform or carbon tetrachloride, and, on warming, a violent reaction takes place; when this is ended, the mixture is thoroughly shaken with an aqueous solution of oxalic acid, separated, and the insoluble bromides and stannic acid collected. The antimony is precipitated from the solution with hydrogen sulphide, and the remaining tin subsequently by electrolysis. F. M. G. M.

Estimation of Glycerol. W. STEINFELS (*Seifensieder Zeit.*, 1910, **37**, 793—795).—The author discusses the various methods advocated for the estimation of glycerol, and suggests some modifications to the one introduced by Hehner. The alkaline liquid containing glycerol (not more than 2 grams) is acidified with sulphuric acid, rendered feebly alkaline with sodium hydroxide, and treated with 20 c.c. of 10% zinc sulphate solution; it is then filtered, and made up to 250 c.c.; 25 c.c. of this are oxidised by heating on the water-bath for two hours with 25 c.c. of Hehner's potassium dichromate solution and 50 c.c. of dilute sulphuric acid (1 : 4). After cooling, it is diluted to 500 c.c. with cold water. Twenty-five c.c. are run into a $\frac{3}{4}$-litre flask containing 2 grams of potassium iodide, dissolved in the least possible amount of water and 10 c.c. of hydrochloric acid (1 : 2), diluted to 1 litre, and titrated with sodium thiosulphate.

F. M. G. M.

Colorimetric Estimation of Dextrose in Urine. WILHELM AUTENRIETH and THEODOR TESDORPF (*Münch. med. Woch.*, 1910, **37**, No. 34, Reprint 13 pp.)—The authors find that the end-point in the titration of urinary dextrose by Bang's method (Abstr., 1907, ii, 136) is not sharp, and, moreover, is dependent on various factors, such as temperature, concentration, and rapidity of working. Better results may be obtained by employing an excess of Bang's copper solution, and estimating the unaltered copper with the help of the colorimeter previously described (Autenrieth and Koenigsberger, Abstr., 1910, ii, 910). The copper solution changes slightly when kept or when boiled, but the accuracy of the results is not affected if the same duration of ebullition (three minutes) is always employed. A curve is prepared showing the amounts of dextrose corresponding with the scale divisions of the colorimeter.

The agitation with blood-charcoal suggested by Bang and Bohmansson (Abstr., 1910, ii, 163) for the removal from urine of reducing substances other than dextrose is not to be recommended, because the charcoal absorbs dextrose as well Loss of dextrose also occurs when the agitation with charcoal is effected in presence of hydrochloric acid. R. V. S.

The Micro-Chemistry of Inulin. O. TUNMANN (*Ber. Deut. pharm. Ges.*, 1910, **20**, 577—585).—The so-called amorphous inulin granules in cellular tissues are not of a uniform nature; inulin crystals occur in them, and these crystals are bound together by other substances. The most useful reactions for detecting inulin are given by pyrogallol and resorcinol-hydrochloric acid (0·1 gram of resorcinol dissolved in 5 c.c. of alcohol and 5 c.c. of hydrochloric acid); the former yields a violet-red coloration on warming for a short time, and the latter a red coloration. Before applying the test, the preparation should be immersed for eight days in alcohol containing tartaric acid to remove alkaloids, then for eight weeks in alcohol to harden the inulin, and, finally, be washed with water to remove sugars. The membrane of the cells and starch do not give a coloration with the reagents. W. P. S.

A New Mode of Estimating Pentosans by the Copper Reduction Method. J. TH. FLOHIL (*Chem. Weekblad*, 1910, **7**, 1057—1063).—The amount of furfuraldehyde generated by boiling pentosans with dilute hydrochloric acid can be estimated by its reducing action on Fehling's solution, the cuprous oxide being weighed, or the excess of cupric salt ascertained by iodometry. The procedure is to prepare 400 c.c. of the furfuraldehyde distillate, and to add sodium hydroxide (1 : 3) to 50 c.c. of the cooled distillate until the reaction is slightly alkaline. To the mixture are added 10 c.c. of a solution containing 69·28 grams of crystallised copper sulphate per litre, and 10 c.c. of one containing 346 grams of Rochelle salt and 100 grams of sodium hydroxide per litre. After diluting the solution to 100 c.c. with distilled water, it is boiled in a reflux apparatus for thirty-five minutes, pieces of ice being placed in the open end of the condenser to ensure complete condensation of the furfuraldehyde. When the operation is finished, the liquid is cooled quickly, and the extent of the oxidation is ascertained by the gravimetric or volumetric method. Each c.c. of $N/10$-sodium thiosulphate corresponds with 0·0024 gram of furfuraldehyde, and each mg. of copper with 0·0003775 gram. The percentage of pentosan can be calculated by means of Tollens's formula. The amount of reduction of the Fehling's solution in the absence of furfuraldehyde must be ascertained by the aid of a blank experiment carried out with similar conditions, and deducted from the analytical results before calculating the percentage of furfuraldehyde. A. J. W.

Estimation of Lactic Acid. ELIAS ELVOVE (*Amer. J. Pharm.*, 1911, **83**, 14—19).—The United States Pharmacopeia specifies a lactic acid containing 75% of true lactic acid and having D^{25} 1·206. An acid of this specific gravity should contain about 85% of true lactic acid, and this anomalous specification is due to the inaccuracy of the pharmacopeial method of estimation, which involves direct titration of the boiling acid. The author recommends instead the addition of 50 c.c. of normal sodium hydroxide solution to 2 grams of the acid, and titration of the excess of alkali with normal sulphuric acid after the mixture has remained for thirty minutes in the cold. Phenolphthalein should be used as indicator. T. A. H.

The Anhydride of Lactic Acid. A. A. BESSON (*Chem. Zeit.*, 1911, **35**, 26).—Attention is drawn to the fact that specimens of lactic acid frequently contain quantities of the anhydride, and that the latter is not estimated when the acidity of a sample is determined by direct titration. The total amount of acid is found by treating the neutralised solution with an excess of alkali, leaving the mixture for ten minutes, then adding an excess of acid, boiling the solution, and neutralising. The quantity of alkali used in these operations is a measure of the total lactic acid present (that is, acid *plus* anhydride) in the sample. In cases where dextrin has been removed from the sample by treatment with alcohol and the alcoholic solution of the acid evaporated before the titration, it is necessary to collect the distillate and titrate its acidity, as a small quantity of the acid distils over with the alcohol. W. P. S.

Influence of Potassium Dichromate on Certain Analytical Constants of Milk. LEON GARNIER (*J. Pharm. Chim.*, 1911, [vii], **3**, 55—59).—Samples of milk collected officially in France in connexion with the food adulteration law of 1905 are ordered to be preserved by the addition of 1 gram of potassium dichromate per litre. The author points out that in analysing milk so treated, allowance must be made for the increase in specific gravity, acidity, refraction, "dry extract," and ash, due to the addition. He also finds that milk preserved by means of dichromate, when kept, increases steadily in acidity and refraction and decreases in optical activity, these changes being no doubt in part due to conversion of lactose into lactic acid. The changes induced are irregular in amount, but the variations are usually within limits narrow enough to permit of corrections being made in analytical results. T. A. H.

Simple Method for the Estimation of Formaldehyde. FELIX HERRMANN (*Chem. Zeit.*, 1911, **35**, 25—26).—The formaldehyde solution is mixed with ammonium chloride and treated with a definite volume of standard sodium hydroxide solution; the ammonia liberated combines with the formaldehyde to form hexamethylenetetramine, and the excess of alkali is then titrated. The difference between the quantity of alkali added and that found by titration represents the amount of ammonia which has combined with the formaldehyde and is a measure of the quantity of the latter present. A correction must be made for the amount of free acid which is always present in commercial formaldehyde solutions. W. P. S.

Estimation of Cyanogen Compounds in Coke Oven Gases. EMLIE LECOCQ (*Bull. Soc. chim. Belg.*, 1910, **24**, 439—445).—Fifty to 100 litres of the gas are passed through absorption tubes containing 2·5 grams of lead acetate dissolved in 200 c c. of a 10% potassium hydroxide solution. The precipitated lead sulphide is removed by filtration, and the filtrate transferred to a 500 c.c. flask; the lead is then precipitated by addition of dilute sulphuric acid, the solution being cooled during the process to prevent the escape of hydrogen cyanide. After making up to the mark, 400 c.c. of the clear solution are removed for the estimation of cyanide and thiocyanate.

For this purpose, 10 c.c. of a solution containing 10% of a mixture of equal parts of ferrous and ferric sulphates are added, followed by potassium hydroxide solution sufficient to precipitate a considerable proportion of the iron in solution. After about an hour, the contents of the flask are acidified by addition of sulphuric acid, heated on the water-bath for a quarter of an hour, and left for some hours. The reddish-coloured solution is then decanted off, and the Prussian-blue separated by filtration through a small, fine-grained filter-paper. The proportion of cyanide in the precipitate is now estimated by Feld's method, which consists in converting the complex cyanide into mercuric cyanide by heating with an alkaline solution of magnesium and mercuric chlorides.

For the estimation of the thiocyanate, the decanted solution and the wash liquors are combined, made up to a definite volume, and the colour of the solution compared with that of a similar solution containing a known quantity of thiocyanate.

Actual experimental results are recorded, according to which the average amount of cyanogen is 0·093 gram, and that of thiocyanogen 0·189 gram, per cubic metre of gas. H. M. D.

Estimation of Cyanamide, Dicyanodiamide, and Carbamide in Calcium Cyanamide (Kalkstickstoff). NIKODEM CARO [with B. SCHUCK] (*Zeitsch. angew. Chem.*, 1910, **23**, 2407—2411).—See this vol., i, 119.

Tests for Cocaine and Certain other Anæsthetics. ERNEST H. HANKIN (*Analyst*, 1911, **35**, 2—6).—The permanganate test for cocaine is extremely sensitive if the cocaine is dissolved in alum solution and the permanganate is used in the form of a dried film; the test readily distinguishes between cocaine and certain cocaine substitutes. Of these substitutes, alypine, tropacocaine, and scopolamine form crystalline permanganates which can easily be distinguished from each other and from cocaine permanganate. β-Eucaine, stovaine, novocaine, holocaine, and nirvane do not form crystalline permanganates, but bromine-water furnishes a means of distinguishing them. With bromine-water, cocaine, scopolamine, stovaine, and novocaine give a yellow precipitate which dissolves on heating; β-eucaine yields a precipitate which dissolves on warming, but is re-precipitated on boiling the solution. Nirvane also gives a yellow precipitate, soluble on heating the solution; the liquid acquires a red colour. Holocaine yields a yellow precipitate with bromine-water; when the mixture is boiled, the precipitate dissolves, and a pinkish-white opalescence is produced in the liquid. W. P. S.

New Reaction of Cupreine. GEORGES DENIGÈS (*Compt. rend.*, 1910, **151**, 1354—1355. Compare this vol., ii, 79).—Ten c.c. of a solution of a cupreine salt (about 0·2%) is mixed with 1 c.c. of ammonia and 1 c.c. of 1 vol. hydrogen peroxide. After shaking, 0·1 c.c. of copper sulphate solution, containing 3—4% of the crystalline salt, is added, and the mixture again shaken. The liquid becomes green, and shows greenish-blue particles in suspension; an absorption band is visible in the infra-red. On the addition of an equal volume of alcohol to the solution, it changes to deep emerald-green. The reaction is visible in solutions considerably more dilute than the one mentioned. W. O. W.

Estimation of Morphine. RUDOLF GOTTLIEB and O. STEPPUHN (*Arch. exp. Path. Pharm.*, 1910, **64**, 54—66. Compare Abstr., 1910, ii, 558).—Rübsamen's method is defended, and details given of the method and of the sources of error and how to avoid them. W. D. H.

Estimation of Nicotine in Concentrated Tobacco Juice. JOHANNES SCHRÖDER (*Chem. Zeit.*, 1911, **35**, 30).—Very varying results are obtained by the processes which have been proposed by different workers (Kissling, Heut, Keller, Biel, Schloesing, Tóth, etc.) for the estimation of nicotine in tobacco, although fairly concordant figures are yielded by each particular method. The discrepancy is particularly marked in the case of products containing considerable quantities of nicotine, such, for instance, as the concentrated tobacco extracts which are used as insecticides. The method described by Tóth has been recommended as being trustworthy for technical purposes, but the author points out that the results obtained for one sample may vary by as much as 20% of the quantity of nicotine actually present. He considers that the subject needs further investigation. W. P. S.

Volumetric Estimation of Phenolphthalein. V. ZOTIER (*Bull. Soc. chim.*, 1910, [iv], **7**, 993—995).—A weighed quantity of the material containing phenolphthalein is triturated with sodium hydroxide, free from carbonate and mixed with a few c.c. of water, and the solution made up to 50 c.c. and filtered. To 25 c.c. of the filtrate, dilute hydrochloric acid is added until phenolphthalein begins to be precipitated, any precipitate formed being then just re-dissolved by a drop or two of $N/10$-sodium hydroxide. $N/10$-Sulphuric acid is then added until the red colour disappears, the liquid being vigorously shaken after each addition of acid. If n be the quantity in c.c. of $N/10$-acid added, and V the volume of the liquid after titration, the quantity in centigrams of phenolphthalein in the material used is given by the formula: $2[1{\cdot}59n+(V-n)0{\cdot}0092]$. It is convenient to use the second 25 c.c. of filtrate as a control. T. A. H.

Estimation of the Tannin in Tanning Liquids by means of the Zeiss Immersion Refractometer. PIETRO FALCIOLA and M. CORRIDI (*Gazzetta*, 1910, **40**, ii, 229—236).—The change of refractive index caused by removal of the tanning substance from the solutions is compared with the weight of tanning substance precipitated, and in this way the amount of the latter corresponding with one-scale division of the refractometer is ascertained. The results agree fairly closely with those of Zwick (*Chem. Zeit.*, 1908, **32**, 405) and Sager (*Collegium*, 1909, 146), and indicate that the refractometric equivalents for tanning substances of different origins do not differ more than those for different samples of the same origin, so that it would not seem possible to identify the source of a given extract by this means, as was suggested by Zwick. R. V. S.

Estimation of the Amide Nitrogen in Proteins. W. DENIS (*J. Biol. Chem.*, 1910, **8**, 427—435).—Folin's method for the estimation of ammonia in urine can also be used with good results for the estimation of ammonia in the cleavage products of proteins; amino-acids are not affected. W. D. H.

Method for the Estimation of the Aliphatic Amino-group. Application to the Chemistry of the Proteins, Urine, and Enzymes. DONALD D. VAN SLYKE (*Ber.*, 1910, **43**, 3170—3181).—The apparatus described, in which the principle of Sachs and Kormann is adopted, allows of the determination of aliphatic amino-groups within a few minutes, with an accuracy of ± 1/20 mg. of nitrogen. A flask containing 35—37 c.c. is nearly filled with a mixture of sodium nitrite and acetic acid, and closed with a cork through which pass capillary tubes closed by stopcocks connecting with a gas burette, a tube containing the amino-acid solution, and a tube containing water. The air is entirely displaced from the flask by nitric oxide, and about 20 c.c. of solution are driven back into the tube containing water by the pressure of the gas formed. The flask is then connected to the burette, and the amino-acid run in. Nitrogen is evolved, and passes together with much nitric oxide into the burette. After about five minutes, all the gas is expelled from the flask by running in water, and the mixture of gases collected is passed into an absorption pipette containing alkaline potassium permanganate. The residual nitrogen is measured. A few drops of amyl alcohol are introduced when protein solutions, which are inclined to froth, are analysed.

The simple amino-acids give up all their nitrogen. Arginine, histidine, and tryptophan give up one molecule of nitrogen. In leucylleucine the peptide amino-group does not react; this group is partly active in glycylglycine. Cytosine and guanine react only slowly with the primary amino-groups. Proline and oxyproline do not react.

By determining the total and amine nitrogen in an impure proline fraction, the amount of this present is accurately obtained; thus casein contains 6·7% proline.

It is possible almost completely to analyse a protein, even when only small amounts are available, by hydrolysis and determination of the nitrogen as ammonia, melanine nitrogen, total and total amino-nitrogen, and also of the total and amino-nitrogen in the phosphotungstic acid precipitate and filtrate. The method is applicable to urine after removal of the carbamide and ammonia; 1·5 to 2·5% of the total nitrogen is urine in amino-nitrogen.

By taking proofs from time to time, it is possible to follow the course of protein hydrolysis by trypsin or by sodium hydroxide. The amino-acid nitrogen increases as hydrolysis proceeds. E. F. A.

General and Physical Chemistry.

Character of the Double Refraction of Liquid Crystals. DANIEL VORLÄNDER and M. E. HUTH (*Zeitsch. physikal. Chem.*, 1911, **75**, 641—650. Compare Abstr., 1908, ii, 88).—Further evidence has been obtained of the rule already enunciated, that all liquid crystals are optically uniaxial. Pleochroism, surface colours, and iridescence of liquid crystals are only observed with substances showing circular polarisation, but crystals showing no pleochroism or play of colours may be optically active. All liquid crystals showing pleochroism and iridescence show negative double refraction; all other crystals show positive double refraction. The latter rule also applies to crystals which exist in more than one liquid-crystalline phase. In such a case, the region of the phases showing pleochroism and iridescence occurs regularly between those of the amorphous liquid and of the colourless, crystalline liquid. G. S.

The Variation of the Refractive Index with the Temperature in the Ultra-red Region for Rock Salt, Sylvine, and Fluorite. ERIK ZIEBREICH (*Ber. Deut. physikal. Ges.*, 1911, **13**, 1—18).—Measurements of the variation of the refractive index with the temperature have been made for wave-lengths extending to $\lambda = 6{\cdot}5\mu$ in the case of fluorite and to $\lambda = 9\mu$ and 21μ for rock salt and sylvine. The temperature-coefficients are negative, a result which is identical with that obtained for rays of the visible spectrum. In contrast with the behaviour of visible rays, the temperature-coefficient for the ultra-red rays diminishes as the wave-length increases. This difference is attributed to a shift of the region of absorption in the direction of greater wave-lengths as the temperature is raised.

H. M. D.

Structure of Liquids with Conical Focal Lines. GEORGES FRIEDEL and F. GRANDJEAN (*Compt. rend.*, 1911, **152**, 322—325. Compare Abstr., 1910, ii, 809, 1018).—Contrary to the view upheld in a previous paper, the author now agrees with Mauguin (*Compt. rend.*, 1910, **51**, 1141) that liquids such as azoxyphenetole are doubly refractive throughout their whole mass and optically homogeneous. This is not evident from the appearance of a film of the substance in polarised light, unless the utmost precautions are taken to ensure the purity of the compound, the cleanliness of the glass plates between which it is viewed, and their freedom from relative movement. The geometrical nature of the phenomena observed when these precautions are taken is discussed. W. O. W.

Optical Dispersion: An Analysis of its Actual Dependence on Physical Conditions. T. H. HAVELOCK (*Proc. Roy. Soc.*, 1911, *A*, **84**, 492—523).—The effect of the physical state of a medium on its optical dispersion can be represented by means of two variables, one of which is the density (ρ), and the other a factor (σ) which expresses the effect of surrounding molecules. For two different states of aggregation of the same substance, it is found that the difference, $\rho_2/(n_2^2-1)-\rho_1/(n_1^2-1)=\rho_1\sigma_2-\rho_2\sigma_2$, is independent of the wave-length of the rays passing through the substance, and is a function only of physical conditions, such as pressure, temperature, and density. Experimental data for gases and liquids are shown to be in satisfactory agreement with this deduction. By assigning a zero value to σ in the case of a gas at 0° and 760 mm., numerical values can be obtained which express the effect of the molecular aggregation in different states. Anomalies in the refractivity are to be ascribed, in part, to variations in the magnitude of the factor σ. H. M. D.

The Doppler Spectrum of the Hydrogen Canal Rays. E. Gehrcke and O. Reichenheim (*Ber. Deut. physikal. Ges.*, 1911, **13**, 111—118.)—The Doppler effect exhibited by the line H_β in the canal-ray spectrum of hydrogen has been investigated. For a given fall of the cathode potential, the distribution of intensity in the Doppler spectrum is dependent on the size of the cathode. With a cathode of 1·5 mm. diameter, the intensity of the two Doppler lines is approximately the same when the cathode fall amounts to 730—800 volts. The sharpness of the Doppler lines increases as the pressure of the hydrogen in the discharge tube diminishes. From the observations at higher pressures it is found that the wave-lengths of the Doppler lines do not correspond with velocities of particles in the ratio of $\sqrt{2}:1$, and this is considered to be irreconcilable with the hypothesis that the lines are due to hydrogen atoms and hydrogen molecules respectively under the influence of the same driving force. H. M. D.

Normals from the Arc Spectrum of Ion in the International System. Heinrich Kayser (*Zeitsch. wiss. Photochem.*, 1911, **9**, 173—185).—To supplement the determinations of the normal lines of the second order, measurements have been made of further lines in the arc spectrum of iron of wave-lengths differing by 5—10 Å. These normal lines of the third order were obtained by means of a concave grating having 20,000 lines to the inch, and a radius of curvature of 6·5 metres. The measurements extend from $\lambda=4120$ to $\lambda=6495$. The recorded wave-lengths were obtained by an interpolation method in which the data for several pairs of adjacent secondary normal lines were made use of, and the several interpolated values were then combined to give a mean value.

On comparison of the differences between the corresponding wave-length numbers in Rowland's and the international system, it is found these increase from about 0·16 at $\lambda=4100$ to about 0·21 at $\lambda=6500$. H. M. D.

Absorption Spectra of Certain Salts of Cobalt, Erbium, Neodymium, and Uranium as Affected by Temperature and by Chemical Reagents. I. and II. Harry C. Jones and W. W. Strong (*Amer. Chem. J.*, 1911, **45**, 1—36, 113—159).—The work of Jones and Anderson (Abstr., 1909, ii, 359) on the absorption spectra of cobalt, erbium, and neodymium salts has been continued.

I. Solutions of cobalt chloride and bromide in glycerol do not give any of the fine red cobalt bands. A rise of temperature of the more concentrated solutions causes the yellow absorption band at λ 5100 to widen, so as finally to absorb all the red, and thus cause the solution to appear blue. Concentrated aqueous solutions of cobalt chloride show an enormous increase in the absorption with rise of temperature; this increase takes place at lower temperatures as the concentration is increased. In the case of the more dilute solutions, the widening of the absorption with rise of temperature is quite symmetrical. The effect of a rise of temperature on the absorption of cobalt nitrate or sulphate is very small as compared with its effect on the chloride. The presence of calcium or aluminium chloride in aqueous solutions of cobalt chloride increases the effect of temperature on the absorption, and causes the red absorption to take place in more dilute solutions. The temperature at which the absorption in the red increases so greatly is termed the "critical colour temperature," and seems to depend on the existence of some solvate or peculiar condition of the cobalt molecule; it is much higher in water and glycerol than in other solvents.

A review is given of Becquerel's investigations of the effect of low temperatures and magnetic fields on the absorption spectra of erbium and neodymium.

The absorption in solutions of erbium chloride in glycerol is very similar to that in aqueous solutions, but the bands, in general, are shifted towards the red, and most of them are of greater wave-length than those of aqueous solutions. A rise of temperature from 15° to 200° produces no appreciable change in wave-length, but at the higher temperature the bands are much less distinct and considerably weaker. An examination of the spectra of aqueous solutions of erbium nitrate has shown that the NO_3 group does not exert a hypsochromous effect such as has been found for the uranyl bands.

It has been found that Beer's law holds for solutions of neodymium salts in glycerol, except in the case of the more dilute solutions, which show greater general absorption in the ultra-violet. A rise of temperature of a solution of neodymium chloride in glycerol effects scarcely any noticeable shift in the bands. The presence of calcium chloride causes the temperature shift of the bands to be increased, but the effect is not so great as in aqueous solutions. The absorption spectra of neodymium chloride in glycerol are very similar to those of aqueous solutions. The "glycerol" bands closely resemble the "water" bands, but are all of slightly greater wave-length. The presence of free nitric acid in aqueous solutions of the nitrate causes the bands to become much broader and more diffuse than those of the neutral salt. A study has been made of the effect of nitric acid, hydrobromic acid, and hydrochloric acid on neodymium acetate solutions, and of hydrochloric acid on neodymium citrate solutions. The spectra indicate that in some of these reactions there probably exist several systems or compounds between the acetate and the salt of the acid added.

An investigation of concentrated solutions of erbium and neodymium salts and of the salts themselves has shown that the spectra are entirely different for the different salts. It has also been found that the absorption of different salts in the same solvent is very similar, which indicates that the solvent plays an important part in the absorption of light.

II. It is unusual for the absorption spectra of solutions of salts to show much, if any, influence of the acid radicle, but an exception exists in the case of aqueous solutions of uranium salts, the uranyl nitrate bands being all of shorter wave-length than those of other uranyl salts.

The absorption spectra of the uranyl salts have been photographed over a wide range of concentration, and the results show that the wave-lengths of the bands do not depend on the concentration.

Experiments have been made on the influence of nitric acid on the absorption spectra of uranyl nitrate, of sulphuric acid on those of the sulphate, of acetic acid on those of the acetate, and of hydrochloric acid, calcium chloride or aluminium chloride on those of the chloride. In general, the presence of these reagents causes the uranyl bands to become more intense, and, in some cases, narrower. The action of all the reagents, except nitric acid, is to cause the uranyl bands to be shifted towards the red. Nitric acid, however, causes a considerable shift towards the violet. Similar effects are produced on the bands of the corresponding uranous salts. These effects are probably due to the formation of aggregates.

A study has also been made of the effect of gradually adding sulphuric or hydrochloric acid to uranyl nitrate, and it has been found that the spectra change gradually as one salt is transformed into the other (compare Abstr., 1910, ii, 247).

It has been shown previously (Abstr., 1909, ii, 360) that the spectrum of any one salt often varies greatly with different solvents. Uranous salts have been found to show very characteristic bands in water, methyl and ethyl alcohols, acetone, and glycerol. In mixtures of two solvents, both sets of solvent bands appear, the intensity of any solvent band being a function of the relative amounts of the solvents present.

A rise of temperature causes the general absorption of an aqueous solution of any salt to increase, and also causes the bands to become wider and more intense. The uranyl chloride bands are shifted towards the red as the temperature increases, but those of uranyl nitrate do not appear to shift. Uranyl nitrate, dissolved in concentrated nitric acid, however, shows a considerable shift. The bands of uranyl acetate and sulphate are only slightly shifted.

It is pointed out that the results of this investigation furnish additional evidence that ions and certain molecules combine to some extent with the solvent. These so-called solvates have very different compositions and absorption spectra, depending on the solvent employed for the solution of a particular salt.

The paper concludes with a discussion of the bearing of the solvate hypothesis on the theory of electrolytic dissociation (compare Abstr., 1909, ii, 221 ; and *Zeitsch. physikal. Chem.*, 1910, **74**, 325). A bibliography of the work of Jones and others on this subject is appended.

E. G.

Selective Oxidation. XXXIII. Harry C. Jones and W. W. Strong (*Amer. Chem. J.*, 1911, **45**, 36—38).—The absorption spectrum of a solution of uranous bromide in a mixture of methyl alcohol and water shows two well-defined sets of bands, the "methyl alcohol bands" and the "water bands." On adding a small quantity of potassium perchlorate to such a solution, the uranous "water bands" disappear, whilst the "methyl alcohol bands" remain, thus showing that the portion of the uranous salt combined with the water has been oxidised, whilst that combined with the methyl alcohol has not undergone any change. Calcium nitrate produces the same effect, but hydrogen peroxide oxidises both the "hydrated" and "alcoholated" uranous bromide to the uranyl state. Similar results are obtained with uranous chloride. E. G.

The Destruction of the Fluorescence of Iodine and Bromine Vapour by other Gases.

ROBERT W. WOOD (*Ber. Deut. physikal. Ges.*, 1911, **13**, 72—77 *).—The intensity of the fluorescent light which is emitted by iodine vapour when subjected to sunlight decreases when foreign gases are admixed with the vapour. From a series of comparative measurements it has been found that the fluorescence is diminished in the ratio 5·3 to 1 by ethyl ether, carbon dioxide, air, and hydrogen when the pressures of the admixed gases are respectively 3, 7, 11·5, and 24 mm. The influence of the foreign gas increases with its molecular weight, but there is no simple connexion between the two quantities.

In the absence of traces of foreign gases, the intensity of the fluorescence of iodine increases in a linear manner with the temperature between $-20°$ and $+20°$. At 30° the intensity is the same as at 20°, but diminishes with further rise of temperature. It is probable that at the higher temperatures the increase in the fluorescence is more than counterbalanced by the increased absorption.

Some experiments with bromine vapour show that this can be made to fluoresce if the tube containing it is cooled by means of solid carbon dioxide. This indicates that the density of the vapour must be reduced below a certain value before the molecules of the vapour show fluorescent effects. H. M. D.

The Influence on the Fluorescence of Iodine and Mercury Vapour of Gases with Different Affinities for Electrons.

J. FRANCK and ROBERT W. WOOD (*Ber. Deut. physikal. Ges*, 1911, **13**, 78—83 †).—The effect of varying quantities of helium, argon, nitrogen, oxygen, and chlorine on the intensity of the fluorescence of iodine vapour has been examined. On comparing the results with those obtained in presence of hydrogen, air, carbon dioxide, and ethyl ether (see preceding abstract), it is found that the reduction in the intensity of the fluorescence for a given pressure of the admixed gas increases as the electro-negative character becomes more pronounced. The inert gases are least active, whilst chlorine is the most effective. Preliminary experiments with mercury vapour in presence of helium and oxygen have given similar results. In presence of oxygen at a pressure of 3 mm., mercury cannot be made to fluoresce, whereas helium at a pressure of one atmosphere is apparently without influence.

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* and *Phil. Mag.*, 1911, [vi], **21**, 309—313.

† and *Phil. Mag.*, 1911, [vi], **21**, 314—318.

These observations are connected with the fact that the pressures at which fluorescence can be excited in the case of mercury, iodine, and bromine are very different. The optimum pressure for mercury amounts to several atmospheres; for iodine it is 0·2 mm., and for bromine it is very small. The fall in pressure with increase in the electro-negative character of the vapour is supposed to be due to the increasing influence of the vibrating molecules on one another.

H. M. D.

The Transformation of the Resonance Spectrum of Fluorescing Iodine into a Banded Spectrum by Addition of Helium. Robert W. Wood and J. Franck (*Ber. Deut. physikal. Ges.*, 1911, **13**, 84—87; also *Phil. Mag.*, 1911, [vi], **21**, 265—268. Compare preceding abstracts).—Spectroscopic examination of the fluorescent light emitted by iodine vapour exposed to the green mercury line has shown that the presence of helium at a pressure of 2 mm. of mercury causes a marked change in the spectrum. The series of lines which are observed in pure iodine vapour are greatly diminished in intensity, and this change is accompanied by the appearance of a banded spectrum. This spectrum appears to be identical with that which is obtained when the iodine vapour (without helium) is excited by means of white light. When the pressure of the helium is raised to 10 mm., the series of resonance lines can no longer be observed. When the helium is replaced by chlorine, there is no trace of this banded spectrum.

In explanation of these observations it is supposed that impacts of iodine molecules with molecules of helium set up vibrations in all the contained systems of electrons, the energy of the original vibrating systems being thereby diminished. The change in the colour of the fluorescence from green to red when increasing quantities of helium are admixed with the iodine vapour is consistent with this hypothesis. The absence of the banded spectrum in presence of chlorine is due to the damping effect of the strongly electro-negative molecules.

H M. D.

Photolysis of Acids with a Complex Grouping by Ultra-violet Light. Action of Uranium Salts as Luminous Catalysts. Daniel Berthelot and Henry Gaudechon (*Compt. rend.*, 1911, **152**, 262—265. Compare Abstr., 1910, i, 349, 543; ii, 564, 606, 813, 814).—Dibasic acids in the solid state or in aqueous solution lose carbon dioxide on exposure to ultra-violet light, and form monobasic acids, which, on prolonged exposure, undergo further decomposition as previously indicated. Maleic and fumaric acids give a mixture of carbon monoxide and dioxide. Pyruvic acid is decomposed in the same way as by heat, but lævulic acid behaves differently, yielding carbon dioxide, carbon monoxide, and gaseous hydrocarbons. Lactic acid forms mainly carbon dioxide, with carbon monoxide, hydrogen, and methane.

The action of the rays on the foregoing substances is accelerated by the presence of uranium salts, which act as catalysts. Other fluorescent substances, such as thorium sulphate or eosin, are without action. The presence of fluorescent substances diminishes the decomposition of simple compounds, such as alcohol or acetaldehyde. W. O. W.

The Re-combination of Ions Produced in Gases by α-Rays. M. MOULIN (*Le Radium*, 1910, 7, 350—354).—Curves are given showing the relation between the ionisation current and voltage for carbon dioxide, air, and hydrogen ionised by the α-rays of polonium when the electric field acts in the direction of, at right angles to, and at 45° to, the path of the rays through the gas. It is possible to predict the form of saturation curve for different inclinations of the electric field to the trajectories of the rays by supposing that only the component of the field perpendicular to the trajectories acts. This would not be the case if the phenomenon of lack of saturation with α-ray ionisation were due to initial re-combination of ions produced from the same molecule, but is well explained on the view that the ions are formed in columns along the trajectory of the rays, and are not uniformly distributed throughout the volume of the gas.

F. S.

The Different Influences of α-, β-, and γ-Rays on the Colours of Solid Substances. CORNELIO DOELTER and HEINRICH SIRK (*Monatsh.*, 1910, 31, 1057—1066).—Rock salt, quartz, fluorspar, and barytes were exposed for four months to the α-rays of polonium deposited on a platinium foil. Only the first-named showed coloration, which was brownish, and extended only some hundredths of a millimetre into the material. A glass vessel in which a radium preparation had been kept showed, in addition to the brown coloration throughout due to β-rays, an intense surface coloration due to α-rays. Glass cubes exposed to the β- and γ-rays of radium showed an intense dark brown coloration, diminishing with depth, due to β-rays, and a much lighter uniform yellowish-brown coloration beyond, due to the γ-rays.

A cylinder of salmon-red gold-ruby-glass, covered on all sides but one with 5 mm. thickness of tin foil and exposed to two radium preparations consisting of 1·0 and 0·5 gram of radium chloride, one acting directly and the other through the foil, showed after twenty-three days a uniform orange-brown colour, showing that the β-rays were without action in this case.

A clear rock-crystal after exposure to the rays showed a remarkable distribution of colour, reminiscent of what is often seen in natural amethysts, consisting of lighter and darker shades of colour parallel to the hexagonal contour. From the centre extended three rhomb-shaped streaks parallel to the crystal axes. The darker streaks were all dichroic. There was no alteration of the rotatory power or of the interference figure of the crystal. Coloured zircons are coloured more deeply, and those rendered colourless by heating are re-coloured by the rays. Solutions of barium and calcium chloride were not coloured by thirty days' exposure to the rays from 0·5 gram of radium chloride, but those of mercuric chloride, potassium chloride, and sodium sulphate showed respectively faint yellowish, milky-blue, and yellow coloration, as is the case for the solid salts. F. S.

Scattering During Radioactive Recoil. WALTER MAKOWER and SYDNEY RUSS (*Mem. Manchester Phil. Soc.*, 1910, **55**, No. 2, 1—4). —In experiments on the recoil in a vacuum of radium-*B* from a wire coated with radium-*A*, surfaces out of the direct line-of-fire also received some active deposit. Under conditions where the surface could only receive active deposit by reflexion from an opposite surface, the decay curve showed that more than one-half of the active matter deposited was radium-*C*, and not radium-*B*. The latter is probably due to reflexion and the former to recoil from radium-*B* deposited on the reflector. The large proportion of radium-*C* under these conditions is surprising, as in ordinary circumstances only one-thousandth of the atoms of radium-*C* formed recoil from radium-*B*. It is probable that the absence of films on the surface in this experiment is the cause of the greater proportion of the radium-*C* recoiling. F. S.

The Chemical Reactions of Radioactive Elements. BÉLA SZILARD (*Le Radium*, 1910, **7**, 366—372).—The views that the fixation of radioactive elements by precipitates formed in their solutions is due to chemical similarity between the precipitant and the substance fixed, or to the great insolubility of the radioactive substance, the precipitant acting as a nucleus, or to the electro-positive character of the elements, like barium, most used as precipitants, or to isomorphism, or to the lowering of the solubility of the radio-element by addition of another electrolyte, are dismissed as untenable. The view is advanced that the precipitates are charged particles in suspension which attract the charged ions of the dissolved radio-element, forming complexes less highly charged.

Precipitates like barium sulphate and ferric hydroxide, formed in non-radioactive solutions and afterwards mixed with them, still fix the radioactive substance. The precipitates most useful, as barium sulphate, carbon, &c., are extremely insoluble substances, capable of existing undissolved in the state of fine suspensions. Whether radioactive substances act differently in neutralising the charge on these fine particles from ordinary electrolytes cannot at the present time be decided. F. S.

Some Probable Chemical Properties of Radium and its Compounds. ROBERT DE FORCRAND (*Compt. rend.*, 1911, **152**, 66—69).—The heats of solution and of formation, respectively, augment or diminish regularly for the halogen salts and the oxides of the alkali and alkaline earth metals, in the order: calcium, lithium, strontium, barium, sodium, potassium, rubidium, cæsium. So far as is known, the same is true for the sulphates and selenates, and for the hydrides and carbides. The affinity of the oxides for oxygen, water, or carbon dioxide, and the solubility of the fluorides, oxides, and, with some irregularities, the carbonates augment progressively in the order given. Similar considerations apply to the solubility in alcohol or in hydrochloric acid of most of the halides and carbonates, and to the formation from the fluorides of more and more stable compounds with hydrofluoric acid. In this scheme radium, by analogy, is to be placed between barium and sodium, and by taking the mean of the values for these elements, the heat of formation of the halogen salts and oxide, in solution, can be approximately calculated for radium ($\frac{1}{2}$Ra) as follow: chloride, 98·5; bromide, 91·0; iodide, 79·0; fluoride, 112·0; oxide, 79·6 Cal. The solubilities at 15° per 100 parts of water, calculated in the same way, are: chloride, 35 to 36; bromide, 100; iodide, 180; fluoride, 1 to 2; oxide, 10 to 20. The calculated heat of reaction between radium ($\frac{1}{2}$Ra) and excess of water is 45 Cal. The hydroxide should be more stable than that of barium, and less stable than sodium hydroxide. The oxide should be peroxidised easily at a red heat with development of 19 Cal., and the carbonate should be formed from the oxide with 70 Cal., and should be with difficulty decomposed at a red heat. The heat of formation of the hydride ($\frac{1}{2}$Ra) should be 17·7 Cal., and it should decompose at about 900°. It is to be expected that the metal should be formed by the action of calcium or lithium on the fluoride, or by calcium or aluminium on the oxide. F. S.

The Density of Niton (Radium Emanation) and the Disintegration Theory. R. WHYTLAW GRAY and Sir WILLIAM RAMSAY (*Proc. Roy. Soc*, 1911, *A*, **84**, 536—550).—By means of a modified form of the micro-balance described by Steele and Grant (Abstr., 1909, ii, 876) the authors have succeeded in determining the density of niton from experiments with about 0·1 cubic mm. of the gas weighing approximately 1/1400 mg. The balance employed was sensitive to about 2.10^{-6} mg., and its zero was found to remain constant for days together. As in Steele and Grant's balance, a small silica tube containing air was used as counterpoise, its capacity being about 20 cubic mm. Instead of weighing by displacement from the zero position, a null method was adopted, the pressure in the balance being altered until the spot of light reflected from a platinised silica mirror, and deflected by movement of the beam, was brought back to its initial position.

The volume of niton at disposal, representing the equilibrium amount yielded by the available radium, was known from previous experiments, and the proportion of this actually present in the weighing tube was ascertained by measurements of the γ-ray activity. In five independent experiments, the values obtained for the density of niton corresponded with molecular weight values of 227, 226, 225, 220, and 218, mean = 223.

After the lapse of sufficient time for the decay of the niton and the conversion of its quick-change products, *A*, *B*, *C*, into radium-*D*, the density tube was opened, and the loss of weight corresponding with the helium produced was determined. After correction, this diminution in weight was found to correspond with the loss of three atoms of helium from each atom of niton. Since four atoms of helium are emitted by an atom of radium during its conversion into radium-*D*, and the atomic weight of radium is 226·4, it follows that the true atomic weight of niton is 222·4. H. M. D.

The Half Period of Actinium-*C*. ALOIS F. KOVÁŘIK (*Physikal. Zeitsch*, 1911, **12**, 83).—The period of decay of actinium-*C* obtained by recoil methods has been frequently measured. From 150 curves

the mean value of the half-period, 4·71 minutes, was found, no single value being so great as five minutes. Hahn and Meitner found by several methods the value 5·1 minutes (compare Abstr., 1908, ii, 920).
F. S.

Radioactive Equlibrium in Vesuvian Cotunnite. Paolo Rossi (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 578—583. Compare Abstr., 1908, ii, 9; and Zambonini, Abstr., 1907, ii, 663).—From theoretical considerations the author deduces what measurements are necessary for ascertaining whether a given specimen of cotunnite (containing radium-*D*, radium-*E*, and radium-*F*) has reached radioactive equilibrium. The question may be settled either by examining the radioactivity of the specimen at intervals of a few months, or by comparing its activity with that of a sample known to be in equilibrium. For the latter purpose the author has employed a cotunnite dating from 1872, and has found that the sample of the mineral of 1907, examined by Zambonini (*loc. cit.*), was by no means in equilibrium, and contained in fact at that time very little radium-*F*. It had attained to an equilibrium condition by July, 1910. In this connexion interest attaches to the observation of Piutti (*Rend. Acad. Sci. fis. mat. Napoli*, 1910, [iii], **16**, 30), who found no helium in the mineral, and suggested that possibly this disintegration product of radium-*F* had not had time to accumulate.
R. V. S.

The Radioactivity of Rocks. Albert Gockel (*Jahrb. Radioaktiv. Elektronik*, 1910, **7**, 487—527).—The α-radioactivity, and in some cases the β-activity also, of a great variety of rocks and minerals from all parts of the world has been examined. The radioactivity was found to vary within far wider limits than when determined by means of the emanation method. Igneous rocks may be divided into three classes. The first is strongly radioactive, and comprises granite, porphyry, syenite, and pegmatite, the activity being due to zircon, rutile, titanite, and rare earths. The second class, comprising diabase, andesite, and gabbro, are almost inactive. The third class, comprising the remainder, are of intermediate activity. The activity of the first class varies over a range of 1 to 280, due to variation in the amount of active constituent minerals. Among sedimentary rocks, quartz sand, rock salt, gypsum, anhydrite, and chalk are inactive, the activity of the others averaging only one-tenth of that of the first group of igneous rocks. Many rocks send out β-rays in considerable intensity, and of penetrating power varying with the nature of the rock. Potassium accounts for this in some cases, but in others the rays are much more penetrating, and may be due to mesothorium-2 or to unrecognised radioactive substances.
F. S.

Radiation from Quinine Sulphate, Ionisation, and Luminescence. Maurice de Broglie and L. Brizard (*Compt. rend.*, 1911, **152**, 136—138).—The ionisation produced in a gas when quinine or cinchonine sulphate is heated, or allowed to cool after heating, appears to be connected with the production of small electrical discharges due to disruption of the crystals. Thus, on heating cinchonine sulphate at 120° for half an hour and allowing it to cool in the air, brilliant scintillations are visible under a lens recalling those seen in a spinthariscope. The scintillations increase under diminished pressure. The luminous and electrical phenomena are more marked in hydrogen than in air. W. O. W.

The Isolation of an Ion and the Exact Measurement of its Charge; Correction to the Law of Stokes.

R. A. MILLIKAN (*Le Radium*, 1910, 7, 345—350).—A cloud of droplets of oil, mercury, or other non-volatile liquid is produced by spraying in dust-free air above a condenser with horizontal plates. A few droplets are allowed to fall through a small hole in the upper plate, which is then closed, and one droplet, illuminated by a horizontal beam from an arc lamp passed through a long column of water, is kept under observation in a cathetometer. By alternately applying a suitable electric field to the plates of the condensor and discharging them, the same drop may be watched for many hours at a time, falling under gravity and ascending against it under the field in the same vertical line. In absence of the field during the fall of the drop, the air is always ionised to a certain extent naturally, and this ionisation may be increased at will by the presence of radioactive preparations. The speed of fall is throughout independent of the charge on the drop if precautions are taken against air currents, but as, during the fall, one or more ions of either sign may join themselves to the drop, altering by definite increments the value of its charge, the speed of ascent, which is a simple function of the charge on the drop, varies step-wise in successive measurements. In one case the speed of fall and ascent were observed for a single negatively-charged drop for four and a quarter hours, during which the number of atomic charges on the drop varied from 4 to 17. The value of the charge can be altered at will by holding the drop with a suitable field near to either plate with the air uniformly ionised by radium. Near the plate the concentration of the ion of opposite sign to the plate is the greater, so that to increase the charge on a positively charged drop, it is kept near the negative plate, when more positive than negative ions attach themselves to it. The spontaneous alteration of the charge during descent must be due to the kinetic energy of the ion, assisted or opposed by the electrostatic attraction or repulsion, according to the sign, projecting the ion against the drop. Since the spontaneous accretion of negative ions by a drop already charged negatively with 126 to 150, but never more, units has been observed, it follows that the kinetic energy of the ion must be greater than 4·6 to 5·47 ($\times 10^{-14}$ ergs). This agrees with the accepted value ($5·756 \times 10^{-14}$ ergs) for the kinetic energy of a molecule at ordinary temperatures, as deduced from the kinetic theory, and furnishes a direct experimental proof of the existence of this kinetic energy. The results of forty-seven days consecutive observations, comprising 33 drops, ranging in radius from 313 to 6581 ($\times 10^{-7}$ cm.), as determined from the velocity of fall under gravity, gives a mean value for, e, the atomic charge, $4·9016 \times 10^{-10}$ *E.S.U.*, with a probable error of 1 in 1000, although the value involves that of the coefficient of viscosity of the air, taken as 0·0001785 at 15°, which may be wrong to 5 in 1000. By assuming always a multiple of this charge and measuring the departures from it for drops comparable in diameter with the mean free path of the molecule, it is deduced that Stokes' Law gives velocities of fall for such drops which must be multiplied by $1 + Al/a$, where l is the mean free path of the molecule, a the radius of the drop, and A a constant found equal to 0·815. This is in agreement with the theory of Cunningham based on kinetic considerations. F. S.

The Ions and Neutral Particles Present in Certain Gases when Recently Prepared. LÉON BLOCH (*Le Radium*, 1910, 7, 354—362).—It is probable that ions produced by spraying, bubbling, and splashing are produced in the same way as those produced in chemical reactions. A liquid surface disengaging very fine bubbles of hydrogen by chemical action was made one plate of a condenser, and it was found that the current was nearly proportional to the voltage, no indication of saturation being obtained with fields exceeding 1100 volts. This is shown to be due to the projection from the surface of neutral particles which, when a field is applied, become charged electrostatically, carrying away part of the surface charge. The larger part of the ionisation due to chemical reactions is due to these "neutral particles," which become charged electrostatically and which are to be sharply distinguished from true ions, because their charges and mobilities are functions of the electric field where they originate. They are to be distinguished from dust particles, etc., which attract "small ions" forming "large ions," for they do not form "large ions" in this way. They are formed in liquids which give ions by bubbling, whilst the "neutral centres," similar to those investigated by others, which are produced by bubbling are only formed in liquids which do not give ions. They are too small to be visible in the ultramicroscope, and may be present in large numbers in a gas optically void. Determination of their diffusion coefficients and mobility gave 2·5 units for the mean value of their charge, but the particles are too small to obey Stokes' Law, and probably have a radius of the order of 10^{-7} cm. Their production is prevented by a layer of benzene, petroleum, and various oils, also by alcohols and ethyl ether, but acetone and aldehyde do not stop their formation. In the first case the action cannot be explained by supposing that the surface liquid stops the formation of spray. Since a liquid does not lose its charge by evaporation, there must exist somewhere between the dimensions of these new "neutral particles" and that of the molecule a critical diameter at which the particle loses its power of becoming electrified by contact. F. S.

A Relationship between the Temperature-coefficient and the Specific Resistance of Certain Metals, with Special Reference to Copper. STEPHAN LINDESK (*Ber. Deut. physikal. Ges.*, 1911, 13, 65—71).—From a comparison of the data for a large number of samples of copper, it is found that the product of the specific resistance (c) and the temperature-coefficient (a) at a given temperature is very nearly constant. At 15° the mean value of the product is $6·78 \times 10^{-5}$, and the relationship holds good for samples of copper the specific resistances of which vary as much as 3 : 1. For copper containing a considerable proportion of arsenic, the conductivity of which is only one-eleventh of that of pure copper, the product ca has nearly the same value as that for the pure metal.

Similar relationships have been found in the case of samples of commercial aluminium and iron. For aluminium the value of $c_{15^\circ}a_{15^\circ}$ is $11 \cdot 6 \times 10^{-5}$, and for iron, $58 \cdot 5 \times 10^{-5}$. The relationship appears therefore to be of a general nature. H. M. D.

Experiments with Metallic Conductors of Very High Resistance and the Application of the Electron Theory. HILDA VON MARTIN (*Physikal. Zeitsch.*, 1911, **12**, 41—48).—The conduction of electricity through columbite and stibnite, both of which have a specific resistance of the order of 10^7 ohms, takes place according to Ohm's law. From observations on the variation of the resistance with the temperature, the heat of dissociation is calculated to be about 4400 for columbite and about 10,000 for stibnite. According to this, the latter occupies a position between those substances for which the conduction is electronic in character, and those for which the conduction is due to ions.

Various anomalous phenomena have been observed in the further investigation of the conducting properties of stibnite. On prolonged passage of a current through the substance in one direction, the conductivity increases, but this increase is accompanied by a diminution of the conductivity when the current is passed in the opposite direction. The original direction of the flow of the current is without influence on this phenomena. After the lapse of a considerable time, during which no current is passed through the stibnite, it returns to its original condition. This unipolar effect, which is quantitatively reproducible, cannot be attributed to polarisation.

A further primary unipolar effect is also observable which cannot be reproduced in a quantitative manner, and this is supposed to be due to lack of homogeneity in the crystal under examination.

H. M. D.

Regularities in the Changes of the Electrical Conductivity of Metals on Liquefaction. ERNST WAGNER (*Ann. Physik*, 1910, [iv], **33**, 1484—1492).—A comparison of the electric conductivities of solid and liquid metals at the melting point shows that in many cases the conductivities are related to one another in a simple manner. For mercury the ratio of the conductivity of the solid to that of the liquid is approximately 4; for lead, zinc, tin, cadmium, thallium, and tellurium 2; for sodium, potassium, rubidium, and cæsium 1·5, and for bismuth and gallium 0·5.

If the number of free electrons in unit volume is the same for the two states of aggregation, the changes in the conductivity must be attributed to simply related changes in the mobilities of the electrons. The possibility that these changes are connected with variations in the molecular complexity in the solid and liquid states is discussed.

H. M. D.

The Thomson Effect and its Variation with Temperature in Lead, Mercury, Tin, Zinc, Cadmium, and Aluminium. PAUL CERMAK (*Ann. Physik*, 1910, [iv], **33**, 1195—1215).—Measurements of the Thomson effect in the above six metals have been made at various temperatures reaching up to 350°. In general, the magnitude of the effect increases as the temperature rises, but this increase is not consistent with the assumption that the Thomson effect is proportional to the absolute temperature. At the melting point, the curves which show the relationship between the Thomson effect and the temperature are apparently quite continuous, in spite of the very considerable change in the conductivity. H. M. D.

The Dielectric Constants of the Halogen Compounds of Lead. AUGUST LENERT (*Ber. Deut. physikal. Ges.*, 1910, **12**, 1051—1053).—The fact that the pure halogen compounds of lead have a very small electric conductivity has led the author to measure their dielectric constants. The substances were examined in the form of powder or compressed plates by Nernst's method, and gave the following values: lead chloride, 4·20; bromide, 4·89; iodide, 2·35, and fluoride, 3·62. A determination of the dielectric constant of the chloride by Drude's method comfirmed these results. After the substances had been melted and solidified, much higher values were obtained, and this is attributed to the loss of halogen and the formation of sub-halides. H. M. D.

The Cathode Fall in Argon (Air, Nitrogen, Hydrogen), and the Periodic System of the Elements. KARL ROTTGARDT (*Ann. Physik*, 1910, [iv], **33**, 1161—1194).—Observations have been made relating to the distribution of potential in discharge tubes containing different gases and cathodes of different metals.

A considerable difference of potential exists between the two ends of the negative glow region. This varies from 26 to 60 volts in argon, from 26 to 56 volts in air, from 26 to 49 volts in nitrogen, and from 30 to 60 volts in hydrogen. By using different metals as cathodes, it is found that the potential fall in the glow light increases as the cathode fall increases. Although the fall of potential in the glow light is practically constant when the cathode fall is normal, it appears to increase slightly with increasing current density and with diminution in the pressure.

The normal cathode fall is defined as the minimum value of the potential difference between the earthed cathode and that part of the negative glow region which is in immediate contact with the cathode dark space. For variations in pressure, current strength, and dimensions of the discharge tube, the normal cathode fall, defined in this way, appears to be constant within 5% when the tube contains argon, and within 3% for the other gases investigated.

In argon the normal cathode fall has the same value for series of metals which have the same valency, and diminishes as the valency increases. For copper, silver, and gold it is 131 volts; for magnesium, zinc, and cadmium 119 volts, and for aluminium 100 volts. Tin and lead gave 123·5, and approximate therefore to the bivalent metals, while antimony and bismuth gave 135·5. Similar relationships are found between the cathode falls in nitrogen. In hydrogen the normal cathode potential increases in most cases with the passage of the discharge, and this is attributed to the conversion of the metal into a hydride.

When small quantities of foreign gases are admixed with argon, the normal cathode fall is altered to a considerable extent, hydrogen having the smallest, oxygen and water the greatest, effect. With a zinc cathode, the change brought about by 2% of moist oxygen is equal to that effected by 10% of nitrogen or 35% of hydrogen.

H. M. D.

Value of the Components of the Electromotive Force of the Voltaic Couple. GIOVANNI GUGLIELMO (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 572—577).—If V be the electromotive force of the couple, V' and V'' the difference of potential between the metals and the electrolyte respectively, C' and C'' the respective heats of combustion (in Joules) of 1 gram-equivalent of the metals with the electronegative constituent of the solution, and e the quantity of electricity which produces this amount of chemical action (for 1 gram-equivalent, e will be 96540 coulombs), then $V = V' - V'' = (C' - C'')/e$, whence $V' = C'/e + K$, and $V'' = C''/e + K$. If K be negligibly small, $V' = C'/e$ and $V'' = C''/e$. The value of K can be calculated, however: (1) by using Helmholtz's formula $V' = C'/e + dV'/TdT$, from which it follows that $K = dV'/TdT = dV''/TdT$; the value of K calculated by this means from the experimental results of previous workers is 0·22 volt; (2) by applying the fact that of the total heat of combination, C', of one of the metals only a fraction, c', appears locally, the rest manifesting itself in the whole circuit: hence $V' = (C' - c')/e$, and $V'' = (C'' - c'')/e$, and therefore $K = c'/e = c''/e$; the value of K obtained by this method is also about 0·2 volt. R. V. S.

Mercurous Sulphate as Depolariser in Weston and Clark Normal Cells. P. J. H. VAN GINNEKEN (*Zeitsch. physikal. Chem.*, 1911, **75**, 687—709).—A theoretical paper. Hulett (Abstr., 1904, ii, 695) observed that the *E.M.F.* of a cadmium element rose on shaking to a value higher than the normal, but slowly recovered the former value when kept. He gave an explanation of this based on the slow hydrolysis of mercurous sulphate and the consequent increase of the "mercury concentration" in the solution. It was further assumed that the hydrolysis is accelerated by the catalytic action of the mercury surface. It is not clear exactly what Hulett means by "mercury concentration" in this case. The author accepts Hulett's assumptions in the main, but shows as the result of a detailed consideration of the equilibria in the system that the mercury ion concentration would be diminished and not increased by hydrolysis. The author's explanation of the observations is as follows. On remaining quiescent, hydrolysis takes place fairly rapidly in the layer in contact with the mercury surface, owing to the catalytic action of the latter, but is very slow in the main bulk of material. The result is that the mercury ion concentration in the surface layer diminishes and the *E.M.F.* falls, but, on shaking, the mercury concentration in the surface layer becomes practically the same as that in the main bulk of material, and the *E.M.F.* rises. In normal circumstances, therefore, the *E.M.F.* is depressed owing to hydrolysis. G. S.

Thermodynamics of Normal Cells. Ernst Cohen (*Chem. Weekblad,* 1911, 8, 1—4. Compare Abstr., 1910, ii, 176).—The values obtained by the thermochemical method for the chemical energy of the normal cells of Clark and of Weston differ from those derived from Gibbs and von Helmholtz's equation by the aid of electro-measurements. The author attributes the discrepancies to errors in the temperature formulæ employed. For neither cell can the relation of *E.M.F.* to temperature be represented by a continuous curve. A. J. W.

Determination of Specific Heats at Low Temperatures and Their Use in the Calculation of Electromotive Forces. F. Pollitzer (*Zeitsch. Elektrochem.,* 1911, 17, 5—14).—The method of measuring the rise of temperature produced by the addition, electrically, of a known quantity of heat, described by Nernst (Abstr., 1910, ii, 263), is employed. The specific heats of zinc, mercury, heptahydrated zinc sulphate, and of mercurous sulphate and chloride are determined at temperatures between $-200°$ and $-30°$. The results are calculated by means of the formula given by Magnus and Lindemann (Abstr., 1910, ii, 580), the values of the constants being :

	n.	$\beta\nu$.	a.
Zn	1	173	$5{\cdot}4 \times 10^{-5}$.
Hg (solid)	1	80	$21{\cdot}0 \times 10^{-5}$.
Cl	1	236	—

The specific heat of mercurous chloride is calculated by adding the expressions for one atom of mercury and one of chlorine, the value of a for the compound being 12×10^{-5}. With the more complicated substances, zinc sulphate and mercurous sulphate, empirical expressions were used instead of attempting to introduce a special value for the frequency of each kind of atom.

The heat of fusion of mercury is found to be 554·5 cals. per gram-atom at the melting point, $-38{\cdot}7°$.

Using these data, the following *E.M.F.*'s are calculated by means of Nernst's theorem :

Zn | $ZnSO_4,7H_2O$ | Hg_2SO_4 | Hg ($-7°$), 1·4610 volt (calculated), 1·4556 volt (obs.).
Hg | HgCl | $PbCl_2$ | Pb ($-39°$), 0·4636 volt (calculated), 0·5216 volt (obs.).
Hg | HgCl | AgCl | Ag ($-39°$), 0·0341 volt (calculated), $-0{\cdot}0270$ volt (obs.).

The differences between the observed and calculated values in the last two cases are possibly due to errors in the values of the heats of formation of the compounds. T. E.

Calculation of Electromotive Force from Thermal Effects. Ernst Cohen (*Chem. Weekblad,* 1911, 8, 51—52; *Zeitsch. Elektrochem.,* 1911, 17, 143—145. Compare Pollitzer, preceding abstract).—The great discrepancies between the values deduced by the aid of Nernst's theorem for the *E.M.F.* of galvanic combinations and those obtained by experiment are attributed by Pollitzer to errors in the thermochemical determinations involved. The author points out that for a cell $Hg\text{–}HgCl\text{–}PbCl_2\text{–}Pb$, the difference is due to the use of an electrode of lead amalgam instead of pure lead. A. J. W.

Mathematical Theory of the Changes of Concentration at the Electrode brought about by Diffusion and by Chemical Reaction. T. R. ROSEBRUGH and W. LASH MILLER (*J. Physical. Chem.*, 1910, **14**, 816—883).—A mathematical paper, in which the changes in concentration at the electrodes which take place as the result of electrolysis under different conditions have been deduced from a consideration of the effects of ionic migration and diffusion.

H. M. D.

The Behaviour of Copper Anodes in Chloride Solutions. SAUL DUSHMAN (*J. Physical Chem.*, 1910, **14**, 885—908).—The behaviour of copper anodes in the electrolysis of solutions of hydrochloric acid in the absence of air has been investigated. In an extensive series of experiments, in which the concentration of the hydrochloric acid was varied from 0·00465 to 0·01615 mol. per litre, the current from 0·013 to 0·051 ampere, the anode area from 18 to 47 square cm., and the rate of circulation of the electrolyte from 0·242 to 2·361 c.c. per second, it was found that the proportion of the copper which passed into solution as cuproion varied from 25 to 74%. By taking into account the change resulting from diffusion, values have been obtained for the constant $K=[Cu^{\cdot\cdot}]/[Cu^{\cdot}]^2$ corresponding with the equilibrium $Cu^{\cdot\cdot}+Cu \rightleftharpoons 2Cu^{\cdot}$. The numbers so obtained vary from $0·5$ to $3·5\times10^{-4}$, whereas the value obtained by Bodländer and Storbeck from experiments in which finely divided copper and cuprous chloride were shaken with solutions of potassium chloride was $1·5\times10^{-4}$.

The proportion of copper dissolved as cuprous salt at a rotatory anode in hydrochloric acid with different concentrations of acid, current densities, rates of rotation of the anode, and rates of circulation of the electrolyte, is found to be in accord with the assumption of the above equilibrium condition. H. M. D.

Velocity of Anodic Solution of Nickel in Normal Sulphuric Acid. C. RUSSO (*Gazzetta*, 1910, **40**, ii, 491—508).—The rate at which nickel functioning as anode passes into solution in normal sulphuric acid is proportional to the strength of the current when this is not great. After a certain critical strength of current has been reached (usually about 0·1 ampere), the electrode is passive, and the rate of solution decreases, being a linear function of the current strength. A minimum is plainly observable when the current is 0·4 ampere, and thereafter the velocity of solution increases again, forming a linear function of the strength of the current. R. V. S.

Comparison between the Velocity of Solution and the Anodic Polarisation of Nickel in Normal Sulphuric Acid. C. RUSSO (*Gazzetta*, 1910, **40**, ii, 508—518. Compare preceding abstract).—The results obtained by the author support the theory of Muthmann and Frauenberger that the passivity of nickel is due to the formation of a solid solution of oxygen at the surface of the anode. In following the variation of anodic polarisation with increasing current, no sudden change is observed which could correspond with the singular point (at 0·4 ampere) in the curve of velocity of anodic solution, so that the existence of the latter must be due to some cause which does not sensibly affect the polarisation. It is suggested that it may be connected with the discharge of the ion HSO_4'. When a certain degree of polarisation has been exceeded, the nickel anode no longer remains practically unattacked by the solution; in spite of the gaseous envelope of oxygen which surrounds it, it is in a semi-active condition, and this forms another argument in favour of the hypothesis that the passivity of the metal is due to dissolved, not to enveloping, oxygen. R. V. S.

Planck's Formula for Diffusion Potentials. NIELS BJERRUM (*Zeitsch. Elektrochem.*, 1911, **17**, 58—61).—Planck's formula for the difference of potential between two solutions of electrolytes is obtained on the assumption that two solutions of constant concentration are separated by a layer the composition of which is also not changed by the diffusion going on through it. This condition is not fulfilled in general. The real state of affairs is better represented by a formula obtained by Henderson from Nernst's theory (Abstr., 1907, ii, 426; 1908, ii, 655), in deducing which it is supposed that the two solutions are separated by a fairly thick layer in which they have simply mixed together. It is shown that when such a layer is formed, the potential difference changes with the time, the change being inversely proportional to the thickness of layer. For 0·1*N*-potassium chloride and 0·01*N*-hydrochloric acid and a layer of separation 1 cm. thick, the change is about 0·2 millivolt in a quarter of an hour; usually it is much smaller and quite negligible. T. E.

Electrometric Measurements [of Acidity] in Liquids containing Carbon Dioxide. K. A. HASSELBALCH (*Biochem. Zeitsch.*, 1910, **30**, 317—331).—The measurements were made with the hydrogen electrode by a slight modification of the usual method. Hydrogen was passed for half an hour through the electrode vessel containing the electrode only until the latter was thoroughly saturated. The solution to be examined, saturated with air or oxygen, was then drawn in until its upper surface just touched the bottom of the electrode, the electrode vessel was then shaken to establish equilibrium between the liquid and the gas space, and the potential measurements made in the usual way. This method gives satisfactory results for solutions saturated with air or oxygen (the latter gas produces no depolarising effects on the electrode), but is not satisfactory for solutions containing carbon dioxide, as the latter escapes into the gas space, and the measured $H^{\cdot}$ ion concentration is too low. This difficulty has been overcome by shaking one portion of the solution until equilibrium is established with the gas space; this portion is then replaced by a second portion, and as the gas space already contains carbon dioxide, none of the gas escapes from the liquid. A series of measurements with blood shows that the previous methods of measurements (compare Michaelis and Rona, Abstr., 1909, ii, 680) give rather too low values for the $H^{\cdot}$ ion concentration, as would be anticipated from the source of error above referred to. G. S.

Rationality of the Ratios of the Magnetic Moments of Atoms and a New Universal Constituent of Matter. PIERRE WEISS (*Compt. rend.*, 1911, **152**, 187—189. Compare this vol., ii, 91).—Values have been calculated for the magnetic susceptibility at absolute specific saturation of a number of metals in the form of aqueous solutions of their salts. To explain the results, which together with those of Pascal and others are shown in graphic form, the author is led to assume the existence in all forms of matter of *magneton*, a substance having a definite determinable magnetic moment.

W. O. W.

New Method for Investigation of the Magnetic Permeability of Gases. W. P. ROOP (*Physikal. Zeitsch.*, 1911, **12**, 48—56).—A method of determining the difference between the magnetic permeabilities of two gases is described, which depends on the deflexion of a jet of the one gas streaming through the other under the influence of a magnetic field in which the lines of force are very unevenly distributed. From experiments with carbon dioxide and air, for the former of which the magnetic susceptibility is probably nil, the susceptibility of air has been found to $0{\cdot}0260 \times 10^{-6}$. H. M. D.

The Magnetism of the Copper–Manganese–Tin Alloys under Varying Thermal Treatment. ALEXANDER D. ROSS and ROBERT C. GRAY (*Proc. Roy. Soc. Edin.*, 1910, **31**, 85—99. Compare Abstr., 1909, ii, 859).—A series of ternary alloys has been prepared in which copper and manganese are present throughout in the ratio 7 : 3, whilst the alloys contain respectively 14, 16, 18, 30, 38, and 48% of tin. The alloys, cast in the form of rods, were tested magnetically as cast, and also after normalising by heating and cooling fairly rapidly. Other specimens were tested after baking for several hours at 180° or 200°, and after annealing at higher temperatures. Baking diminishes the susceptibility, and increases the coercive force and hysteresis. The three alloys containing the smallest quantity of tin are much more magnetic at −190° than at the ordinary temperature. Quenching from 350° or 580° produces complex changes, the coercive force being always diminished, and the effect cannot be reversed by again annealing. The quenched alloys are more improved in magnetic properties by cooling to −190° than those in the normal condition. C. H. D.

The Magnetisation of Ferro-magnetic Substances above the Curie Point. PIERRE WEISS and G. FOËX (*Arch. Sci. Phys. Nat.*, 1911, [iv], **31**, 5—19).—In connexion with an investigation of the variation of magnetisability with the temperature, preliminary measurements of the coefficient of magnetisation of anhydrous cobalt sulphate and the heptahydrated salt and of solutions of cobalt and nickel nitrate have been made with a specially designed form of apparatus. H. M. D.

Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. VI. PAUL PASCAL (*Bull. Soc. chim.*, 1911, [iv], **9**, 79—84. Compare Abstr., 1910, ii, 100, 179, 580; this vol., ii, 91).—The method of calculating magnetic susceptibilities of carbon compounds has been described previously, and it has been shown that although this property is additive, a correction *B* must be made, the value of which varies with the structure of the group of compounds under consideration.

The present communication deals with cycloid substances, and it is shown that ring-formation invariably exalts the magnetic susceptibility. For purposes of calculation in these cases, a definite value is assigned to each carbon atom, apart from its intrinsic value as a carbon atom, according as it occurs in one ring only (mononuclear carbon, as in benzene), two rings (binuclear carbon, as in naphthalene), or three rings (trinuclear carbon, as in chrysene). The values of *B* for carbon atoms so linked are $-2{\cdot}5\times10^{-7}$, $-32{\cdot}0\times10^{-7}$, and $-42{\cdot}0\times10^{-7}$ respectively. The magnetic susceptibility of indene, C_9H_8, calculated according to these rules and those already given (*loc. cit.*) is $(-9\times62{\cdot}5+-8\times30{\cdot}8+-2\times32{\cdot}0+-6\times2{\cdot}5)10^{-7}=-885{\cdot}5\times10^{-7}$, which compares well with the experimental value -883×10^{-7}. The magnetic susceptibilities found experimentally are best explained by the Claus formulæ for cycloid substances, but they are not entirely in harmony with any formulæ yet put forward. A long list of calculated and experimental values for compounds of various types is given, showing, as a rule, good agreement between the two values. T. A. H.

Electrical Double Refraction (Kerr Effect) in Liquids and its Relation to Chemical Composition and Constitution.

ALEXANDER LIPPMANN (*Zeitsch. Elektrochem.*, 1911, **17**, 15—20).—The values of the electro-optical constants of some eighty-eight substances dissolved in benzene are determined. It appears that this constant is influenced enormously by the constitution of the substances, depending, for example, in the case of benzene derivatives on the number, nature, and relative positions of the substituting groups. T. E.

Experiments Relating to the "Swarm" Theory of Anisotropic Liquids.

EMIL BOSE (*Physikal. Zeitsch.*, 1911, **12**, 60—62. Compare Abstr., 1909, ii, 383).—Observations relating to the behaviour of anisotropic liquids in a magnetic field are described as evidence in support of the theory which the author has put forward previously. In a magnetic field, the lines of force in which are parallel to the line of sight, a clearing of the turbid liquid has been observed in the case of anisaldazine, *p*-azoxyanisole, *p*-azoxyanisolephenetole, and a mixture of anisylidenepropionic acid with anisic acid. With cholesteryl benzoate, which is much more viscous than the other substances examined, no effect was obtained even when a strong magnetic field was employed. With a weak field, the clearing takes an appreciable time, but the clearing period diminishes rapidly with increase in the strength of the field.

When the lines of force of the applied field were at right angles to the line of sight, no clearing effect was observed in any of the substances examined. H. M. D.

Density, Coefficient of Expansion, and Variation in Volume on Fusion of the Alkali Metals.

Louis Hackspill (*Compt. rend.*, 1911, **152**, 259—262).—A description is given of the methods whereby the following results have been obtained:

Column *A* contains the coefficients of expansion of the solid metals, *B* the same constants for the liquid metals at temperature *t*, and *C* the percentage increase in volume on fusion.

	D°.	$D^{96\cdot5}$.	*A*.	*B*.	*t*.	*C*.
Cs	1·9029	—	0·000291	0·000341	28— 50°	2·32
				0·000348	50—123°	
Rb	1·5248	—	0·00027	0 000339	40—140°	2·28
K	0·859	—	0·00025 at 0—58°	0·000280	70—100°	2·42
				0 000285	100—150°	
Na	0·9725	0·9385	0·000216 at 0—80°	0·000275	100—180°	1·50

Toluene and benzene are rapidly attacked by liquid cæsium. The compounds formed are under investigation. W. O. W.

Anomalous Expansion of Nickel Steels.

Charles Édouard Guillaume (*Compt. rend.*, 1911, **152**, 189—191).—The coefficients of expansion of reversible alloys of iron and nickel have been determined, and the results plotted in the form of a curve, showing the variation of the coefficient as a function of the proportion of nickel. Owing to the small cohesion of the pure alloys, specimens containing a small proportion of manganese (or chromium), silicon, and carbon were employed. The curve shows a well-marked minimum, corresponding with about 36% of nickel; as the percentage of the latter rises, it gradually approaches, and finally coincides with, the line representing the expansion as calculated from the law of mixtures.

The effect of the manganese and chromium in the alloys has also been studied. The influence of these metals on the expansion is somewhat complex; in general, the addition of small amounts of manganese diminishes the expansion in the neighbourhood of the minimum of the curve. W. O. W.

The Variation of the Thermal Conductivity of Solid Non-Metals with the Temperature.

Arnold Eucken (*Ann. Physik*, 1911, [iv], **34**, 185—221).—Two forms of apparatus are described which have been used in the investigation of the thermal conductivity of crystalline and amorphous substances. From experiments with crystals of sodium chloride, potassium chloride, fluorspar, calcspar, sodium chlorate, and sucrose between −190° and +100°, it is found that the thermal resistance increases in approximately the same ratio as the absolute temperature. This holds with greater exactness for quartz in a direction perpendicular to the axis than for any of the other substances examined. The magnitude of the thermal conductivity does not depend on the system to which a particular crystal belongs. In general it is found to increase with a diminution in the number of atoms in the molecule of the substance and with increase in the melting point. Crystals containing two and three atoms in the molecule have approximately the same thermal conductivity at their respective melting points.

For substances in the form of crystalline aggregates, the above relationship between thermal conductivity and temperature does not hold. This is attributed to the existence of thermal resistance between the individual small crystals, and this effect becomes relatively more important as the conductivity of the substance increases.

According to experiments with various kinds of glass, the behaviour of amorphous substances is quite different from that of crystals, for the thermal resistance of these diminishes as the temperature rises. A comparison of the conductivity of the same substance in the crystalline and amorphous form shows that the crystalline form always conducts better than the amorphous. At 0° crystalline quartz conducts 7·5 times, and at −190° fifty-five times, as well as fused quartz. At the melting point the conductivities are probably equal. H. M. D.

Connexion between the Elastic Properties and the Specific Heat of Solid Substances Consisting of Monatomic Molecules.

Albert Einstein (*Ann. Physik.*, 1911, [iv], **34**, 170—176).—Reference is made to the calculation by Sutherland (Abstr., 1910, ii, 946) of the wave-lengths which correspond with the fundamental mechanical vibrations of the atoms of the alkali metals and the halogens, and it is pointed out that the frequencies corresponding with the molecular vibrations of monatomic substances can be calculated from the variation of the specific heat of these substances with the temperature. The wave-lengths, which have been deduced from the elastic properties for ten different metals, vary from $\lambda = 45 \times 10^{-4}$ for aluminium and nickel to $\lambda = 163 \times 10^{-4}$ for bismuth. The value for silver is $\lambda = 73 \times 10^{-4}$, whereas that calculated from the variation of the specific heat with the temperature is $\lambda = 90 \times 10^{-4}$. For the other metals, the specific heat at low temperatures is not known accurately enough to permit of a comparison, but the agreement in the case of silver affords strong evidence of the correctness of Sutherland's views relating to the nature of the ultra-red rays. H. M. D.

Specific Heat of Carbon Tetrachloride and of its Saturated Vapour.

James E. Mills and Duncan MacRae (*J. Physical Chem.*, 1911, **15**, 54—66. Compare Abstr., 1910, ii, 932).—The method previously described for benzene has been used to determine the specific heat of carbon tetrachloride with a maximum error of ±0·001. The purified tetrachloride of b. p. 76·64° to 76·69° at 760 mm. has a specific heat which increases regularly from 0·2010 at 0° to 0·2031 at 70°. This value is somewhat lower than that obtained by Hirn and by Winkelmann at the same temperatures.

The specific heat of the saturated vapour is calculated from the sp. heat of the liquid and the latent heat. The values obtained are somewhat lower if the latent heat is calculated by the thermodynamical equation than if by the equation given by Mills (Abstr., 1909, ii, 861).

The specific heat of the vapour falls from 0·140 at 0° to 0·115 at 70°

according to the latter method of calculation, which is preferred by the authors.

When the quantities of heat employed in doing external work, in increasing the kinetic energy of the molecules, and in overcoming molecular attraction are subtracted from the specific heat, there remains about 0·3 cal. in the case of benzene liquid or vapour, and of 0 16 cal. in the case of carbon tetrachloride, unaccounted for.

Nearly as much energy is required to raise carbon and hydrogen, combined as benzene, from $-273°$ to $+20°$ as when they exist separately. R. J. C.

The Specific Heat of Liquid Benzene and of its Saturated Vapour. James E. Mills and Duncan MacRae (*J. Physical Chem.*, 1910, **14**, 797—815).—Measurements have been made of the specific heat of liquid benzene at temperatures ranging from the freezing point to 70°, a Dewar vessel being employed as calorimeter and the heat supplied by an electrical current. The specific heat varies with the temperature in a linear manner, the straight line representing the data giving the values 0·3970 and 0·4369 at 0° and 70° respectively.

From the heats of vaporisation of benzene at different temperatures, the authors have also calculated the specific heat of the saturated vapour. It is shown that the heats of vaporisation obtained in different ways are not in satisfactory agreement, and as a consequence the calculated specific heat values differ considerably according to the vaporisation data which are utilised. The values, adopted tentatively, lie on a straight line corresponding with the specific heats 0·284 and 0·268 at 0° and 70° respectively. H. M. D.

The Latent Heat of Fusion of Antimony Trichloride and Tribromide, Arsenic Trichloride, and Stannic Bromide in Relation to the Molecular Depression of their Freezing Points. Stanislaw Tołłoczko and M. Meyer (*Chem. Zentr.*, 1910, ii, 1024—1025; from *Kosmos*, 1910, **35**; *Radziszewski-Festband*, 641—648).—The latent heats of fusion of antimony trichloride and tribromide, arsenic trichloride, and stannic bromide were determined from the measurement of the heats of solution of the substances in solid and liquid (supercooled) states, in 20·5% hydrochloric acid solution, and 25% hydrobromic acid solution, and the results are given. The molecular depression of the freezing points calculated from these latent heats of fusion agree with those obtained by cryoscopic methods. At the same time it is shown that the latent heat of fusion given by Berthelot (*Thermochimie*, 1897, **2**, 156) for stannic bromide, 7·07 cal., was much too high. The specific heat of a 25% dilute hydrobromic acid solution is 0·715 cal. N. C.

Use of a Dewar Flask in Measurements of Heats of Neutralisation. J. Howard Mathews and A. F. O. Germann (*J. Physical Chem.*, 1911, **15**, 73—82).—By the use of a silvered Dewar flask as calorimeter in measurements of heats of neutralisation, the radiation correction is much reduced and the error due to thermometric lag is minimised. The acid is placed in the Dewar flask and is stirred by an inner reciprocating tube containing the equivalent of alkali, which in turn contains a rotating stirrer. The liquids are brought into contact by tearing with the rotating stirrer the rubber disc which forms the bottom of the inner vessel. Only one thermometer is required.

Parallel determinations of the heats of neutralisation of sodium hydroxide by hydrochloric, nitric, sulphuric, and acetic acids in $2N$, N, $N/2$, and $N/4$ strengths were in very close agreement in every case, and show that the method is susceptible of great accuracy. Stress is not laid on the actual values obtained in this investigation, since the thermometer was not specially standardised. R. J. C.

Thermochemical Analysis of Tautomeric Compounds. WOJCIECH SVENTOSLAVSKY (*Chem. Zentr.*, 1910, ii, 1022; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 469—477).—The analysis of the thermochemical data of organic compounds led the author to study the thermochemical characteristics of some atomic linkings. These characteristics make it possible to state the energy contents of tautomeric forms of the same compound. The author explains the results for some examples of well known tautomeric compounds, and shows that the mutual interconversion of tautomeric forms of ethyl acetoacetate, isatin, and benzoquinoneoxime takes place either without any heat change, or is accompanied by very slight thermal disturbance. In the two tautomeric forms of methylisatin, the energy content is decidedly different; the mutual interconversion of the two forms would be accompanied by considerable heat effect, and therefore it does not take place. N. C.

The Influence of Temperature on the Compressibility of Metals. EDUARD GRÜNEISEN (*Ann. Physik*, 1910, [iv], **33**, 1239—1274).—An apparatus is described by means of which measurements of the compressibility of metals at different temperatures have been made. Iron, copper, silver, and platinum were investigated between $-190°$ and $+165°$, aluminium between $-190°$ and $+125°$, and tin and lead between $-190°$ and $+16°$. These data show that in some cases the compressibility increases with the temperature according to a linear equation, whilst in others the increase is more rapid. At low temperatures the magnitude of the temperature-coefficient of the compressibility increases as the coefficient of thermal expansion increases. H. M. D.

Thermal Molecular Pressure of Gases in Tubes. MARTIN KNUDSEN (*Ann. Physik*, 1910, [iv], **33**, 1435—1448).—A method of measuring small differences of pressure is described. This has been employed to determine the molecular pressures of hydrogen and oxygen contained in a tube, different parts of which are at different temperatures. If p_1 and p_2 denote the molecular pressures observed at points the absolute temperatures of which are T_1 and T_2, these are found to be connected by the equation: $p_1^2 - p_2^2 = C(T_1^2 - T_2^2)/273(\frac{\text{dynes}}{\text{cm.}^2})^2$, where C is a constant which depends on the diameter of the tube, on the viscosity of the gas, and on its density. H. M. D.

Application of the Principle of Archimedes to the Exact Determination of the Densities of Gases. ADRIEN JAQUEROD and M. TOURPAÏAN (*Arch. Sci. Phys. Nat.*, 1911, [iv], **31**, 20—35).—A method of measuring gas densities is described which depends on changes in the weight of a closed cylindrical glass tube when suspended in the different gases. This cylinder is suspended by a thin platinum wire from one arm of a balance, and is surrounded by a wider tube immersed in a thermostat. The wider tube is provided at its lower end with an inlet, through which the gas to be examined is introduced. At its upper end the containing tube is drawn out to a capillary sufficiently wide to permit of the free movement of the platinum wire suspension. For experiments with chemically active gases, an attachment is provided above the hydrometer tube by means of which the gases can be removed from the neighbourhood of the balance. With this apparatus the density of oxygen at 0° and 760 mm. was found to be 0·0014290, and the coefficient of expansion, between 10° and 37°, 0·003674 at 730 mm. pressure.

In the case of hydrogen, the rapid diffusion of gas through the capillary was found to introduce an error into the density measurements. This can be eliminated by making weighings when hydrogen is passing through the containing tube at different rates, and extrapolating the results to the stationary condition. It is shown that this method yields satisfactory results, and that the density found for hydrogen agrees with Morley's value. H. M. D.

Determination of Degree of Molecular Association in Liquids. ALEXIUS BATCHINSKI (*Zeitsch. physikal. Chem.*, 1911, **75**, 665—673. Compare Abstr., 1902, ii, 444).—It is shown that the familiar Ramsay-Shields' formula, $\gamma(xMv)^{2/3} = 2{\cdot}12(T_k - T - 6)$, for determining the molecular complexity of liquids from measurements of surface tension requires a correction which can be made by substituting for T_k the magnitude T_m, the "metacritical temperature" already defined by the author (*loc. cit.*). The metacritical temperature can be obtained from the results of viscosity measurements by means of the equation: $T_m[\rho_k/(\eta T^3)^2]^{1/7} = 16{\cdot}31$, where ρ_k is the critical density and η is the viscosity at the absolute temperature T. When the critical density is not known, the density at 0°, ρ_0, may be used; the formula then becomes $T_m[\rho_0/(\eta T^3)^2]^{1/7} = 19{\cdot}4$. By means of these formulæ the molecular complexities of methyl and ethyl alcohols, acetic acid, and water have been calculated. G. S.

Surface Tension of Solutions of Salts in Alcohol. IVAR W. CEDERBERG (*J. Chim. Phys.*, 1911, **9**, 3—14).—The surface tension of purified alcohol and of alcoholic solutions of sodium bromide, sodium iodide, and potassium acetate was determined from the capillary rise in tubes of Jena glass. Care was taken to maintain the temperature constant and to compensate for evaporation of solvent during the determinations.

The surface tension of alcohol is increased by each of the salts, the bromide being most effective and the acetate least. The increase is relatively rapid with the first additions of salt, but afterwards falls, and becomes a linear function of the salt added when the concentration of the latter is more than about 0·3 mol. per litre.

The highest surface tension observed was 22·93 dynes with a solution of 0·9381 mol. of sodium iodide per litre. The increment, 1·72 dynes, is the same as that produced in water by 0·94 mol. of sodium chloride per litre.

Quincke found (1877) that lithium chloride and calcium chloride increase the surface tension of alcohol in proportion to their concentration, but his measurements were made before the sources of error in capillary rise determinations had been studied by Volkmann.

R. J. C.

Degree of Dispersity and Viscosity. H. W. Woudstra (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 73—80).—The influence of the degree of dispersity of the disperse phase on the viscosity of colloidal solutions of ferric and chromic hydroxides has been investigated. On addition of successive small quantities of electrolytes, the viscosity diminishes at first, attains a minimum, and afterwards increases. Small quantities of a non-electrolyte, such as sucrose, have no influence on the viscosity. When the colloidal solutions are kept at 45°, a gradual diminution in the viscosity is observed both in presence and absence of electrolytes. Continued shaking of the colloidal solutions has no measurable effect on the viscosity. Since addition of electrolytes, rise of temperature, and shaking reduce the degree of dispersity of the hydrosol, it is supposed that the changes in viscosity are dependent on the changes in the character of the disperse phase. For small variations in the degree of dispersity, the viscosity diminishes, whereas the formation of much larger particles results in an increase of viscosity. H. M. D.

Balling-together Phenomena. J. Hertkorn (*Chem. Zeit.*, 1911, **35**, 89).—The various phenomena in connexion with the balling-together of precipitates (this vol., ii, 98) are readily explained by the convection currents set up by the difference in temperature between the liquid in which the precipitate is suspended and the surrounding atmosphere. T. S. P.

Adsorption of Neutral Salts. Hilary Lachs and Leonor Michaelis (*Zeitsch. Elektrochem.*, 1911, **17**, 1—5).—It is first shown that potassium and sodium chlorides are adsorbed (from aqueous solutions) by blood charcoal in a normal way (the quantity adsorbed per gram of charcoal is nearly proportional to the square root of the equilibrium concentration of the salt) and that the cation and anion are adsorbed in equivalent quantities. The adsorption is not affected by the addition of acetone, amyl alcohol, or phenol to the solution, and, conversely, the adsorption of these substances is not affected by the presence of the salts. On the other hand, the addition of a salt (sodium or potassium nitrate or sodium sulphate) to the solution diminishes the quantity of the chloride adsorbed in a very marked way.

The addition of a basic substance (sodium or potassium hydroxide, ammonia, sodium carbonate, trisodium phosphate) to the solution prevents the adsorption of chlorine ion altogether, whilst acids have the opposite effect. This effect of acids is not entirely dependent on the hydrion, but depends also on the nature of the anion. Sulphuric and phosphoric acids were the most active of those tried, nitric acid had but little effect, and the halogen hydracids diminished the adsorption instead of increasing it.

The authors draw the conclusion that whilst the adsorption of non-electrolytes is probably due to changes of surface tension, that of electrolytes must be ascribed to some different cause, probably of electrical origin. T. E.

Adsorption Experiments. K. SCHERINGA (*Chem. Weekblad*, 1911, **8**, 11—12).—The author describes experiments on the diminution of the lead content of lead solutions by contact with paraffin-wax, and states that the amount of lead abstracted from the solutions is independent of the surface area of the wax. His inference is that the action is due to solution and not to surface condensation. A. J. W.

Ostwald's Dilution Law. JAN ŠEBOR (*Zeitsch. physikal. Chem.*, 1911, **75**, 685—686).—It is shown mathematically that the dilution law is only valid when no reaction takes place between the electrolytes in the mixture. G. S.

Relation of Osmotic Pressure to Temperature. I. Manufacture of the Cells employed in the Measurements. HARMON N. MORSE, WILLIAM W. HOLLAND, JOSEPH C. W. FRAZER, and B. MEARS (*Amer. Chem. J.*, 1911, **45**, 91—113. Compare Morse and Frazer, Abstr., 1905, ii, 575).—Morse and Holland (Abstr., 1909, ii, 386) have given an account of measurements of the osmotic pressure of sucrose solutions at 20°, and have compared the results with those obtained at 0°, 5°, 10°, 15°, and 25° (Abstr , 1907, ii, 744; 1908, ii, 671, 1019; 1909, ii, 216). It has been found that within this range of 0—25°, the temperature-coefficient of osmotic pressure in the case of sucrose solutions of concentration from $0{\cdot}1N$ to N is practically identical with that of gas pressures.

The method of investigation has now been further improved, and the work at the six temperatures mentioned has been repeated. The results obtained confirm the conclusion arrived at previously, but a few preliminary experiments with concentrated solutions at 30°, 40°, and 50° indicate that at these higher temperatures the ratio of osmotic to gas pressure does not remain constant, but tends to diminish, beginning at some point between 25° and 30°. A detailed account of the work is to be published in a series of papers, of which this is the first.

A full description is given of the method of manufacturing the cells, including the treatment of the clays, the burning and glazing of the cells, and the mode of attaching the manometer. The cells are glazed, both inside and outside, from the middle upwards. They have been found satisfactory in all respects, except that there is a chance that dissolved matter may diffuse in between the two glazed surfaces and afterwards affect the pressure measurement by diffusing downwards and distributing itself about the membrane. It is considered probable that the results of the experiments have not been vitiated in the slightest degree by this defect, but efforts will be made to obviate the risk by making a cell half porous and half porcelain.

E. G.

Theory of the Isoelectric Point. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1910, **30**, 143—150).—In previous papers (Abstr., 1910, ii, 592, etc.) it has been shown by experiments with protein solutions that the so-called isoelectric point and the point of optimum coagulation coincide. The acidic and basic dissociation constants of these proteins are, however, not known, and experiments have now been made with simpler compounds for which both dissociation constants are known. The rate of crystallisation from fairly concentrated solutions of these electrolytes in $N/1$-sodium hydroxide to which different proportions of acid had been added was observed; the hydrogen concentration of the solution showing the maximum crystallisation velocity was determined by *E.M.F.* measurements, and the $H^{\cdot}$ ion concentration, J, at the isoelectric point thus obtained compared with that calculated by means of the formula $J=\sqrt{K_aK_w/K_b}$, where K_a and K_b are the acidic and basic dissociation constants of the electrolyte, and K_w is the ionic product for water.

With *m*- and *p*-aminobenzoic acids there is excellent agreement between the observed and calculated values of J, with aspartic acid the agreement is moderate, with theobromine unsatisfactory, and with arsenious acid the velocities of crystallisation were so irregular that no definite results were obtained.

G. S.

Ideal Solutions. L. GAY (*J. Chim. Phys.*, 1911, **9**, 103—104).—Polemical. Criticism of a recent paper by Washburn (Abstr., 1910, ii, 1044).

R. J. C.

Transference and Transformations of Energy with Applications to the Theory of Solutions. MADISON M. GARVER (*J. Physical Chem.*, 1911, **15**, 20—44. Compare Abstr., 1910, ii, 935).—The second law of thermodynamics may be enunciated thus: "In an isolated system work or potential energy appears only during the spontaneous transfer of energy from points of higher to points of lower intensity, accompanied by an equilibrating of the various energy intensities." All natural processes are equilibrating processes, during which each type of energy independently tends to become uniformly distributed.

Equilibrium may be established between a solution and the pure solvent by (1) raising the temperature of the solution until its vapour pressure equals that of the solvent, or (2) raising the level of the solution so that the difference in vapour pressures is compensated by the higher barometric pressure of the vapour on the solvent, or (3) increasing the pressure on the solution. If any two of these conditions are prevented, the spontaneous transfer of solvent vapour to the solution will establish the third. The solution is therefore in a state of less potential (free) energy than the pure solvent at the same temperature, although the energy per molecule is unchanged. If it is assumed that dissolution entails no chemical union, but merely the distribution of the energy of the N-molecules of solvent among the $(N+n)$ molecules of solution, the abs. temperatures before and after dissolving the solute should be as $(N+n):N$. The fall in temperature on dissolving 1 gram-mol. of sucrose in a litre of water at 20° would be 5° instead of the actual 0·8°. The difference must be supplied by chemical union with a decrease in the number of reacting molecules and the liberation of a definite amount of energy.

R. J. C.

The Critical Phenomena of Dissolution of Mixtures with Normal Components Examined under Variable Pressure. JEAN TIMMERMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 507—526).—The influence of pressure on the critical solution temperature has been investigated for mixtures of *cyclo*hexane and aniline (31·05°), nitrobenzene and hexane (21·00°), and nitrobenzene and *iso*pentane (32·20°). For the first pair of liquids the critical solution temperature rises with increase of pressure, the rise per atmosphere being about 0·0065°. For the other two pairs the temperature falls with increase of pressure, the fall per atmosphere decreasing as the pressure becomes greater. In the case of a mixture of nitrobenzene and hexane, dt/dp is equal to 0·0186° at low pressures, and 0·0122° at 220 atmospheres. For a mixture of nitrobenzene and *iso*pentane, dt/dp is equal to 0·0413° at low pressures and 0·0200° at 250 atmospheres.

H. M. D.

Crystallisation from Aqueous Solutions. V. Adsorption by Crystals. ROBERT MARC (*Zeitsch. physikal. Chem.*, 1911, **75**, 710—732. Compare Abstr., 1909, ii, 798, 983; 1910, ii, 834).—In connexion with the observation that the presence of dyes retards the velocity of crystallisation, the equilibrium between certain crystals and dyes in solution has now been systematically investigated. As dyes, methylene-blue, Bismarck-brown, methyl-violet, and ponceau-RR, and as adsorbing surfaces, crystals of uric acid, barium sulphate, and barium and strontium carbonates were used.

It is shown that the colouring of crystals is an adsorption phenomenon, and follows the well-known exponential law $a=kl^{1/n}$, where a is the amount adsorbed by a definite surface, l is the concentration of the dye in the solution, and k and n are constants. With different substances the values of $1/n$ vary between 1/3 and 1. Further, for every crystalline substance with definite surface, there is an upper limit of saturation, beyond which a no longer increases as l is increased. The bearing of the saturation limit on the phenomena of crystallisation from coloured solutions is discussed in detail.

The same crystal does not adsorb to the same extent on all its surfaces, and in this connexion it is shown generally that the ratio in which the different dyes are adsorbed does not depend on the chemical nature of the adsorbent, but on the crystallographic nature of the adsorbing surface.

G. S.

Crystallisation through Membranes. JAMES H. WALTON, jun. (*J. Physical Chem.*, 1911, 15, 45—53. Compare Abstr., 1909, ii, 649).—Supercooled phosphorus, which crystallises at a speed of 60,000 mm. per minute, cannot transmit its crystallisation through goldbeater's skin, or through 0·005 in. of rubber, although salol with a crystallisation speed of only 4 mm. per minute is able to pass its solid phase through these membranes. Aqueous supersaturated solutions of sodium acetate, potassium alum, and lead acetate are unable to crystallise through rubber membranes 0·0003 to 0·0004 in. thick. The necessary contact with the solid phase is not established unless the membrane is wetted by the solvent as in the case of aqueous solutions with parchment or collodion. In order that an aqueous solution shall crystallise through either of these membranes, a definite minimum degree of supersaturation is necessary, depending on the particular salt and membrane. Potassium alum appears to pass through parchment less readily than through collodion, and the reverse holds for sodium acetate. The author suggests that there is a concentration of the water in the pores of the membrane, so that in order to produce a saturated solution in the membrane, a definite degree of supersaturation is necessary outside it. R. J. C.

Solid Colloidal Solutions. ALFRED LOTTERMOSER (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 95—96).—In reference to the views of Benedicks on the nature of troostite (this vol., ii, 25), the author calls attention to the similarity between the phenomena which are observed in the slow and rapid cooling of iron carbon alloys on the one hand, and gold glasses on the other. H. M. D.

Emulsion Colloids (Emulsoids) and Observations on the Methods of Counting Ultra-microscopic Particles. GEORG WIEGNER (*Koll. Chem. Beihefte*, 1911, 2, 213—242).—It has been found that independent estimations of the number of ultra-microscopic particles in a solution of colloidal gold, carried out by different observers at different times, exhibit discrepancies such as can be entirely accounted for on the basis of the law of probability.

Experiments are described which show that olive oil–water emulsions can be prepared by means of a Laval emulsifier which contain as many as $5\cdot10^9$ colloidal particles in 1 c.c. Emulsoids containing from 2 to $3\cdot10^9$ particles per c.c. are quite stable, but those containing a larger or a smaller number of particles are comparatively unstable.

The olive oil–water emulsoids exhibit the characteristic properties of colloidal solutions. Coagulation takes place on addition of electrolytes. Corresponding with the fact that the emulsoid particles are negatively charged, it is found that acids cause coagulation even in very dilute solution. In very small quantities (less than 2·5 millimols. per litre), hydroxides have no effect, but above this limit the activity of hydroxides exceeds that of acids. This is attributed to the greater readiness with which the $OH^{\cdot}$ ions are adsorbed as compared with the $H^{\cdot}$ ions.

In presence of egg-albumin, coagulation takes place more readily, and this is supposed to be an effect of the same kind, although opposite in sign, as that which is involved in the action of protective colloids.

H. M. D.

Some General Properties of the Binary Equilibrium Diagram. KARL BORNEMANN (*Metallurgie*, 1910, 7, 740—747).—Complete immiscibility of the components in two co-existing phases is impossible, and every homogeneous field of the equilibrium diagram must therefore have a certain extension in the direction of the axis of concentration. As two co-existing saturated phases cannot have the same composition, the heterogeneous field separating these two phases must also have a definite extension in the same direction. These rules apply to all systems which are not in invariant equilibrium. Their effect on the diagram is illustrated by application to the nickel-sulphur system (Abstr., 1910, ii, 1072). C. H. D.

The Analysis of Binary Compounds by a Method Based on the Law of Mass Action. IWAN OSTROMISSLENSKY (*Ber.*, 1911, 44, 268—273).—It is shown that if two substances, A and B, unite to form an unstable compound, and if varying amounts represented by a and b (in gram-mols.) of the two are mixed in solution so that $a+b$ is always constant, then the maximum yield of the compound is formed when the two components are present in the proportions in which they combine with one another. The maximum yield of compound can be determined by some physical method, such as change in colour. It is shown that in the case of aniline and nitrobenzene, a definite compound of molecular proportions of the components is formed in the absence of a solvent. The coloration was determined with a Krüss spectrophotometer, using an incandescent gas lamp and a thickness of liquid 10 mm., at 22—23°.

The formula $a/s.(9M+3M')/R$ can be used for calculating the relative amounts of product in the solution when $a+b=12$ and $a/b=3$. M and M' represent the mol. wts. of the two components, S the sp. gr. of the mixture, and R the proportionality factor. J. J. S.

Equilibrium Diagram of Silver Iodide. GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1911, 75, 733—762).—In a previous paper (*Ann. Phys. Chem.*, 1899, [ii], 68, 643) evidence was obtained that three solid forms of silver iodide exist. As a result of the present investigation, this conclusion is confirmed, the three forms being silver iodide, I, the ordinary yellow modification ; II, a red modification, and III, which is only stable when the pressure exceeds 3000 kilog./cm.^{2}.

The equilibrium curves I—III and I—II have been determined in detail, and also the position of the triple point at which the three forms are in equilibrium ; the latter point lies at 100° and 2940 kilog. pressure. The change of volume when modification I changes to the denser form III is about 0·0265 c.c. per gram, whereas the converse change from III to I is attended by an expansion of only 0·0233 c.c. per gram. The cause of this discrepancy is so far undetermined. The average change of volume in changing II to III is about 0·0115 cm. per gram. The velocity of transformation of I to III, and vice versâ, does not take place like a system of one component, for example, like the transformation ice I—ice III. In the range of temperature from 90° to 20° the transformation I—III takes place at a definite pressure, which only depends on the rate of change of volume; in the converse transition III—I, the maximum velocity is reached at 2700 kilog./cm.^{2}, practically independent of the temperature. At the end of the transformation I—III, the pressure must exceed 3200 kilog. in order to complete the change; similarly, to complete the converse transformation, the pressure must be very considerably lowered. As an explanation of these peculiarities it is suggested that both I and III form saturated mixed crystals, the composition of which depends on the temperature and pressure.

When III is cooled to −80° and the pressure reduced, the change III—I occurs at 1700 kilog. pressure, but when the same form is cooled to −180°, the transformation does not occur even at 1 kilog. pressure.

In the course of the investigation it was shown that the precipitated, so-called amorphous silver iodide is identical with the crystalline modification. G. S.

Mixed Crystals in Liquid-Crystalline Systems and the Phase Rule. Ada Prins (*Zeitsch. physikal. Chem.*, 1911, **75**, 681—684).—An answer to the criticisms of Lehmann (Abstr., 1910, ii, 772) on the author's work (compare Abstr., 1909, ii, 869). The importance of quantitative observations as opposed to purely qualitative microscopic observations is emphasised. G. S.

Periodic Reactions. Julius Hirniak (*Zeitsch. physikal. Chem.*, 1911, **75**, 675—680. Compare Lotka, Abstr., 1910, ii, 401).—It is shown mathematically that under certain conditions a periodic chemical reaction may occur in the unimolecular reversible transformation of three isomerides. G. S.

Speed of Reaction in Heterogeneous Systems. J. Boselli (*Compt. rend.*, 1911, **152**, 256—259).—The following conclusions, derived from theoretical considerations to be published hereafter, refer to that particular type of reaction illustrated by the dissolution of magnesia in dilute hydrochloric acid, a case in which the velocity of reaction depends on the rate of diffusion of the acid towards the solid.

(1) The velocity of dissolution or vaporisation of a solid in a liquid is proportional, other conditions being equal, to a power, slightly less than the 4/3, of the difference between the mean concentration of the dissolved solid at an infinitely small distance from the undissolved surface, and its average concentration in the solution. The velocity is also proportional to the 1/3 power of the coefficient of diffusion of the solute in the solvent.

(2) The speed of dissolution is proportional to the square root of the coefficient of diffusion, to the square root of the velocity of the stream of liquid (moving uniformly in a straight line), and to the difference between the concentration at saturation and the average concentration.

(3) The following expressions indicate the speed of total dissolution, Q, of a rectangular plate (dimensions $l \times y$) and of a circular plate, radius R, respectively, each being parallel to the flow of liquid:

$$Q = 2By\sqrt{VKl/\pi}; \qquad Q = 2^{\frac{5}{2}}R^{\frac{3}{2}}\sqrt{VK/\pi}.B\int_0^1(1-a^2)^{\frac{1}{4}}.da.$$

K is the coefficient of diffusion, V the velocity of the liquid, and B the difference between concentration at saturation and mean concentration.

These expressions have an advantage over those of Nernst, inasmuch as they contain no arbitrary constant. W. O. W.

Comparison of Reaction Velocity and the Fluidity of the Medium.

ERNEST S. GRUMELL (*J. Chim. Phys.*, 1911, **9**, 143—159).—The rates of hydrolysis of sucrose and ethyl acetate by hydrogen chloride have been compared with the viscosities of the same solutions at various temperatures from 0° to 98°. In neither case does the progress of the hydrolysis introduce any appreciable change in the viscosity of the solutions.

No quantitative relation between viscosity and chemical activity could be traced, and the introduction of solubility considerations in the case of sucrose led to no better result.

The coefficients of increase of velocity and decrease of viscosity with temperature both show a diminution as temperature rises. The ratios of the temperature-coefficients of velocity and viscosity at any temperature were appreciably constant in both reactions. This is held to demonstrate a connexion between the phenomena. It is suggested that connexion is to be sought in Trautz' hypothesis (Abstr., 1909, ii, 651), according to which the variations in the temperature-coefficient of reaction velocity are due to changes in the specific heat of the solution, to which also the viscosity is closely connected. R. J. C.

The Velocity of the Ring Opening in Connexion with the Composition of the Unsaturated Ring Systems.

JACOB BÖESEKEN and A. SCHWEIZER (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 534—536).—The rates of hydration of succinic and malic anhydrides have been compared at 0° by means of measurements of the electrical conductivities of the aqueous solutions. The observed rate of change indicates that the reaction is unimolecular, and that maleic anhydride takes up water 14·2 times as fast as succinic anhydride (compare Rivett and Sidgwick, Trans., 1910, **97**, 1677). H. M. D.

Repeating Figures in the Atomic Weight Values.

HEINRICH LOEWEN (*Chem. Zeit.*, 1911, **35**, 55).—A severe adverse criticism of Loring's suggestion (compare Abstr., 1910, ii, 1053) that there is some significance in the occasional recurrence of the figure in the unit's place in the second place of decimals. G S

Atomic Weight Relations.

F. H. LORING (*Physikal. Zeitsch.*, 1911, **12**, 107—112).—The paper consists mainly of tables and curves illustrating relationships between the atomic weights, some of which have already been given in previous papers (compare Abstr., 1909, ii, 392, 562, 715; 1910, ii, 26). The inactive gases are supposed to be formed by the association of acid and basic principles, and a number of methods of arriving at their atomic weights on this basis are indicated. The atomic weights of these elements are also derived by a geometrical method. In the course of the investigation, the atomic weights of a number of elements so far unknown are deduced.

G. S.

Periodic System [of the Elements]. CURT SCHMIDT (*Zeitsch. physikal. Chem.*, 1911, **75**, 651—664).—The author considers that the weaknesses of Mendeléeff's classification of the elements can be avoided by dividing the elements into four groups which are genetically connected. The first group comprises hydrogen, certain gases present in stars, and "proto-metals." The second group consists substantially of the members of the even series of Mendeléeff's table, which are characterised by pronounced chemical individuality and the division into metals and non-metals, separated by a neutral zone of inactive gases. The third group, which consists mainly of the uneven series of Mendeléeff's table, consists of metals only, and the members form no definite chemical compounds among themselves, but merely alloys. The fourth group comprises the metals of the rare earths.

The advantages of this system of classification, and the possible stages in the genesis of the elements are discussed in detail. Finally, as regards tendencies now at work, the development is towards the elimination of chemical differences, and therefore towards the disappearance of chemical affinity. This is brought about by the formation of systems of elements, the members of which become chemically more alike and finally identical. G. S.

Helix Chemica. Study of the Periodic Relations of the Elements and Their Graphic Representation. BENJAMIN K. EMERSON (*Amer. Chem. J.*, 1911, **45**, 160—210).—The elements have been arranged in the form of a spiral based on the idea of Crookes' spiral (Trans., 1888, **53**, 503). The curve begins with "der Urstoff" or ether with valency and density of zero. From this an initial half-circle rises with coronium at its summit. The second curve is a half-octave circle passing from hydrogen through nebulium and "protofluorine" to helium (compare Jessup and Jessup, Abstr., 1908, ii, 96). This is followed by two octave circles in which the elements sink through lithium to carbon, rise through fluorine to neon, and repeat the curve through sodium to silicon and on through chlorine to argon. The spiral is continued by four double-octave circles, and terminates in a quadruple octave. The first double octave begins with potassium and ends with krypton; the second begins with rubidium and ends with xenon; the third begins with cæsium and ends with an unknown element; the fourth begins with an unknown element and ends with "radium emanation." The quadruple octave contains radium, ionium, thorium, and uranium.

The position of the elements in the spiral are correlated with the atomic weights, densities, valencies, refractivities, specific volumes, compressibilities, electropotential relations, crystallographic forms, fusibilities, volatilities, hardness, ductility, and other properties.

The paper is illustrated with numerous diagrams. E. G.

The State of Aggregation of Matter. I.—III. SAMUEL B. SCHRYVER (*Proc. Roy. Soc.*, 1910, *B*, **83**, 96—123).—See this vol., i, 245.

The History of the Name "Gas." EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1911, **35**, 41—43, 62—64, 70—72).—Historical.
L. DE K.

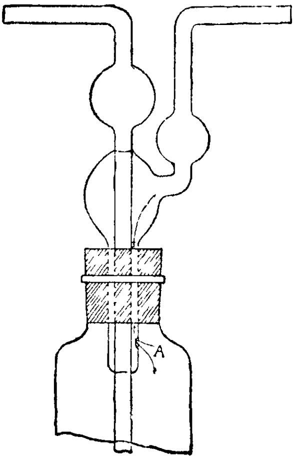
Congress of Chemists at Karlsruhe in 1860. ERNST VON MEYER (*J. pr. Chem.*, 1911, [ii], **83**, 182—189).—Historical.
C. S.

Gas Regulator for Thermostats. ARTHUR SLATOR (*J. Soc. Chem. Ind.*, 1911, **30**, 61—62).—The part of the regulator containing the mercury is provided with a side-tube which is bent slightly downwards close to the junction and then rises vertically. By means of a glass rod fitted into the upper end of this side-tube, the level of the mercury in the main tube may be regulated as desired, the rod being moved up or down for this purpose. The rod passes through a rubber stopper fitted in a cup at the top of the tube, and this cup is filled with a mixture of glycerol and water. W. P. S.

New Form of Constant Temperature Drying Oven. RAYMOND L. SIAU (*J. Soc. Chem. Ind.*, 1911, **30**, 61).—The oven consists of a round or square cylinder mounted horizontally and surrounded by a jacket of similar shape. The jacket is united to the cylinder at one end, and this end of the oven is closed by means of a closely-fitting door. Steam, or the vapour of any other liquid, is admitted to the jacket, which is provided with a condenser, and a current of air is drawn through the oven itself, this air, before entering the oven, having been passed through a spiral tube situated in the jacket and surrounding the cylinder forming the oven. A tube, leaving the oven at the opposite end to the door, is connected with a pump in order to draw the current of heated air through the spiral tube and oven. W. P. S.

Cheap Crucible Supports. VON HEYGENDORFF (*Chem. Zeit.*, 1911, **35**, 139).—The disused fire-clay supports of inverted incandescent mantles will be found suitable for supporting red-hot crucibles either on the bench or in a desiccator. L. DE K.

A Closing Contrivance for Gas-washing Bottles, Wash-Bottles, etc. FRANZ MICHEL (*Chem. Zeit.*, 1911, **35**, 72).—The arrangement (see Fig.) renders unnecessary the use of stopcocks or pinchcocks, and allows the current of the gas to be regulated or to be shut off. All that is necessary is to move the bulb-tube upwards or downwards in the cork, so as to partly or totally close the opening *A*.



The same principle may be applied to ordinary wash-bottles.

L. DE K.

A New Gas-generating Apparatus. FRANZ MICHEL (*Chem. Zeit*, 1911, 35, 52).—An Improved Kipp Apparatus.—An exit tube for the gas generated is fused on to the neck of the lower vessel. Corresponding in position with this, a groove is cut in the upper vessel where it is ground into the neck of the lower vessel, so as to form a passage from the lower vessel to the exit tube. On rotating the upper vessel this passage is closed, thus replacing the usual external stopcock on the exit tube. L. DE K.

Inorganic Chemistry.

Influence of Organic Liquids on the Interaction of Hydrogen Sulphide and Sulphur Dioxide. DAVID KLEIN (*J. Physical Chem.*, 1910, 15, 1—19).—Dry hydrogen sulphide will not react with dry sulphur dioxide (Cluzel, *Ann. Chim. Phys.*, 1812, 84, 162). Brereton Baker has recently stated that liquid alcohol and liquid sulphur dioxide can liberate sulphur from the dried mixture of gases, whereas carbon tetrachloride is inert (*Mem. Manchester Phil. Soc.*, 1909, 53, Part 3). The author's experiments confirm and extend these observations.

Immediate action is produced by water, ethyl alcohol, *iso*butyl alcohol, *iso*amyl alcohol, acetone, propyl acetate, benzaldehyde, and carvone. A slower decomposition occurs with methyl ethyl ketone, acetonitrile, propionitrile, valeronitrile, phenylacetonitrile, methyl benzoate, *iso*butyl acetate, and ethyl ether. On the other hand, carbon disulphide, ethyl disulphide, benzene, amylene, chloroform, nitrobenzene, acetyl chloride, benzoyl chloride, ethyl chloride, and carbon tetrachloride are quite inert. There appears to be no connexion between the dielectric capacity or association factor of a liquid and its activity as a catalyst in this reaction. Many of the active liquids are known to form compounds with hydrogen sulphide, notably the nitriles, the aldehydes, and carvone. The results generally support the intermediate compound theory of catalysis.

Care was taken to eliminate water as far as possible from the mixed gases and the various solvents, but it is admittedly impossible to prove that water was entirely absent in those cases where action occurred. R. J. C.

Nitrosulphonic Acid: "Blue Acid". FRITZ RASCHIG (*Zeitsch. angew. Chem.*, 1911, 24, 160. Compare Abstr., 1910, ii, 1055).—Polemical. A reply to Manchot (this vol., ii, 107). T. S. P.

Tellurium. ALEXANDER GUTBIER and FERDINAND FLURY (*J. pr. Chem.*, [ii], **83**, 145—163).—See this vol., i, 182.

Action of Hydrazine Hydrate on Sodamide. ROBERT STOLLÉ (*J. pr. Chem.*, 1911, [ii], 200).—Almost anhydrous hydrazine is obtained by distilling sodamide and hydrazine hydrate in a vacuum (compare Raschig, Abstr., 1910, ii, 706). The quantity of sodamide must be rather smaller than that calculated from the equation: $N_2H_4,H_2O + NH_2Na = N_2H_4 + NH_3 + NaOH$; when an excess is used, a violent explosion occurs at about 70°, probably due to the formation and decomposition of sodium hydrazide (compare Ebler, Abstr., 1910, ii, 614). C. S.

Experiments on the Inertness of Oxygen towards Phosphorus. MIECZYSLAW CENTNERSZWER (*Chem. Zentr.*, 1910, ii, 1022; from *Kosmos*, 1910, **35**, *Radziszewski-Festband*, 526—527).—The author determined the partial pressure of oxygen at which luminosity commences in solutions of phosphorus in castor oil, petroleum, and vaselin oil between 0° and 25°. He also measured the speed of oxidation of phosphorus in castor oil at 25°. The experiments show that the apparent inertness of phosphorus for oxygen occurs also in solutions of phosphorus, and that with the decreasing partial pressure of the phosphorus the luminosity pressure decreases for the oxygen. It is also shown that by the solution of phosphorus in non-volatile oils its oxidation power is increased. During the oxidation of phosphorus an unknown compound is formed, which inhibits the oxidation process autocatalytically; this compound is evidently identical with that which inhibits the oxidation of solid phosphorus by oxygen at atmospheric pressure. N. C.

Density of Hydrogen Phosphide and Atomic Weight of Phosphorus. G. TER-GAZARIAN (*J. Chim. Phys.*, 1911, **9**, 101—102). —Replying to the criticism of Baxter and Jones (Abstr., 1910, ii, 288), the author contends that the hydrogen phosphide used in his atomic weight determinations could not have been contaminated with hydrogen and ammonia. Some error may, however, have been introduced by calculating the compression constants from the critical data instead of from the compressibility of the phosphide. R. J. C.

The Volatile Matter of Coal. HORACE C. PORTER and F. K. OVITZ (*Bull. Bureau of Mines*, 1910, I, 1—56).—Nine different coals from various parts of the United States have been investigated with a view to determining the composition of the volatile products evolved at different temperatures. The by-products of coking were determined by tests in an iron retort on 400 grams of coal, whilst the gas evolved was determined by tests on 10 grams of coal, using a platinum retort. The furnace temperatures varied from 500—1100°.

The main features of the results are the comparatively large amounts of inert constituents, such as carbon dioxide and water, in the products from certain western coals, the large amounts of higher methane hydrocarbons, such as ethane, in the products obtained at moderate temperatures, particularly from the Appalachian coals, and the larger amounts of gas and tarry vapours produced quickly at moderate temperatures from the younger western coals. The bearing of these results on smoke-producing tendencies, on studies of the nature of coal substance, and on the calculation of heat value from ultimate analysis is discussed.

Any statement as to the character of the gases or volatile products evolved from coal at specified temperatures has little value, unless it is accompanied by a clear description of the conditions prevailing during the testing, and particularly of the points at which temperatures were taken, and of the mass of coal which was heated. The temperature varies throughout the mass, and is affected by the rate and time of heating. The same temperatures outside the containing vessel produce different temperatures in the coal itself according to the kind of vessel and the duration of heating. The distance of the vessel from the point where temperatures are read influences the difference between the observed temperature and that of the coal within the vessel. T. S. P.

Fractional Crystallisation and Atomic Weight of Argon.

Franz Fischer and Victor Froboese (*Ber.*, 1911, **44**, 92—104).—The discrepancy in the periodic arrangement of the elements which occurs with the pair argon and potassium is due very probably to an error in the atomic weight of argon. The authors have therefore tested the individuality of this element by a process of fractional crystallisation. An apparatus for this purpose is figured and described; the most important part is the fractionating vessel, which is designed to effect a separation of the liquid and the solid phases at any pressure, and in the complete absence of air. Forty litres of argon, D 19·94, isolated from air by the aid of glowing calcium carbide (Fischer and Ringe, Abstr., 1908, ii, 688; Fischer and Hähnel, Abstr., 1910, ii, 608), are used. Argon has b. p. – 186·9°/760 mm. and f. p. – 189·6°, and its freezing and thawing by the aid of freshly-prepared liquid air, b. p. about – 191°, and of stored liquid air, b. p. about – 184°, is a practical operation.

The experiments show that argon cannot be separated into two fractions of different density by fractional crystallisation; the densities of the gaseous argon obtained from the liquid and the solid phases are both 19·95(4), corresponding with an atomic weight of 39·9. In some experiments fractions have been obtained having D 19·86; the depression is due to the presence of neon and air, for when the latter is removed by chemical means the density is increased to 19·92.

C. S.

Isotherms of Monatomic Gases and of their Binary Mixtures. VI. Co-existing Liquid and Vapour Densities of Argon; Calculation of the Critical Density of Argon.

C. A. Crommelin (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 607—613).—From the data obtained in a previous investigation (Abstr., 1910, ii, 709), the author has calculated the differences between the densities of liquid and gaseous argon at a series of temperatures. By combination of these differences with the sum of the densities as represented by the law of rectilinear diameters, values have been obtained for the density of both liquid and saturated vapour. The respective densities are 1·0268 and 0·1073 at −140·8°, 0·9339 and 0·1621 at −134·72°, 0·8581 and 0·2079 at −129·83°, and 0·7557 and 0·2843 at −125·49°. It is shown that the observations can be satisfactorily represented by means of Keesom's formula.

H. M. D.

Isotherms of Monatomic Gases and of their Binary Mixtures. VII. Isotherms of Argon between +20° and −150°. H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 614—625).—The pressure volume relationships of argon have been determined at temperatures between +20° and −150° for pressures ranging up to 60 atmospheres.

H. M. D.

Precipitation of Soluble Chlorides by Hydrochloric Acid. JOHN GIBSON and ROBERT B. DENISON (*Proc. Roy. Soc. Edin.*, 1909–10, **30**, 562—568).—From the point of view of the dissociation theory the precipitation of sodium chloride from solution by the addition of hydrochloric acid is due to a decrease in the dissociation of the salt, and consequent increase in the concentration of the undissociated molecules. Precipitation should occur, therefore, only when the concentration of the chloride ions in the solution of hydrochloric acid is greater than the concentration of the chloride ions in the saturated solution to which it is added.

Experiments at 18° with saturated solutions of sodium, potassium, rubidium, and ammonium chlorides, and at 0° with saturated solutions of sodium and potassium chlorides, showed that precipitation occurred only when the concentration of the hydrochloric acid added was 18—19% or higher, that is, when acid of maximum conductivity was added.

Calculation of the chloride-ion concentrations of the saturated solutions from measurements of the electrical conductivity shows that only in the case of sodium chloride is it less than the concentration of the chloride ion in hydrochloric acid of maximum conductivity, so that if the explanation mentioned above is the correct one, the ionic concentrations calculated from the electrical conductivities cannot be even approximately correct.

Even if the concentration of the chloride ions is at least equal to that of the saturated salt solutions, there is no explanation as to why such solutions, which are all precipitated by hydrochloric acid of the same concentration, are in no case precipitated by a solution containing less hydrogen chloride.

The insufficiency of the dissociation theory to explain these phenomena is probably due to its taking into account only the following equilibria: solid salt $\rightleftarrows$ undissociated salt in solution $\rightleftarrows$ ions, whereas probably there are other factors, such as the hydration of the ions and undissociated molecules, and the formation of complex ions.

The above experiments are further instances of a tendency towards maximum specific conductivity in chemical reactions (compare Abstr., 1897, ii, 437; 1900, ii, 198); the hypothesis of such a tendency is thus shown to be useful, for by it the conditions necessary for these precipitations are correlated and were predicted. T. S. P.

Revision of the Atomic Weight of Calcium. II. Analysis of Calcium Chloride. THEODORE W. RICHARDS and OTTO HÖNIGSCHMID (*Monatsh.*, 1911, **32**, 41—51.* Compare Abstr., 1902, ii, 394, and this vol., ii, 112).—The calcium chloride was prepared from calcium carbonate and hydrochloric acid, and was subjected to three recrystallisations. The calcium carbonate was from two different sources. The first specimen was prepared from calcium nitrate by precipitation with freshly distilled ammonium carbonate, the calcium nitrate having been obtained from marble and nitric acid, and recrystallised ten times. The second specimen was obtained in a similar manner from a pure specimen of precipitated calcium carbonate, the nitrate being recrystallised four times. Calcium chloride was prepared from each of these specimens of calcium carbonate, and also by concentration of the mother liquors resulting from the recrystallisations; this third specimen of calcium chloride was recrystallised four times.

The calcium chloride used in each determination was fused in a current of hydrogen chloride, and cooled in an atmosphere of nitrogen and, finally, of air. It was then analysed by the gravimetric titration method (Abstr., 1910, ii, 292), the chlorine being precipitated by silver nitrate prepared from three different specimens of pure silver. Allowance had to be made for any acidity or alkalinity of the calcium chloride. The average of seven determinations gave the ratio $CaCl_2 : Ag = 0·514405$, corresponding with $40·074 \pm 0·002$, as the atomic weight of calcium [$Ag = 107·88$ and $Cl = 35·457$]. This result is considered to be more accurate than those obtained by analysis of calcium bromide (*loc. cit.*). As a mean of all results, the authors consider $Ca = 40·075$ as the most accurate number. T. S. P.

The Chemical Action of Sea-Water on Portland Cement. LUCIEN POIRSON (*Zentr. hydraul. Zemente*, 1910, **1**, 151—159).—Experiments in which powdered Portland cement was shaken with solutions of the salts contained in sea-water show that the only stable compound formed is calcium sulpho-aluminate, $3CaO,Al_2O_3,3CaSO_4$. Solutions of chlorides react with cement, and form insoluble compounds, such as $2(3CaO,Al_2O_3),CaCl_2$, but these compounds are rapidly decomposed by solution of sulphates, yielding the sulpho-aluminate. Calcium ferrite forms an insoluble compound, $3CaO,Fe_2O_3,CaSO_4$. C. H. D.

The Ternary Alloys of Lead, Tin, and Antimony. RICHARD LOEBE (*Metallurgie*, 1911, **8**, 7—10, 33—49).—The thermal analysis of the tin-antimony alloys confirms the results of Williams (Abstr., 1907, ii, 783) as to the existence of three series of solid solutions, the discontinuities in the freezing-point curve being at 422° and 244° respectively. Thus, two components of the ternary system form three solid solutions with one another, whilst the third component does not form solid solutions with either. The limited miscibility of solid lead and tin may be neglected under the conditions of the investigation.

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* and *J. Amer. Chem. Soc.*, 1911, **33**, 28—35.

The freezing-point surface of the space-model is made up of four surfaces, of which three represent the primary crystallisation of the solid solutions of tin and antimony, and the fourth that of lead. There is no ternary eutectic, the lowest point of the surface being the lead-tin eutectic point at 183°. There are two horizontal planes of invariant equilibrium, at 245° and 191°, limiting the regions of stability of the saturated solid solutions. The process of diffusion in the solid alloys is so slow that equilibrium is not readily reached, and small discrepancies are observed between the thermal and microscopical results. The great differences of density between the phases formed also lead to much segregation during freezing. The lead in these alloys only plays the part of a solvent, and does not otherwise affect the relations of tin and antimony. C. H. D.

A New Property of Copper and the Rapid Combustion of Gases without Flame, or Convergent Combustion. JEAN MEUNIER (*Compt. rend.*, 1911, **152**, 194—196. Compare Abstr., 1908, ii, 11, 276, 376, 463; 1909, ii, 311).—Copper is able to bring about the flameless combustion of mixtures of coal gas and air at its surface in the same way as the metals mentioned in previous communications. The phenomenon may be observed by passing a copper wire into the interior of the luminous flame from a Bunsen burner in such a way that the surface becomes bright by reduction; on allowing air to enter, and pushing the metal into the cool portion of the mixed gases, the wire glows and the flame above becomes green, probably through the formation of a hydride of copper. This property appears to be attributable to the crystalline condition of the metal; electrolytic copper shows it particularly well. W. O. W.

Colloidal Mercury. CONRAD AMBERGER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 88—93).—Colloidal preparations containing about 50% of mercury can be obtained by the reduction of mercurous nitrate in presence of protalbic and lysalbic acids as protective agents. Five grams of sodium protalbate are dissolved in 250 c.c. of water, and sodium hydroxide is added to this solution in quantity somewhat greater than that corresponding with 7 grams of mercurous nitrate. This is also dissolved in 250 c.c. of water acidified with a few drops of nitric acid, and the mercurous salt solution is added in successive small portions to the protalbate solution. On addition of excess of hydrazine hydrate to the reddish-brown solution, the mercurous salt is reduced. Acetic acid is then added, and the dark brown, flaky precipitate, after washing, is dried in a vacuum at the ordinary temperature. The substance thus obtained is an adsorption compound of solid colloidal mercury and protalbic acid. If the flaky precipitate is dissolved in the minimum amount of sodium hydroxide solution before evaporation, a similar absorption compound of colloidal mercury and sodium protalbate is obtained.

Experiments are also described which show that colloidal mercury preparations are obtained by the reduction of mercurous nitrate by means of sodium hyposulphite in presence of sodium protalbate or lysalbate as protective colloid. All these preparations appear to be quite stable, but coagulation takes place when they are dissolved in water. The stability of solutions of the preparations obtained by the hyposulphite reduction is, however, relatively much greater than that of the preparations which result from the reduction with hydrazine. This is attributed to the presence of colloidal mercuric sulphide, which acts as a second protective colloid. H. M. D.

Formulæ of Aluminium Salts. S. C. J. Olivier (*Chem. Weekblad*, 1911, 8, 56—59).—Polemical. A reply to Coops (this vol., ii, 116). A. J. W.

The Influence of Manganese on the Properties of Mild Steel. Georg Lang (*Metallurgie*, 1911, 8, 15—21, 49—53).—The addition of aluminothermic manganese to iron prepared in an electric furnace, and containing 0·1% of carbon, yields alloys the tenacity and hardness of which increases up to 3% of manganese. The ductility is not diminished until the manganese exceeds 1·5%. The electrical resistance is increased, and is independent of the thermal treatment. The magnetic coercive force and hysteresis of iron are increased, and the permeability diminished by the addition of manganese. C. H. D.

Action of Water Containing Carbon Dioxide on Iron. W. Th. Clous (*Chem. Weekblad*, 1911, 8, 10).—When carbon dioxide is passed through a wash-bottle containing water and powdered iron into a eudiometer filled with a concentrated solution of potassium hydroxide until the hydroxide solution is nearly saturated with the gas, a small amount of gas insoluble in the potassium hydroxide is obtained. In the author's experiment, 2·5 c.c. of this gas were collected, and it was proved to be hydrogen by introducing a small amount of oxygen, and exploding the mixture by an electric spark. A. J. W.

Preparation of the Hydrosol of Tungstic Acid. Arthur Müller (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 93—95).—Five grams of tungstic tetrachloride are dissolved in about 50 c.c. of a mixture containing equal volumes of ethyl alcohol and ethyl ether, and the filtered solution is then diluted to 250 c.c. with ethyl alcohol. If this solution is mixed with an equal volume of water, a colloidal solution of tungstic acid is obtained, which can be kept for some days without any appreciable opalescence being observed. With larger quantities of water, coagulation takes place much more quickly. On addition of small quantities of neutral salts or of hydroxides, coagulation occurs immediately; strong acids produce a similar effect after some minutes, but weak organic acids appear to exert no influence on the stability of the colloidal solutions. Rise of temperature is also without influence, but coagulation takes place if the volume is reduced to about a fourth of the original by evaporation.

When an electric current is passed through the colloidal solution, a deep blue precipitate is formed at the cathode. This is attributed to reduction of the positively charged colloidal particles by the discharged hydrogen. The behaviour of the colloidal solutions towards electrolytes is consistent with the supposition that the tungstic acid is a positive colloid, and the spontaneous coagulation of the solutions obtained by the author's method is probably due to the presence of chlorine ions in the solutions. H. M. D.

Metallic Uranium. WILLEM P. JORISSEN and A. P. H. TRIVELLI (*Chem. Weekblad*, 1911, **8**, 59—62. Compare Kohlschütter, Abstr., 1901, ii, 598; Jorissen and Ringer, Abstr., 1907, 422, 731; Olie, and also Jorissen, Abstr., 1909, ii, 10; Olie, Abstr., 1909, ii, 783).—When metallic uranium is exposed to cathode rays, nitrogen is evolved. To ascertain whether this nitrogen is derived from Kohlschütter's uranium nitride, U_3N_4, a sample of uranium was heated in a vacuum with lead chromate. The results indicated the presence in the metal of 0·94% of nitrogen and 1·25% of carbon. The formula U_3N_4 requires 12·9% of uranium. A. J. W.

A New Uranium Colloid. ALEXANDER SAMSONOW (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 96—97).—When a solution of uranyl chloride is electrolysed, a black precipitate is formed by reduction at the cathode. The precipitate is soluble in water, giving a dark-coloured solution which shows the presence of ultra-microscopic particles. A very dilute solution has a yellow tinge, and the absorption spectrum indicates that neither a uranous nor a uranyl salt is present. In an electric field the solution becomes decolorised at the anode, and precipitation takes place at the cathode. On addition of electrolytes, coagulation phenomena characteristic of the positive colloids are observed.

By titration of the solution with potassium permanganate, before and after reduction with zinc, it has been found that the colloidal suspension consists of uranous oxide. The same substance is also obtained in the reduction of uranyl chloride by zinc or copper in dilute acid solution. Uranous chloride acts as a protective, and increases the stability of the colloidal solution. H. M. D.

Thorium Arsenates. GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 642—645. Compare Barbieri and Calzolari, Abstr., 1910, ii, 779).—The author has succeeded in preparing two thorium arsenates similar in constitution and appearance to the two cerium arsenates previously described.

Thorium hydrogen arsenate, $Th(HAsO_4)_2,6H_2O$, is precipitated in crystalline form when to a boiling solution of thorium nitrate (containing 2% of ThO_2) a 40% aqueous solution of arsenic acid (4 mols.) is added. If less arsenic acid is employed, an amorphous precipitate of variable composition is obtained, whilst if the reaction with the quantities mentioned is carried out with dilute solutions in the cold, no precipitate may be formed, but, instead, a gelatinous mass, which eventually becomes crystalline and then has the above composition. *Thorium dihydrogen arsenate*, $Th(H_2AsO_4)_4,4H_2O$, is precipitated in colourless crystals when a solution of thorium nitrate (containing 5% of ThO_2) is treated with a 50% solution of arsenic acid (8 mols.). Water converts it into the monohydrogen salt. R. V. S.

Brown Gold. Maurice Hanriot (*Compt. rend.*, 1911, **152**, 138—141. Compare this vol., ii, 118).—A further study of the influence of temperature, dimensions, mode of heating, impurities, and composition of the original alloy on the contraction undergone when brown gold, the product of the action of nitric acid on gold-silver alloys, is heated. Contraction is not complete below 950°, or until after about six hours' heating. W. O. W.

Mineralogical Chemistry.

Pyrites and Marcasite. VIKTOR PÖSCHL (*Zeitsch. Kryst. Min.*, 1911, **48**, 572—618).—Descriptions are given of the surface characters of crystals of pyrites and marcasite, as seen under a metallographic microscope.

The characters of the faces and the form and orientation of the artificially-produced etched figures suggest that the symmetry of pyrites is tetrahedral-pentagonal-dodecahedral rather than pentagonal-dodecahedral.

Numerous determinations were made of the hardness of natural and of artificially-cut faces. The degree of hardness is assumed to be proportional to the volume of material removed (that is, proportional to the square of the width of the scratches produced) by a weighted diamond point moved across the surface. The hardness of pyrites, relative to that of topaz = 1000, is 199·1 under a load of 50 grams and 182·2 under a load of 20 grams; of marcasite, 134·1 and 140·2 under the same loads respectively. On one and the same crystal no differences in hardness were detected on different faces, or along different directions on the same face. Different crystals, however, differ slightly in hardness, and it is noticed that those which are softer are at the same time less dense. The specifically lightest and heaviest crystals of each lot experimented on were analysed, with the following results, but no essential differences are shown in chemical composition:

	Fe.	Ni.	Co.	Cu.	S.	As.	Total.	Sp. gr.
I.	46·02	0·04	—	0·59	51·70	0·93	99·28	5·098*
II.	46·19	0·07	—	0·63	51·55	0·78	99·22	5·153*
III.	46·32	trace	0·06	0·09	51·78	1·52	99·77	5·078
IV.	46·18	trace	0·09	0·04	51·90	1·73	99·94	5·113
V.	46·07	0·03	0·16	0·26	51·83	1·28	99·63	5·068†
VI.	45·98	0·02	0·18	0·29	51·95	1·19	99·61	5·101†

* Trace Ag. † Trace Mn.

I and II, pentagonal-dodecahedral crystals {210} of pyrites from

Elba; III and IV, ditto, from Hüttenberg, Carinthia; V and VI, ditto, from Seegraben, near Leoben, Styria. L. J. S.

Composition of Jamesonite and Warrenite. WALDEMAR T. SCHALLER (*Zeitsch. Kryst. Min.*, 1911, 48, 562—565).—The jamesonite formula proposed by Spencer (Abstr., 1907, ii, 700) is replaced by the simpler formula, $4PbS,FeS,3Sb_2S_3$, proposed by Loczka (Abstr., 1909, ii, 153), the calculated percentages corresponding with these formulæ being:

	S.	Sb.	Pb.	Fe.
$7(Pb_{\frac{4}{5}},Fe_{\frac{1}{5}})S,4Sb_2S_3$	21·70	34·23	41·29	2·78
$4PbS,FeS,3Sb_2S_3$	21 86	35·10	40·32	2·72

Warrenite (Eakins, 1888) is shown to be a mixture of the brittle "feather-ore" jamesonite and the flexible "feather-ore" plumosite (PbS,Sb_2S_3). L. J. S.

Optical Characters of the α- and β-Modifications of Quartz and Leucite. FRITZ RINNE and R. KOLB (*Jahrb. Min.*, 1910, ii, 138—158).—The refractive indices are given for lines of several wave-lengths at various temperatures ranging from −140° to +765°. These were determined with prisms enclosed in a specially constructed electric oven or cooling chamber attached to the goniometer. The curves showing the results obtained with quartz exhibit an abrupt break at 570°, corresponding with the change from α- to β-quartz. The values for α-quartz at 23° are $\omega = 1·5442$, $\epsilon = 1·5533$; for β-quartz at 580°, $\omega = 1·5328$, $\epsilon = 1·5404$ (line D_2). Leucite becomes optically isotropic at 714°, and the plotted curves of the refractive indices deviate in direction near this point, but show no sudden break; the change from α- to β-leucite therefore takes place over a considerable interval of temperature. L. J. S.

Artificial Production of Nesquehonite. GIUSEPPE CESÀRO (*Bull. Acad. Roy. Belg.*, 1910, 844—845. Compare *ibid.*, 1910, 749; Abstr., 1910, ii, 49, 613).—A solution of sodium hydrogen carbonate and magnesium chloride was exposed outside to the low temperature at the end of November, and the next day there were formed small, transparent crystals of lansfordite ($MgCO_3,5H_2O$), together with crystalline globules composed of fine needles having the optical characters of nesquehonite ($MgCO_3,3H_2O$). The simultaneous formation of these two substances thus depends on the low temperature and not on pressure. L. J. S.

Thaumasite from Beaver County, Utah. B. S. BUTLER and WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1911, [iv], 31, 131—134).—This mineral has hitherto been found only in Sweden and at Paterson in New Jersey. It has now been found as a filling in small fissures in metamorphosed dolomitic limestone in the Old Hickory copper and magnetite mine in the Rocky Range of Beaver Co., Utah. It is a pure white mineral with a fibrous structure and silky lustre, and its lightness (sp. gr. 1·84) is a noticeable feature. Between crossed nicols the minute, slender prisms give straight extinction; the refractive indices are $\omega > 1\cdot500$, $\epsilon > 1\cdot464$. Analysis agrees with the usual formula $3CaO,SiO_2,SO_3,CO_2,15H_2O$.

SiO_2.	SO_3.	CO_2.	CaO.	H_2O.	$(Al,Fe)_2O_3$.	MgO.	Alkalis, P_2O_5.	Total.
10·14	12·60	6·98	26·81	42·97	0·20	0·23	trace.	99·93

L. J. S.

Are Allophane, Halloysite, and Montmorillonite Simple Minerals or Mixtures of Colloidal Alumina and Silica?

STANISLAUS J. THUGUTT (*Centr. Min.*, 1911, 97—103).—A review of the literature on this question is given (compare Stremme, Abstr., 1908, ii, 1041). The various clay minerals are capable of taking up organic colouring matters (methylene-blue, rhodamine, methyl-orange), but the varying nature of the colour reactions suggests that these minerals possess individuality, and are not merely mixtures of colloidal hydrated alumina and silica. When moistened with cobalt nitrate solution and ignited, some of these minerals do not give a blue colour, whilst others become blue only in part. This indicates that the alumina and silica must be chemically combined. The patchy distribution of the colours sometimes obtained indicates that the materials are not always homogeneous. L. J. S.

Deposit of Alunite in the Liparite of Torniella in the Province of Grosseto.

UGO PANICHI (*Atti R. Accad. Lincei*, 1910, [v], **19**, ii, 656—664).—Analysis of a typical liparite of the district gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	Loss on heating	Total.
72·29	14·40	1·69	0·31	1·34	0·48	4·18	2·67	2·39	99·75

A white deposit which occurs in abundance at Marmaio and Pianale is not kaolin, as has been hitherto believed, but consists of alunite containing a little more silica and iron than the alunite of Tolfa. The mineral loses sulphur trioxide when heated, and this loss of weight has been assumed to be due to water by previous investigators. Analysis of a sample of the mineral gave

SiO_2.	Al_2O_3.	Fe_2O_3.	SO_3.	H_2O.	K_2O.	Na_2O.	Total
1·99	38·04	0·53	33·26	13·74	9·77	2·94	100·27

The rock at the base of the deposit at Marmaio is impregnated with the substance, which when separated by levigation gave similar analytical figures. It is noted that the rocks of the neighbourhood of the deposit of alunite have suffered more change into kaolin than other similar rocks of the same district further removed from it.

R. V. S.

Physiological Chemistry.

The Respiratory Exchange as Affected by Body Position. L. E. Emmes and J. A. Riche (*Amer. J. Physiol.*, 1911, **27**, 406—413).—When the person investigated is sitting quietly in a chair the muscular activity involved causes an increase in metabolism of 8% as compared with that in the same person when lying down.

W. D. H.

The Respiratory Exchange of Mice Bearing Transplanted Carcinoma. R. A. CHISOLM (*J. Path. Bact*, 1910, **15**, 192—206).—No noticeable difference was found in mice with carcinoma and normal mice so far as respiratory exchange is concerned.

W. D. H.

Influence of Preceding Diet on the Respiratory Quotient after Active Digestion has Ceased. FRANCIS G. BENEDICT, L. E. EMMES and J. A. RICHE (*Amer. J. Physiol.*, 1911, **27**, 383—405).—The respiratory exchange was examined twelve hours after a meal in the human subject. The most important fact which came out of the investigation is the rise in the respiratory quotient if the preceding meal is rich in carbohydrates. W. D. H.

The Regulation of Breathing by the Blood. HANS WINTERSTEIN (*Pflüger's Archiv*, 1911, **138**, 167—184).—The method adopted was that of artificial perfusion with Ringer's solution of new-born mammals. If the tension of carbon dioxide in the perfusing fluid is low, apnœa is the result; but the addition of more of the gas excites rhythmical breathing. Lack of oxygen during the apnœic period does not interrupt the apnœa, but leads without excitation to death. The addition of acids to the fluid excites respiratory movements, and within certain limits the excitation of the respiratory centres is parallel to the concentration of hydrogen ions. W. D. H.

The Influence of Oxygen Breathing. OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1911, **70**, 413—432).—The microscopic appearances in red corpuscles and echinoderm eggs produced by oxygen, and by agents which inhibit oxidation, are described and figured. The part played by the cell-membrane and the effect on it of the reagents form the main points investigated. W. D. H.

The Effect of Altitude on the Dissociation Curve of Blood. JOSEPH BARCROFT (*J. Physiol.*, 1911, **42**, 44—63).—The experiments recorded were made on certain members of the recent antituberculosis party which visited Teneriffe. Without going into details of technique and argument, the main practical outcome of the investigation is that some acid substance appears in the blood in increasing quantities as the altitude increases. This change compensates the change in alveolar carbon dioxide tension to such an extent that the actual dissociation curve under the conditions locally established did not alter. W. D. H.

Solubility of Gases in Ox-blood and Ox-serum. ALEXANDER FINDLAY and H. JERMAIN M. CREIGHTON (*Bio-Chem. J.*, 1911, **5**, 294—305).—The solubility of oxygen, carbon monoxide, and carbon dioxide in blood and of carbon dioxide in serum is greater than in water; that of nitrogen and nitrous oxide in blood and serum and of oxygen and carbon monoxide in serum is less than in water. When the solubility is increased, the solubility curves fall with increasing pressure; when it is lessened, the curves rise with increasing pressure. The increased absorption of oxygen, carbon monoxide, and carbon dioxide is ascribed mainly to chemical combination. In cases of diminished solubility, the rise in the curve is ascribed to adsorption.

W. D. H.

Trimethylamine as a Normal Constituent of Human Blood, Urine, and Cerebro-spinal Fluid. CHARLES DORÉE and F. GOLLA (*Bio-Chem. J.*, 1911, **5**, 306—324).—Trimethylamine is a normal constituent of blood and cerebro-spinal fluid. The evidence as to urine is not so clear. Filippi's method of estimation was employed with some modifications which considerably shorten it, and good results were obtained. Choline is normally absent in all these fluids. In most of the methods at present in use for the detection of choline, trimethylamine would be driven off. The acidity of laboratory alcohol is another possibly source of error. Trimethylamine gives most of the reactions (including the periodide reaction) considered to be characteristic of choline. The present observations are confined to normal fluids.

W. D. H.

Action of Arsenic on the Red Corpuscles. MORIZO ONAKA (*Zeitsch. physiol. Chem.*, 1911, **70**, 433—440).—Arsenious acid was found next to hydrocyanic acid to be most powerful in reducing respiratory changes in red corpuscles. Larger doses destroy the cell-membrane. This substance, in view of the lipoid constitution of this membrane, has very small partition-coefficients between oil and water.

W. D. H.

The Absorption of Hæmolytic and Agglutinating Substances. J. DUNIN-BORKOWSKI (*Bull. Acad. Sci. Cracow*, 1910, *B*, 608—617).—The paper consists of a brief account of the results of experiments published in detail in Polish in the *Rozprawy Wydz. Mat. Przyr., Acad. Sci. Cracow* (1910 B).

In the agglutination of red-blood corpuscles by silver nitrate, mercuric nitrate, and ferrous chloride, the relation was determined between the concentration of the salt and the amount taken up by the corpuscles. From the value of the constant n in the equation $A = c^{1/n}$, where A is the amount absorbed, and c the concentration of the salt, it was found that agglutination was accompanied by an adsorption of the salt in the cases of both silver and mercuric nitrates. With ferrous chloride, however, none of the salt was taken up by the corpuscles. Agglutination may thus take place without adsorption, and the theory of Arrhenius, that only those substances which are absorbed have any action on the red corpuscles, is not in accordance with these results.

The coefficients of partition of the hæmolytic agent between the red corpuscles and the solution were determined in hæmolysis brought about by means of acetic acid, boric acid, and potassium cyanide. The results were found to be in contradiction to the hypothesis of Arrhenius that in hæmolysis the red corpuscles absorb a quantity of the hæmolysin sufficient to bring about their complete dissolution.

W. J. Y.

The Law Regulating Hæmolysis of Erythrocytes in Hyposmotic Saline Solution or Distilled Water. U. N. BRAHMACHARI (*Bio-Chem. J.*, 1911, 5, 291—293).—The amount of hæmoglobin dissolved in a given volume of hyposmotic sodium chloride solution or water is proportional to the amount of hæmoglobin in the corpuscles presented for solution in the form of a suspension. In the animals examined, the ratio between the above two factors is smallest for the frog, and greatest for the rabbit and sheep. It is fairly constant in healthy persons, but varies widely in disease. The same law regulates the solution of hæmoglobin within red corpuscles which regulates the solution of globulin in neutral salt solutions. W. D. H.

The Platelets of Human Blood. M. AYNAUD (*Ann. Inst. Pasteur*, 1911, 24, 56—78).—The blood was collected in such a manner as to avoid contact with the tissues, and all the vessels employed were lined with paraffin to preserve it from the action of the glass. Under these conditions blood may be kept for some hours (one to five) without coagulating. The blood was allowed to sediment, and the colourless plasma containing the platelets drawn off. In fresh plasma the platelets occur as clear, round, plain discs having a rapid oscillatory movement which causes them to appear as spindle-shaped bodies. On keeping they alter in shape, become granular in structure, and finally disappear. Anti-coagulants vary in their action on the platelets; thus sodium fluoride produces granular changes in them, whilst citrates, oxalates, and metaphosphates preserve the platelets and retard their agglutination. A number of substances, such as quinine and cocaine, produce changes in the form of the platelets when added to the plasma in the presence of oxalates and citrates. Human blood-platelets show very little tendency to agglutinate on the addition of peptone, gelatin, metallic colloids, or other substances which readily bring about agglutination in the platelets of dogs' blood.

Reactions with staining agents show them to have a complex structure and to contain at least two different substances, whilst no differences could be detected by these means between the platelets of human blood and those of other mammals.

No numerical relation could be established between the platelets and the red corpuscles and leucocytes, and they are considered as quite independent of the other elements of blood. W. J. Y.

Effects of Copious Water Drinking with Meals on Intestinal Putrefaction. W. M. HATTREM and PHILIP B. HAWK (*Proc. Amer. physiol. Soc.*, 1910, xxv; *Amer. J. Physiol.*, 27).—The drinking of copious (1000 c.c.) or moderate doses (500 c.c.) of water with meals reduces the output of urinary indican, but increases that of ethereal sulphates. W. D. H.

Effects of Copious Water Drinking with Meals on the Pancreatic Function. PHILIP B. HAWK (*Proc. Amer. physiol. Soc.*, 1910, xxvi; *Amer. J. Physiol.*, **27**).—The effect is that the pancreatic activity is increased, as judged by the amount of amylase in the fæces. W. D. H.

Effects of Copious Water Drinking with Meals on Gastric Secretion. F. WILLS and PHILIP B. HAWK (*Proc. Amer. physiol. Soc.*, 1910, xxxii; *Amer. J. Physiol.*, **27**).—The urinary ammonia is increased, and this is considered to be an index of a rise in the secretion of gastric juice. The acid concentration of the stomach contents is thus maintained, in spite of the large amount of water taken. W. D. H.

Comparative Study of Four Digestive Diastases from Certain Species of Coleoptera. L. BOUNOURE (*Compt. rend.*, 1911, **152**, 228—231).—The digestive enzymes of *Coleoptera* include a lipase, a proteolytic diastase, an amylase, and an invertase. Experiments have been conducted on a number of different species with the object of determining the relative activity of the different ferments in each, and their variation with the natural diet of the insects. The results are tabulated.

It is found that the more carnivorous the species, the greater the proteolytic, and the smaller the lipolytic, activity. Amylolytic and sucroclastic activity is at a maximum with those insects which favour a mixed diet (*Hydrophilus piceus*), and at a minimum with the carnivorous species, such as *Dysticus marginalis*. Proteolytic enzymes are practically absent from the entirely vegetarian species (*Polyphylla fullo*). W. O. W.

The Metabolism of Dogs with Functionally-resected Small Intestine. FRANK P. UNDERHILL (*Amer. J. Physiol.*, 1911, **27**, 366—382).—When 39% of the small intestine is short-circuited, foods are utilised for many months in a normal way. When 66% is similarly resected, fat utilisation is decreased, and there is a small loss of body-nitrogen and of body weight, which is specially noticeable some time after the operation. When 75% is resected, food utilisation is seriously impaired, and this is particularly the case for fat. Indican elimination is not altered, as in the normal dog, by replacing meat in the diet by gelatin. Ability to utilise carbohydrate is increased; this may be of importance in cases of intestinal resection in man. W. D. H.

The Influence of Meat-extractives on the Absorption of Nutritive Material. The Physiological Value of Meat Extract. WILHELM VÖLTZ and AUGUST BAUDREXEL (*Pflüger's Archiv*, 1911, **138**, 275—291).—The addition of meat extract to a mixed diet has no effect on the absorption of nitrogenous or non-nitrogenous foods. The nitrogen of the extractives can, under very favourable conditions, lead to a retention of nitrogen, or a lessening of loss of nitrogen, which accounts for at least 11% of the extractive nitrogen. The physiological utilisation of the extractives averages about two-thirds of their potential energy. W. D. H.

The Utilisation of Yeast in the Human Body. WILHELM VÖLTZ and AUGUST BAUDREXEL (*Biochem. Zeitsch.*, 1910, **30**, 457—472). —Dried yeast, from which the bitter principles had been extracted, can be tolerated in relatively large quantities by man (100 grams within one to two hours). The food-value was determined by feeding experiments on man in the usual way, and it was found that 86% of the protein was resorbed and 88% of the caloric value was utilised. The physiological food-value, calculated from nitrogenous equilibrium experiments, was 74·8% of its total energy content. S. B. S.

Intravenous Injection of Pineal Extracts. J. A. E. EYSTER and H. E. JORDAN (*Proc. Amer. physiol. Soc.*, 1910, xxiii—xxiv; *Amer. J. Physiol.*, **27**).—Aqueous extracts of the sheep's pineal cause a fall of arterial blood pressure in the dog, which is stated to be greater than that obtained from other parts of the brain. This is associated with dilatation of the splanchnic vessels. W. D. H.

The Dichromate Hæmatoxylin Method of Staining Tissues. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1910, **15**, 179—181. Compare this vol., i, 44).—The substance in the nervous system which is stained in the Weigert method is not only cholesterol, but also the cerebroside separated by the authors. The relative insolubility of this substance in fat solvents accounts for the staining with hæmatoxylin observed in specimens treated with alcohol and ether. It is only present in traces in the brain of the new-born infant; hence the greater difficulty in staining such tissue. The cerebroside has a fluid crystalline phase extending over a wide range of temperature, and on exposure to water it gives "myelin forms." W. D. H.

The Alleged Presence of an Alcoholic Enzyme in Animal Tissues and Organs. ARTHUR HARDEN and HUGH MACLEAN (*J. Physiol.*, 1911, **42**, 64—92).—The experiments recorded establish a strong presumption that alcoholic fermentation cannot be produced by animal tissues or juices, or powders prepared from them. With the onset of putrefaction, evolution of gases (carbon dioxide and hydrogen) occurs, but not otherwise. W. D. H.

A Method of Removing Glycogen from the Human Subject. GRAHAM LUSK (*Amer. J. Physiol.*, 1911, **27**, 427—437).—Exposure to cold (baths in ice water) lowers the respiratory quotient in various men to 0·75 to 0·67; this corresponds with Benedict's figure after a prolonged fast, and isbelieved to indicate the disappearance of glycogen. W. D. H.

The Position Occupied by the Production of Heat in the Chain of Processes Constituting a Muscular Contraction. ARCHIBALD V. HILL (*J. Physiol.*, 1911, **42**, 1—43).—Muscle is not a heat engine, for the heat may not appear until the tension has returned to normal. On excitation, some substance (or substances) is liberated which affects the colloidal tissues of the muscle and sets up a tension proportional to its concentration. The substance is then destroyed or replaced in its original position (the presence of oxygen being favourable for both), and the heat then evolved is proportional to the amount of the substance (for instance, lactic acid) in question.

W. D. H.

Purine Metabolism. V. The Behaviour of the Purine Bases in Muscle during Work. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1911, 30, 473—480).—The purine-base content in the striated muscles of the frog and toad is smaller than in mammals and fish, and diminishes considerably after work (up to 17%); this diminution is derived chiefly from the combined bases, the free bases remaining unchanged in quantity or even increasing. No uric acid was found in the muscles of the frog and toad either in rest or after work. S. B. S.

The Distribution of the Nitrogen of the Extractive Substances from Mammalian Muscle. OTTO VON FÜRTH and CARL SCHWARZ (*Biochem. Zeitsch.*, 1911, 30, 413—432).—The nitrogen was estimated in the following fractions of the extractives: total bases (precipitated by phosphotungstic acid), colloidal substances of albumose character (precipitated by zinc sulphate by Böhmer's method), creatine and creatinine (determined by Folin's process), ammonia (determined by distillation with magnesium oxide), purine substances (determined by Krüger and Schmidt's method), carnosine (determined by Gulewitsch and Krimberg's method), polypeptides and amino-acids (determined by the Sörensen-Henriques method), and urea (determined by Braunstein's method). The materials employed were the muscles of the extremities and of the horse's heart. The chief constituents were found to be creatine and carnosine. No material difference could be detected in the extractives of resting and fatigued muscle in experiments carried out on the muscular tissue of dogs. The authors tabulate several series of results. S. B. S.

Occurrence of Betaine in Cephalopods. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1911, 70, 253—255. Compare Abstr., 1905, ii, 270).—Octopus muscle, in addition to the taurine previously recorded, contains betaine and two substances yielding sparingly soluble picrates, the one m. p. 215—220° (decomp. 225°), and the other decomposing still higher and giving an aurichloride, m. p. 137—148°, crystallising in slender needles (Au = 31·9%). E. F. A.

Isolation of an Hepatic Antithrombin. Description of Some of its Properties. MAURICE DOYON, ALBERT MOREL, and A. POLICARD (*Compt. rend.*, 1911, 152, 147—148).—The isolated liver of a dog is perfused with blood from the carotid vein of another dog which has previously received an injection of peptone. Antithrombin is present in the plasma after centrifugation, It is not destroyed or precipitated by heating the plasma at 100°. If the medium is acid, however, the antithrombin is precipitated at 100°, but can be redissolved in an alkaline solution. W. O. W.

Demonstration of the Exclusively Hepatic Origin of Antithrombin. Extraction of this Substance by a Solvent for Nuclear Substances. MAURICE DOYON, ALBERT MOREL, and A. POLICARD (*Compt. rend* 1911, 152, 282—283).—The antithrombin described in a previous communication (preceding abstract) can be obtained from the liver by perfusion with a slightly alkaline, physiological salt solution. The active substance contains nitrogen and phosphorus, and may be precipitated from the solution by the addition of acetic acid. It gives a slight biuret reaction.

W. O. W.

4-β-Aminoethylglyoxaline, a Depressor Constituent of Intestinal Mucosa. George Barger and Henry H. Dale (*J. Physiol.*, 1911, **41**, 499—503).—Popielski's vaso-dilatin, to which he attributes the activities of commercial peptone and various tissue extracts, contains 4-β-aminoethylglyoxaline. It was in the present research identified chemically and physiologically in intestinal extracts, and is no doubt the substance which in Bayliss and Starling's preparations of secretin lowers blood pressure. The effect of this base in stimulating the pancreas to secrete is very feeble. It also does not affect the coagulability of the blood ; this action of vaso-dilatin must be due to some other substance in it. W. D. H.

Source of Immune Substances in Lymph. The Part Played by the Spleen in the Formation of Immune Substances. Arno B. Luckhardt and Frank C. Becht (*Proc. Amer. physiol. Soc.*, 1910, xi—xii, xvi—xvii; *Amer. J. Physiol.*, **27**).—Hæmolysins, agglutinins, and opsonins pass at about the same rate from the blood into the lymphs, and make their appearance in the thoracic earlier than in the cervical lymph. They are also more concentrated in the former situation. They hardly pass at all in the cerebro-spinal fluid, or aqueous humor.

The formation of such substances is slow and in lessened quantity when the spleen is removed. The experiments were made on dogs.

W. D. H.

Experimental Hyperthyroidism. Anton J. Carlson, J. F. Rooks, and J. F. McKie (*Proc. Amer. physiol. Soc.*, 1910, xiii—xiv; *Amer. J. physiol.*, **27**).—Different animals exhibit great variations in their resistance to thyroid feeding, but the most constant symptoms (emaciation and diarrhœa) may be absent even in fatal cases. The nervous and cardiac phases of the symptom-complex in birds and lower mammals differ from those in man. Feeding on other organs shows that the symptoms are due to thyroid feeding. W. D. H.

Effects of Extracts of Different Parts of the Pituitary Body. J. L. Miller, D. D. Lewis, and S. A. Matthews (*Proc. Amer. physiol. Soc.*, 1910, xvii—xviii; *Amer. J. Physiol.*, **27**).—The experiments show that the pars intermedia is the seat of origin of the pressor substance. The contents of a cyst of this region produced a distinct pressor effect. The substance which slows the heart is confined to the pars nervosa. Extracts of the stalk of the ox hypophysis never gave a pressor effect. W. D. H.

The Neutralisation of Spermotoxins and Alkaloids by Extract of the Testis and Epididymis. S. Metalnikoff (*Pflüger's Archiv*, 1911, **138**, 14—18).—In animals in whose blood strong spermotoxins are contained, the spermatozoa in the epididymis are normal, for the testis and epididymis contain a substance which neutralises spermotoxins or renders them harmless. This material also neutralises certain alkaloids, such as nicotine, which act harmfully on spermatozoa. Curare by itself has but little action on spermatozoa, but mixed with epididymis extract it kills them. W. D. H.

The Amount of Alcohol Excreted by the Animal Organism Under Various Conditions. WILHELM VOLTZ and AUGUST BAUDREXEL (*Pflüger's Archiv*, 1911, **138**, 85—133).—Analytical details are given of the quantity of alcohol excreted in the urine, expired air, etc., when it is given under varying conditions of quantity, volume of diluent, habituation, and so forth. W. D. H.

Allantoin-Purine Excretion of the Monkey. ANDREW HUNTER and MAURICE H. GIVENS (*Proc. Amer. physiol. Soc.*, 1910, xv—xvi; *Amer. J. Physiol.*, **27**).—The analyses show the great relative importance of allantoin as an end-product in purine metabolism in monkeys. From 500 c.c. of urine from two monkeys, 172 mg. of allantoin, no uric acid, and 4·5 mg. of purine bases were obtained. W. D. H.

The Origin of Uric Acid in Man. FRANZ SMETÁNKA (*Pflüger's Archiv*, 1911, **138**, 217—274).—Every protein meal, including those which are purine-free, produces a rise of uric acid excretion which, three hours after the meal, may rise to an 80% increase of the previous value. If the meal is taken late in the day, the rise may extend through the night to the following morning. The increase is attributed to metabolic changes accompanying the activity of the cells of the digestive glands. If polysaccharides are given, the smaller work of the digestive glands is accompanied with a smaller rise in uric acid excretion. After taking honey, there is a large rise, which is explained by the intense activity of the liver cells in forming glycogen. The total excretion of nitrogen is but little altered by carbohydrate food.
W. D. H.

Action of Urinary Antiseptics. ANSON JORDAN (*Bio-Chem. J.*, 1911, **5**, 274—290).—Using a defined arbitrary standard, the average acidity of normal urine is about 4. With large doses of dihydrogen sodium phosphate this can be raised to 9, and the urine can easily be made alkaline with potassium citrate. Putrefaction will readily occur, and *Staphylococcus* and *Bacillus coli* grow easily, in urines of all degrees of acidity and alkalinity which can be produced in the body; acidity, however, exciting a restraining influence.

Urotropine acts as a urinary antiseptic by the formation of formaldehyde; in alkaline urine its action is nil, because no formaldehyde is then formed. In urine of a little over normal acidity, the antiseptic power is sufficient to prevent the growth of all micro-organisms.

Sandal wood oil is quite feeble against *B. coli* and putrefactive organisms; it has a specific antiseptic action against *Staphylococcus*. The power of salicylic acid is not great, but against *B. coli* and putrefactive organisms it is more efficient than sandal wood oil. Neither agent can, however, be compared with urotropine for efficiency. W. D. H.

Chemical Investigation of Atheromatous Aortæ. A. Selig. **Composition of Deposits in Calcified Aortæ.** M. Ph. F. Ameseder. **Remarks on the Foregoing Investigations.** Richard von Zeynek (*Zeitsch. physiol. Chem.*, 1911, **70**, 451—457, 458—463, 464—465).—I. In atheroma the amount of elastin is lessened, the fat (light petroleum extract) is increased, and the calcium in the ash is increased, although the total ash may not be.

II. The second paper gives analytical details.

III. The third paper is explanatory and critical. W. D. H.

Experimental Glycosuria. VI. The Distribution of Glycogen over the Liver under Various Conditions. Post-mortem Glycogenolysis. John J. R. Macleod and R. G. Pearce (*Amer. J. Physiol*, 1911, **27**, 341—366. Compare Abstr., 1910, ii, 144).—The amount of glycogen in different lobes of the liver varies by about 5%. This is due to errors of analysis by Pflüger's method, and to an unequal amount of blood and connective tissue in different parts of the organ. Glycogenolysis is accelerated after death, and this varies in different lobes; it sets in within twenty minutes after death, and proceeds at a uniform speed for several hours. The rate is lessened by absence of blood, and by cutting up the liver. Nervous influences play no part in it. W. D. H.

Uric Acid Excretion in Gout and Rheumatoid Arthritis. William J. Mallory (*J. Path. Bact.*, 1910, **15**, 207—246).—In gout there is a slight fluctuation in the endogenous excretion, a low endogenous average, and a small percentage of exogenous purine nitrogen excretion excreted as uric acid. In cases associated with lead poisoning these characteristics are more marked. Many cases of gout, however, are atypical. In some cases of rheumatoid arthritis there is a somewhat similar disturbance of purine metabolism.

W. D. H.

The Wassermann Reaction in Rabbits Infected with the Trypanosomes of Nagana, and the Effect of Treatment with Arsenophenylglycine (Ehrlich). Carl H. Browning and Ivy McKenzie (*J. Path. Bact.*, 1910, **15**, 182—191).—A full account of experiments previously published (this vol., ii, 59). W. D. H.

The Influence of Quinine and Quinine Derivatives on Experimental Trypanosome Infection. Julius Morgenroth and L. Halberstaedter (*Sitzungsber K. Akad. Wiss. Berlin*, 1911, 30—37).—In continuation of previous investigations (Abstr., 1910, ii, 881), the authors now show that hydroquinine, which is not more toxic than quinine, has a greater trypanocidal action. The method of adding the base to cakes of food-stuff was employed as in former work, and a Nagana trypanosome was the source of infection. S. B. S.

Ingestion of Mineral Acids by the Dog. HENRI LABBÉ and L. VIOLLE (*Compt. rend.*, 1911, **152**, 279—281).—When dogs in a state of nitrogenous equilibrium are dosed with hydrochloric acid in quantity insufficient to affect their general health, an increased urinary excretion of volatile bases takes place, proportional to the amount of acid administered. The ratio between the acid and the bases is practically molecular. The same thing is observed when the diet is insufficiently nitrogenous. The experiments are held to support the view that the organism protects itself against acid intoxication by the increased formation of ammonia. W. O. W.

Migration of Solutions in Bodies Deprived of the Cardiac Circulation. SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1910, xxix—xxx ; *Amer. J. Physiol.*, **27**).—The injection of adrenaline and strychnine into the dorsal lymph sac of the frog produces in time effects on the pupil and spinal cord respectively, even although the circulation has been stopped by removal of the heart. The migration of these substances can therefore take place against gravity through the lymph spaces. W. D. H.

A Second Active Ergot Base. R. ENGELAND and FRIEDRICH KUTSCHER (*Chem Zentr.*, 1910, ii, 1394—1395 ; from *Zentr. Physiol.*, 1910, **24**, 479—480).—The authors have previously obtained an active base from ergot containing a glyoxaline radicle (Abstr., 1910, ii, 881). Another base is now described which has active physiological properties, and is identified with the guanido-butylaminoagmatine of Kossel, both from the properties of the carbonate and sulphate and from the analyses of the aurichloride and picrate. It is precipitated by silver nitrate and baryta after removal of the bases precipitated by ammoniacal silver nitrate. The silver compounds are then converted into the picrolonates, and these into the carbonate and sulphate. Contractions were produced in a cat's uterus suspended in 70% Ringer's solution by 0·001 gram of the dichloride in alkaline solution, and the contraction was only slightly increased by the addition of an equal quantity of 4-β-aminoethylglyoxaline.

Injections of the dichloride into rabbits temporarily increased the blood pressure and respiration. W. J. Y.

[Physiological Action of] Pilocarpine. I. N. WATERMAN (*Zeitsch. physiol. Chem.*, 1911, **70**, 441—450).—Pilocarpine, in addition to its known actions on sympathetic nerves, causes in rabbits an increase in urine, the appearance of sugar in that secretion, and a rise of susceptibility to adrenaline. W. D. H.

[Physiological] Action of Some *iso*Quinoline Derivatives. PATRICK P. LAIDLAW (*Bio-Chem. J.*, 1911, **5**, 243—273).—A review of the action of a number of *iso*quinoline bases is made, and their action compared with their chemical constitution. A law of relationship for one series is put forward. 6 : 7-Dimethoxy-2-methyl-3 : 4-dihydro*iso*quinolinium chloride (Pyman, Trans., 1909, **95**, 1271) has an action very similar to that of hydrastinine. The generally accepted view of the action of hydrastinine on the functions of the body is stated to be erroneous in several points. W. D. H.

Antagonistic Action of Salts. JACQUES LOEB (*Proc. Amer. physiol. Soc.*, 1910, xxxii—xxxiii; *Amer. J. Physiol.*, **27**).—Pure potassium chloride of the same concentration as in sea-water kills *Fundulus* in two days or less, while in sodium chloride of the same concentration the fish live indefinitely. The toxicity of the potassium salts can be neutralised by sodium chloride added in a certain constant ratio. The conclusion is drawn that a partition of some colloidal anion between the two metals occurs in the gills.

There is an upper limit for the concentration of potassium chloride, beyond which its toxic action can be no longer inhibited by sodium chloride. W. D. H.

A Case of Poisoning by Sewer-gas. WILHELM GÖHLICH (*Chem. Zeit.*, 1911, **35**, 129—130).—The investigation arose out of a case of sudden illness, ending in death, in a workman engaged in cleaning a sewer. Samples of the sewer-water were found to contain arsenic and free sulphuric acid in such quantities that the addition of zinc or iron produced an evolution of arsenic trihydride, which could readily be detected with silver nitrate paper. The illness was attributed to poisoning by arsenic trihydride, formed by the action of the sewer-water on the iron tools and zinc bucket, which the man was using at the time. Post-mortem examination revealed the presence of arsenic in the organs and blood. The sulphuric acid and arsenic were eventually traced to the drainage from an artificial manure manufactory. W. J. Y.

Chemistry of Vegetable Physiology and Agriculture.

An Automatic Pipette. CARL PERMIN (*Centr. Bakt. Par.*, 1911, i, 57, 575—576).—The pipette is designed for bacteriological and serological work, and consists of an ordinary graduated pipette connected by a side opening with an india-rubber ball, which is situated on the stem just below the top. The ball serves to fill the pipette, the opening at the top of the stem being closed with the finger. The liquid is run out by removing the finger from the top of the pipette in the usual manner. W. J. Y.

Action of the Bulgarian Ferment on Monobasic Acids Derived from Reducing Sugars. GABRIEL BERTRAND and R. VEILLON (*Compt. rend.*, 1911, **152**, 330—332).—The Bulgarian ferment has no action on solutions of calcium gluconate, galactonate, mannonate, maltobionate, or lactobionate. The first four salts have no influence on the lactic fermentation of dextrose or lactose. In the case of solutions containing lactose and calcium lactobionate, however, the ferment produces more lactic acid than corresponds with the weight of sugar present. This may be explained by supposing that an endolactase is only liberated in media containing lactose; under these conditions the lactobionic acid becomes hydrolysed, the resulting galactose then forming lactic acid. W. O. W.

Fungicidal Properties of Liver of Sulphur. FREDERICK W. FOREMAN (*J. Agric. Sci.*, 1911, **3**, 400—416).—Liver of sulphur contains various oxidation products, and usually free sulphur, in addition to potassium or sodium hydrosulphide, sulphide, and polysulphides. Experiments with spores of *Botrytis cinerea* showed that the oxidation products have little or no fungicidal properties in weak solutions, and that saturated hydrogen sulphide solution and free sulphur have no effect. The chief agent in the mixture is the sodium hydroxide. Potassium hydroxide is less poisonous.

Methods for the analysis of liver of sulphur are described.

N. H. J. M.

Influence of Manganese on the Development of Aspergillus niger. GABRIEL BERTRAND and MAURICE JAVILLIER (*Compt. rend.*, 1911, **152**, 225—228. Compare Abstr., 1908, ii, 124).—*Aspergillus niger* was cultivated in a manganese-free nutrient solution, to which definite quantities of pure manganese sulphate were added. Special precautions were taken to avoid the presence of metals, such as zinc and iron, which favour the growth of the organism. It was found that manganese had a favourable influence on the development of the mould, the yield increasing with the proportion of metal added, from dilutions of 1/1,000,000 to 1/100. At higher concentrations manganese exerted a prejudicial action. W. O. W.

Calcium Requirements of Plants. Different Relations of the Calcium and Magnesium in Nutritive Solutions. IWAN KONOWALOFF (*Landw. Versuchs-Stat.*, 1911, **74**, 343—360).—Results of water-culture and sand-culture experiments with varying amounts of calcium showed that the yields increase up to a certain point with the increase in the amount of calcium. In most cases the highest yield was obtained with solutions containing 0·2% CaO.

With varying relations of calcium (as nitrate) and magnesium, the highest yield was obtained with the ratio $CaO:MgO = 1:1$. When, however, the calcium was in the form of sulphate or carbonate, equally good, or better, results were obtained with the ratio 6·7 : 1.

Comparing different calcium compounds (with a ratio $CaO:MgO = 6·7:1$), it was found that tricalcium phosphate gave the best results. Calcium carbonate (marble) had no injurious effect when the ratio was 53·6 : 1. N. H. J. M.

Basic Components of Bamboo Shoots. GINZABURO TOTANI (*Zeitsch. physiol. Chem.*, 1911, **70**, 388—390).—Fresh bamboo shoots are shown to contain betaine and choline, in addition to tyrosine, asparagine, guanine, xanthine, hypoxanthine and adenine.

E. F. A.

Waxes of the Coniferæ. J. BOUGAULT (*J. Pharm. Chim.*, 1911, [vii], **3**, 101—103).—In addition to juniperic and sabinic acids, already isolated from the wax of *Juniperus sabina*, a small quantity of thapsic acid, which has been shown to be an oxidation product of juniperic acid, has been obtained (compare Abstr., 1909, i, 82; 1910, i, 297). Sabinic acid has also now been obtained from the wax of *Thuja occidentalis*. This wax may also contain a trace of thapsic acid. T. A. H.

The Chromogenic Substances of White Grapes. SERAFINO DEZANI (*Chem. Zentr.*, 1910, ii, 1141—1142; from *Staz. sperim. agrar. ital.*, 1910, **43**, 428—438).—Two chromogenic substances were found in white grapes, of which one only is precipitated by lead acetate. By the action of hydrochloric acid, colouring matters are obtained, which are analogous to the "œnocyanins." The conversion of these substances into colouring matters is due not to oxidation, but probably to hydrolytic scission with simultaneous formation of a reducing substance. In the residue from the chromogenic substances there are other substances which give a red coloration with alkalis.

N. C.

The Tonic Effect of Certain Organic Substances in Solution and as Vapours. HERMANN STADLER (*Arch. Hygiene*, 1911, **73**, 195—217).—The toxicity of the aliphatic alcohols increases as the molecular weight increases; on the other hand, the toxicity of the aliphatic aldehydes falls off with increasing molecular weight. Replacement of oxygen by sulphur in aliphatic compounds leads to a marked increase in toxicity. The effect depends only on the amount of the substance present, and not at all on the form in which it occurs; the compounds examined were equally toxic whether they were used as solutions or as vapours, provided only the partial pressure was the same; indeed, knowing the toxicity of a substance in the liquid form, its toxicity in vapour form is readily calculated from Henry's law. But this rule breaks down when the substance reacts with the nutrient medium on which the organisms are growing; in this case vapours act more powerfully than solutions of the same partial pressure.

A table is given showing the concentrations at which a number of alcohols, aldehydes, and other substances totally inhibit the growth of *Staphylococcus pyogenes aureus*, *Bact. pyocyaneum*, and *B. coli commune*. On the latter organism experiments were made both with solutions and vapours. E. J. R.

Action on Green Plants of Some Substances Extracted from Coal-tar and Employed in Agriculture. MARCEL MIRANDE (*Compt. rend.*, 1911, **152**, 204—206. Compare Abstr., 1909, ii, 824; 1910, ii, 884; this vol., ii, 64).—Insecticides prepared from coal-tar are liable to bring about anæsthesia or blackening of the leaves of plants. Direct contact with the liquids is more injurious to the plants than exposure to the vapours. The action on the chlorophyll appears to be due principally to the phenols present in such preparations.

W. O. W.

Influence of Different Amounts of Water, Different Manures, and Consolidation of the Soil on the Root Development of Wheat and Barley in the First Period of Growth. R. Polle (*J. Landw.*, 1910, 58, 297—344; from *Inaug. Diss. Göttingen*).—Vegetation experiments are described in which wheat and barley were grown in boxes containing loam and sandy soil respectively, both without and with manure, and with low and higher percentages of water. In some the soil was consolidated by pressure, whilst in others it was employed in a looser condition.

Full particulars as to length and weight of the main roots and side roots produced under the different conditions are given, as well as the amounts of growth above ground. N. H. J. M.

Amounts of Ammonia and Nitric Acid in Rain-water in Tonquin. M. Aufray (*Bull. Économ., Hanoi-Haiphong*, 1909, 12, 595—616. Compare Leather, Abstr., 1906, ii, 487; Brünnich, 1910, ii, 647).—The amounts of nitrogen as ammonia and as nitrates were estimated in 123 samples of rain-water collected in the Botanic Gardens, Hanoi, from April, 1902, to March, 1905, and in 313 samples collected from June, 1906, to September, 1909, in an open space in the middle of the same town. Assuming the composition of the samples to approximately represent the whole rainfall, the average amounts of nitrogen per million, and the total amounts per acre, for the six years would be as follows:

	Rainfall, inches.	N per million		N per acre (lbs.)		
		as ammonia.	as nitrates.	as ammonia.	as nitrates.	Total.
1902-3	90·55	0·71	0·66	14·74	13·47	28·21
1903-4	59·68	0·99	0·80	13·34	10·89	24·23
1904-5	84·72	0·64	0·43	12·25	8·26	20·51
1906-7	49·92	0·54	0·36	6·13	4·06	10·19
1907-8	57·91	0·33	0·27	4·39	3·54	7·93
1908-9	77·72	0·23	0·15	4·04	2·65	6·69

Of the total rainfall, about 82% falls from May to October, and this contains about 84% of the total nitrogen. N. H. J. M.

Analytical Chemistry.

Recent Advances in Forensic Chemistry. MAX DENNSTEDT (*Ber.*, 1911, **44**, 5—38).—A lecture delivered before the German Chemical Society. C. S.

Volumetric Analysis with Small Quantities of Liquid. F. PILCH (*Monatsh.*, 1911, **32**, 21—29).—A special form of apparatus is described, which consists essentially of two burettes opening directly into a reaction chamber of 20 c.c. capacity. Each burette is about 40 cm. long, and has a capacity of 3 c.c.; each cubic centimetre is divided into 100 parts, and the accuracy of measurement is 0·001—0·002 c.c.

A Nernst micro-balance is used for weighing out the substances (0·5—2 mg.) to be introduced into the reaction chamber.

Experiments are given showing that accurate results may be obtained in iodimetry, volumetric determinations with silver nitrate, acidimetry, alkalimetry, and in the estimation of nitrogen by the Kjeldahl process. In the last process the ammonia is distilled directly into acid contained in the reaction chamber. T. S. P.

A Micro-filter for the Treatment of Small Quantities of Precipitate. JULIUS DONAU (*Monatsh.*, 1911, **32**, 31—41).—The preparation, from thin platinum foil and asbestos fibre, of a modified Gooch crucible is given. The crucible weighs only 0·02 gram, and can be used with the filtering tube previously described (Abstr., 1910, ii, 152).

Accurate results have been obtained in the gravimetric determinations of antimony, arsenic, tin, iron, potassium, silver, and copper, the weight of substance taken varying from 1—3 mg. T. S. P.

A Simple Flask and an Arrangement for Carrying Out Chemical Reactions. EUGEN SPITALSKY (*Chem. Zeit.*, 1911, **35**, 175).—The apparatus is intended to prevent any loss caused by spirting when the reaction is somewhat violent. A flat-bottomed flask having a very narrow opening into a bulb-shaped neck serves as reaction flask, and the very small amount of liquid which is carried off by the gases is retained by means of a glass ball, or, preferably, a round porcelain sieve placed over the constriction. When the liquid is heated to boiling, any liquid condensed in the neck runs back into the flask, and rinses the porcelain sieve, thus absolutely preventing loss of substance.

The apparatus can also be used for carrying out reactions which take some time to finish, such as the iodometric estimation of chromic acid, or the determination of the iodine number of fats. By carefully pouring a little water or chloroform on to the porcelain sieve, or glass ball, a seal is formed, which prevents any volatilisation of the iodine. L. DE K.

The Yellow Colour of Alcoholic Potash. R. GAZE (*Chem. Zentr.*, 1910, ii, 1499—1500; from *Apoth. Zeit*, 1910, **25**, 668—669). —The best method for the preparation of colourless alcoholic potash consists in placing a cooled solution of 66 grams of potassium hydroxide (purified by alcohol) in 66 grams of water in a litre flask, and, with constant shaking, slowly adding absolute alcohol to the mark. The solution when prepared should be kept in a white glass vessel in the light. To decolorise yellow or brown alcoholic potash, it should be left in contact with fresh animal charcoal for twelve hours, being frequently shaken. N. C.

Method for Complete Destruction of Organic Matter in the Detection of Mineral Poisons. Pierre Breteau (*Compt. rend.*, 1911, **152**, 199—200).—Three hundred grams of the material are gently warmed with 300 c.c. of pure sulphuric acid (D 1·84) in a 2-litre Jena flask, and the mixture treated with a current of oxides of nitrogen, which are best prepared by passing sulphur dioxide into 500 c.c. of nitric acid contained in a Durand wash-bottle. The gas is freed from spray by passage through cotton wool. The temperature is gradually raised, and the process completed as in the Kjeldahl estimation of nitrogen. If necessary, 50 c.c. of sulphuric acid are added to compensate for loss by evaporation. When the liquid has become colourless, it is concentrated in a platinum dish and treated in the usual way. The process is complete in about four hours; the above-mentioned quantity of nitric acid is sufficient for four or five operations. W. O. W.

Simple Method of Applying Boedeker's Reaction. Jaime Ferrer Hernández (*Anal. Fis. Quim.*, 1911, **9**, 16—17).—Test papers are prepared by soaking in 6% zinc sulphate and then in 10% sodium nitroprusside. They keep well in the dark, and are sufficiently sensitive. One part of sodium sulphite in 2500 can be detected. G. D. L.

The Kjeldahl Nitrogen Process. Willem van Ryn (*Pharm. Weekblad*, 1911, **48**, 27—28).—If it should be necessary to temporarily stop the heating with sulphuric acid, the Kjeldahl flask may be fitted with a perforated rubber cork, through which passes a tube bent at right angles and furnished near its lower end with a glass bulb. The end of the tube is made to dip into a small quantity of sulphuric acid. As the flask cools, the acid is drawn up into the bulb, and the air which follows has to bubble through the acid, and is thus freed from water vapour and any ammonia. L. de K.

The Estimation of Small Quantities of Ammonia. Paul Artmann (*Chem. Zeit.*, 1911, **35**, 50—51, 64—65).—For quantities not exceeding 2 mg. of ammonia per litre, the colorimetric (Nessler) process is the best. For larger quantities, the iodometric method (addition of sodium hypobromite, estimating the excess iodometrically) is more suitable. In some cases a preliminary distillation with addition of magnesia is resorted to.

In the presence of nitrites these are rendered harmless by means of potassium permanganate and a little dilute sulphuric acid. The excess of permanganate is reduced by means of ferrous sulphate, any excess of which is oxidised by cautious addition of permanganate. To remove the iron and manganese, the liquid is made alkaline with sodium hydroxide and shaken with a little barium carbonate. After making up to a definite volume with ammonia-free water, the solution is allowed to settle, and an aliquot part is then poured off and treated with hypobromite. L. de K.

Estimation of Nitrates in Vegetable Matter. KARL KROG and JOHN SEBELIEN (*Chem. Zeit.*, 1911, **35**, 145—146).—In order to be able to apply successfully the recent "nitron" process to the estimation of nitrates in such vegetable substances as turnips for instance, it is necessary to remove some of the interfering organic matters. A liquid ready for treatment with the "nitron" reagent may be obtained by macerating 10 grams of the material with a mixture of 300 c.c. of alcohol and 200 c.c. of water; 250 c.c. of the extract are then evaporated to about 80 c.c. to expel the alcohol, the liquid is treated with a little purified animal charcoal, and the filtrate and washings are concentrated to 25 c.c. After adding the reagent and cooling in iced water for two hours, the separation of the "nitron" nitrate will be complete. L. DE K.

Estimation of Phosphoric Acid in Superphosphates and Bone-Meals. ZYGMUNT ROMÁNSKI (*Chem. Zeit.*, 1911, **35**, 163—164). —Fifty c.c. of the prepared solution (= 1 gram of superphosphate or 0·5 gram of raw phosphate) are mixed with 50 c.c. of magnesium solution, and 30 c.c. of 10% ammonia are added. (When dealing with raw phosphates a sufficiency of 20% ammonia is used to neutralise the acidity.) After remaining for an hour with frequent stirring, another 20 c.c. of 10% ammonia are added, and the whole is left overnight. The precipitate is now collected in a Neubauer crucible, washed first with ammoniacal water, then with alcohol, and finally with light petroleum (D 0·64). It is then dried in a vacuum and weighed, or it may be dried in an oven at a temperature not exceeding 40°. The weight multiplied by 28 or 56 respectively = % of phosphoric acid in the sample.

The acid magnesium solution is prepared as follows: 300 grams of magnesium chloride and 400 grams of ammonium chloride are dissolved in 7 litres of water. One litre of 20% ammonia is added, and then 1000 grams of citric acid. L. DE K.

The Estimation of Silver by Electro-Deposition from an Ammoniacal Solution of the Oxalate. FRANK A. GOOCH and J. P. FEISER (*Amer. J. Sci.*, 1911, [iv], **31**, 109—111).—Twenty-five to 50 c.c. of the silver nitrate solution (containing about 0·25—0·50 gram of silver) are precipitated with ammonium oxalate, and the silver oxalate is redissolved by adding ammonia. From this solution, after diluting to 100 c.c., the metal is deposited electrolytically, using a current of 0·25—1·5 ampere and 4—7 volts. The cathode with the deposited silver is dried over a low flame, and then heated to incipient redness. The operation takes from twenty-five to thirty minutes. The best form of apparatus appears to be a gauze cone set point downwards, and so placed with relation to an annular platinum band used as the anode that the end of the axis where the centrifugal effect of rotation is least shall not receive much of the deposit.

The silver nitrate may be also precipitated by hydrochloric acid. The silver chloride is then dissolved in ammonia, and electrolysed in the presence of ammonium oxalate. L. DE K.

The Wartha-Pfeiffer Method of Estimating the Hardness of Natural Waters. J. M. SILBER (*Arch. Hygiene*, 1911, **73**, 171—182).—The ordinary soap method fails to give accurate results in presence of magnesium salts or of dissolved carbon dioxide. Wartha's method, as modified by Pfeiffer, works satisfactorily (compare Pfeiffer, *Zeitsch. angew. Chem.*, 1902, **9**, 128). Complications arise when the saline matter consists chiefly of the sulphates and chlorides of calcium and magnesium, but these are obviated by some modifications in procedure suggested by the author, for details of which the original paper must be consulted. It is claimed that with these modifications the method is easy, rapid, and accurate.

E. J. R.

Physico-chemical Estimation of Calcium in Wine. MARCEL DUBOUX (*Chem. Zentr.*, 1910, ii, 1566—1567; from *Schweiz. Woch. Chem. Pharm.*, 1910, **48**, 592—594).—Calcium cannot be estimated directly in wine by measuring the conductivity of the latter, owing to the presence of substances which interfere with the estimation. It is necessary to separate the calcium from the other electrolytes by treating 50 c.c. of the wine with 2 c.c. of dilute sulphuric acid and 100 c.c. of 35% alcohol; after the lapse of two hours, the precipitated calcium sulphate is collected on a filter, washed with 70% alcohol, and then dissolved in about 30 c.c. of water. The solution is now titrated with $N/1$-potassium oxalate solution, which is added drop by drop, and the conductivity is determined after the addition of each drop. The precipitation curve of the calcium oxalate consists of two straight lines connected by a short curve; the intersecting point of the two straight lines, when these are extended, corresponds with complete precipitation of the calcium oxalate. It is recommended that 1·5 minutes be allowed to elapse after the addition of a drop of potassium oxalate solution before the conductivity is measured. W. P. S.

Quantitative Separation of Barium, Strontium, and Calcium. J. L. M. VAN DER HORN VAN DEN BOS (*Chem. Weekblad*, 1911, **8**, 5—10).—In estimating barium, strontium, and calcium in a mixture of their salts, the barium is precipitated from the boiling solution by addition of a few drops of glacial acetic acid and a slight excess of ammonium chromate solution, the clear liquid decanted through a Gooch crucible, the precipitate washed by decantation several times with a dilute solution of acetic acid and ammonium chromate, transferred to the crucible, and washed with warm water until the filtrate does not react with silver nitrate. The crucible is heated to low redness.

To estimate the strontium, the filtrate from the barium chromate is concentrated to remove excess of acetic acid, diluted with a small quantity of water and made neutral or slightly alkaline with ammonia, treated with ammonium chromate, and evaporated nearly to dryness. After cooling, the residue is triturated with 50% alcohol, and the alcohol decanted through a Gooch crucible, the process being repeated until the alcohol is almost colourless. The precipitate is then transferred to the crucible, and washed with 96% alcohol. It is then dried in an air-oven at 80—90°, and weighed.

The author suggests estimating the calcium in the filtrate from the strontium chromate by precipitation as calcium oxalate, and titration with permanganate, but has not tried the method. The washing of the strontium chromate with alcohol is a slow process, and the percentage of strontium present in the mixture must be low.

A volumetric method of estimating the three metals is recommended. The solution employed contained 0·157 gram barium, 0·1317 gram strontium, and 0·1071 gram calcium. To estimate the barium, it is diluted to about 300 c.c., boiled, acidified with acetic acid, and treated with 50 c.c. of 0·2088/*N*-potassium dichromate solution with constant stirring, the dichromate solution containing sufficient ammonia to produce a yellow colour. After cooling, the liquid is diluted to 500 c.c., the barium chromate allowed to settle, and 100 c.c. of the clear liquid decanted through a filter. To the filtrate is added a solution of potassium iodide in hydrochloric acid, and the liberated iodine is titrated with thiosulphate.

To estimate the strontium, 350 c.c. of the solution are evaporated with 10 c.c. of 0·2088/*N*-potassium dichromate solution, coloured yellow with ammonia, and, when almost dry, triturated with 50% alcohol. It is then diluted with 50% alcohol to 250 c.c., allowed to remain for half an hour with occasional shaking to facilitate solution of the potassium dichromate, 100 c.c. decanted through a filter, and treated with a solution of potassium iodide in hydrochloric acid. After two or three minutes, the solution is diluted with water, and titrated with thiosulphate.

For the estimation of the calcium, 125 c.c. of the filtrate from the strontium chromate are diluted, boiled, made slightly alkaline with ammonia, and precipitated with ammonium oxalate. The precipitate is allowed to settle, and washed by decantation with warm dilute ammonium oxalate to remove the chromate. After washing out the excess of ammonium oxalate with warm water the residual calcium oxalate is titrated with potassium permanganate.

The fact that oxalic acid is readily oxidised by warm acid solutions of chromates precludes estimating the calcium by titration of the excess of ammonium oxalate added. A. J. W.

Waldemar Fisher's Modification of Volhard's Method for the Volumetric Estimation of Manganese, and its Comparison with other Well-known Methods. Edward Cahen and Harry F. V. Little (*Analyst*, 1911, **36**, 52—59).—Fisher's method is the best of all the modifications of Volhard's method from time to time proposed. The authors' method, which is practically the same as that of Fisher, is as follows: The neutral solution of manganese salt containing 10 grams of zinc sulphate is diluted to 500 c.c. and heated to boiling. One gram of pure zinc oxide is added, and the liquid titrated with permanganate until slightly pink. The liquid is then cooled somewhat, and 1 or 2 c.c. of glacial acetic acid are added. The titration of the colourless solution is then continued until the pink colour is permanent. L. de K.

Assay of Bog Ores. August Kaysser (*Chem. Zeit.*, 1911, **35**, 94).—Some practical hints as to the assay of these ores are given.

The analysis should be performed on the sample dried for five hours at 100°, and it must be remembered that the powder is very hygroscopic. The organic substances may be destroyed either by ignition or more conveniently by treating the hydrochloric acid solution with potassium permanganate. The iron is then titrated by Reinhardt's (stannous chloride) method.

It is recommended that the analysis should be done in duplicate, that is, both by the ignition and the permanganate process.

L. DE K.

Deposition of Metallic Chromium in the Electrolytic Estimation of Manganese by Engel's Method. J. KÖSTER (*Zeitsch. Elektrochem.*, 1911, **17**, 57—58).—The deposit of metallic manganese formed on the cathode according to Otin (Abstr., 1909, ii, 703) is shown to consist mainly of chromium. It is only formed when the electrolysis is carried out with too large a current density. T. E.

Analysis of Molybdenum Glanz. WALDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 207).—The process described previously (Abstr., 1909, ii, 942) requires a slight modification when dealing with ores containing zinc blende.

The solution of the molybdenum in ammonium polysulphide should be heated to boiling so as to render the zinc sulphide filterable. The filtrate is then acidified to precipitate the molybdenum trisulphide. After converting this into the trioxide, and weighing, it should be tested for impurities to be deducted from the total weight. The oxide is fused with potassium hydrogen sulphate, the mass is dissolved in hot water, and precipitated by ammonium carbonate. The precipitate, consisting of alumina and silica, is washed with ammoniacal water containing a little ammonium nitrate, ignited, and weighed. L. DE K.

Estimation of Tungsten. B. MDIVANI (*Bull. Soc. chim.*, 1911, [iv], **9**, 122—124; *Bull. Soc. chim. Belg.*, 1911, **25**, 41—42).—The solution should contain the tungsten as ammonium tungstate, or as a potassium or sodium salt. Fifty c.c. of the solution, representing about 0·1 gram of tungsten trioxide, are mixed with 20 c.c. of recently-prepared tin solution containing 50 grams of crystallised stannous chloride per 200 c.c. of strong hydrochloric acid. After boiling for two minutes, the blue precipitate is washed with hot water (first by decantation), collected, ignited, and weighed as trioxide. Experiments have shown it to be absolutely free from tin. The presence of ferric chloride does not interfere with the reaction.

L. DE K.

A Reaction for Uranium Salts. J. A. SIEMSSEN (*Chem. Zeit.*, 1911, **35**, 139).—Any salt of uranium when mixed with a solution of ethylenediamine at once yields a bright yellow, crystalline salt soluble in excess of the reagent. The reaction is almost as delicate as the ferrocyanide or hydrogen peroxide test. L. DE K.

The Separation of Titanium from the Heavy Metals. Karl Bornemann and H. Schirmeister (*Metallurgie*, 1910, 7, 723—729. Compare Abstr., 1910, ii, 1073).—Titanium is readily separated from copper or nickel by precipitation as orthotitanic acid by means of ammonia. Organic acids hinder the precipitation of titanium, and therefore cannot be used for its separation from iron, but the conversion of the iron into ferrocyanide is found to answer the purpose, the iron being previously reduced to the ferrous state.

From 0·3 to 0·5 gram of the substance is dissolved, and the solution, which must not be too acid, is diluted to 500—600 c.c. and warmed to 50° with 20—30 c.c. of a saturated solution of sodium hydrogen sulphite until free from ferric iron. After warming to 40°, 70—100 c.c. of a solution of potassium cyanide in concentrated ammonia are added, with stirring, and the solution is boiled until the precipitate is pure white and the solution pale green. The solution is filtered out of contact with air, and the precipitate is washed with an ammoniacal solution of ammonium sulphite and then with hot water. The iron in the filtrate may be estimated, after evaporation to dryness with sulphuric acid, by dissolving in water, precipitating with ammonia, and dissolving and titrating the precipitate.

Iron may be titrated with permanganate after reduction with stannous chloride if the quantity of titanium present is less than that of the iron, mercuric chloride and a solution of manganous sulphate and phosphoric acid being added. When the proportion of titanium is larger, the greater part of the excess may be removed by precipitating the iron by Classen's hydrogen peroxide method. Titanium and iron may be titrated together after reduction with zinc, and the titanium is then obtained by difference. C. H. D.

Qualitative Reactions of Oil of Turpentine, Pine Wood Oil, and Resin Spirit. Carlo Grimaldi (*Chem. Zeit.*, 1911, 35, 52).—Gross adulteration of oil of turpentine with pine wood oil or with resin spirit may be detected by shaking 4 c.c. of the sample with 200 c.c. of a solution of 27·5 grams of mercuric acetate in a litre of water for an hour; 160 c.c. of diluted nitric acid (3 parts of nitric acid, D 1·4, and 1 part of water) are then added, and the whole is again thoroughly shaken. Pure oil of turpentine gives a clear solution, but if adulterated with either of the above substitutes to a considerable extent, a turbid liquid is obtained, gradually yielding a flocculent deposit. In doubtful cases a larger quantity of the sample may be operated on. L. de K.

Direct Estimation of Caoutchouc in Vulcanised Rubber Materials. Gerhard Hübener (*Chem. Zeit.*, 1911, 35, 113—115).—Asphaltic or bituminous substances interfere with the estimation of caoutchouc in vulcanised rubber by the tetrabromide method, as they yield insoluble bromides and cause the results for the caoutchouc to be too high. The bitumen bromide may, however, be removed by extracting the mixed bromides with a mixture consisting of equal parts of absolute alcohol and carbon tetrachloride; the caoutchouc bromide is insoluble in this solvent. Paraffins and resins also yield insoluble bromine compounds, and it is probable that these would be removed by the alcohol-carbon tetrachloride mixture; in any case, paraffins and resins, if present in the rubber material, can be eliminated by extraction with acetone previous to the bromination.

W. P. S.

Estimation of Sucrose in Beet Sugar Factory Refuse by Clerget's Process, Using Invertase as Hydrolyst. JAMES P. OGILVIE (*J. Soc. Chem. Ind.*, 1911, 30, 62—64).—Distinctly higher results are obtained in estimating sucrose in beet molasses by Clerget's process, using invertase as a hydrolyst, than are found by the ordinary Herzfeld modification, in which concentrated hydrochloric acid is employed as the hydrolyst. But if, in the Herzfeld process, the error due to the influence of the optically active non-sugar substances is obviated, by using the direct acid polarisation, instead of the usual alkaline (basic lead acetate) polarisation, the results do not differ appreciably from those obtained by means of invertase. From this it would appear that invertase is a selective hydrolyst, inverting only the sucrose (and raffinose, if present), without affecting the non-sugar substances. Pellet's method of obviating the error due to the influence of optically active non-sugar substances, by taking the direct polarisation in a solution acidified with sulphurous acid, gives the same results as the method proposed by Andrlík and Staněk, in which concentrated hydrochloric acid and urea are used. As a practical method, Pellet's sulphurous acid process is now recommended as preferable to the Andrlík and Staněk procedure, by reason of its simplicity and several other apparent advantages. W. P. S.

Estimation of Formic Acid in Foods. HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1911, 21, 1—15).—The author has submitted the process described by Auerbach and Plüddemann (Abstr., 1909, ii, 355) to a critical examination, and finds that it yields trustworthy results. When only a few estimations of formic acid have to be made, it is more convenient to collect the precipitated mercurous chloride on a filter and weigh it, as in this case there is no need to prepare the standard solutions required if the estimation is carried out volumetrically. In separating formic acids from foods, the material should be acidified with an organic acid (mineral acids must not be used, as they may cause sugars present to caramelise and yield volatile products which reduce mercuric chloride), and submitted to steam-distillation until about 1500 c.c. of distillate have been collected. When aldehydes are present, the vapours from the distillation flask must be passed, before entering the condenser, through a flask containing water and calcium carbonate; the formic acid is retained in this flask, whilst the aldehydes pass over into the distillate. Sulphur dioxide, if present, is removed by treating the neutralised and evaporated distillate with hydrogen peroxide and sodium hydroxide for four hours at the ordinary temperature; the excess of hydrogen peroxide is then destroyed by the addition of freshly precipitated mercuric hydroxide. Salicylic acid yields an insoluble compound when heated with mercuric chloride in the presence of sodium acetate, but the formation of this compound is prevented by the addition of sodium chloride. Generally, the amount of sodium chloride (15 grams per litre) contained in the mercuric chloride solution employed is sufficient for this purpose, but for the estimation of formic acid in foods containing large quantities of salicylic acid it is recommended that the neutralised distillate be concentrated, and that 1 gram of sodium chloride, 2 grams of sodium acetate, and 0·5 gram of mercuric chloride be added for each 50 c.c. of the concentrated distillate obtained. W. P. S.

Estimation of Total Fatty Acids. P. SIMMICH (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 38—44).—As incorrect results are obtained if fatty acids are dried in their free state before being weighed, the author recommends that, in the estimation of the total fatty acids in fats, oils, and soaps, the fatty acids (liberated from the saponified fat in the usual way) should be separated by means of a mixture of ether and light petroleum; the ethereal solution is then neutralised by the addition of *N*/2-potassium hydroxide solution, and the solvent is evaporated in an atmosphere of hydrogen. The residue of soap is, finally, dried at a temperature of 100° under reduced pressure, and weighed. The weight of the fatty acids is found by subtracting, from the weight of the soap, 0·01907 gram for every c.c. of *N*/2-potassium hydroxide solution used for the neutralisation. W. P. S.

Separation of the Liquid Fatty Acids (Unsaturated) from the Solid Fatty Acids (Saturated) in Natural Mixtures of Fatty Acids. II. PIETRO FALCIOLA (*Gazzetta*, 1910, **40**, ii, 425—435). —See this vol., i, 174.

Employment of the Electrometric Method for the Estimation of the Acidity of Tan Liquors. I. HENRY J. S. SAND and DOUGLAS J. LAW (*J. Soc. Chem. Ind.*, 1911, **30**, 3—5).—The estimation of the acidity of tan liquors is rendered difficult by the dark colour of the liquors masking the colour change of the indicator used. The authors suggest the titration of the liquors by the electrometric method. The hydrion concentration is determined in the usual manner by means of a hydrogen electrode, specially designed for convenient manipulation. It is convenient to use the normal calomel electrode as a standard, and the liquor which is being titrated is taken as neutral when the end-voltage is 0·69 volt.

Experiments in which varying known quantities of acetic, lactic, or butyric acids were added to tan liquors, and the acidity then measured by the above method, gave satisfactory results. T. S. P.

Index of Oxidation of Milk. TEMISTOCLE JONA (*Gazzetta*, 1910, **40**, ii, 414—418).—The index of oxidation of milk is the number of cubic centimetres of *N*/10-permanganate required to oxidise a given volume of it under certain conditions, and is constant unless the milk be watered or deprived of cream (Comanducci, *Proc. Sixth Congress of Applied Chem.*, **5**, 606). In addition to the above index, the author determines in a similar manner the index of oxidation of the whey obtained by treating the milk with acetic acid at the b. p. and subsequently filtering. By means of the double index so obtained it is possible to differentiate between watering and the separation of cream, for the former lowers the index for the whey only. The two indices have been determined for the milk of two hundred cows of the Pavia district, as also the variations caused by definite admixtures of water or losses of cream, so that not only the nature but also the probable extent of frauds on milk practised in that city can be determined. R. V. S.

New Method of Estimating the Lactose and Fat in Milk. TEMISTOCLE JONA (*Gazzetta*, 1910, **40**, ii, 419—424. Compare preceding abstract).—The reduction of permanganate by milk is due solely to the fat and lactose contained in it. Hence, from the amounts of reduction effected by the milk and by the whey respectively, it is possible to estimate these two constituents. With genuine milk or milk merely deprived of cream, the results obtained are accurate; watered milk yields only approximate figures for the lactose if the water added contains substances which reduce permanganate, but the approximation suffices for many purposes. As the mean of his estimations, the author finds that 1 c.c. of $N/10$ permanganate is equivalent to 0·0049 gram of fat. Experiments with milks further show that 1 c.c. of $N/10$ permanganate is equivalent to 0·001401 gram of lactose hydrate, whilst from experiments with pure aqueous lactose solutions, the factor 0·001460 is obtained. R. V. S.

Refractive Constants of Vegetable Oils. ISIDOR KLIMONT (*Zeitsch. angew. Chem.*, 1911, **24**, 254—256).—The values of sp. gravities, refractive indices, specific refractions $(n - 1/d)$, saponification numbers, iodine numbers, and mean molecular refractions have been determined for different samples of the following oils: linseed, cotton, rape, hoof, hedge mustard, maize, olive, soja, sesame, and earth nut. The specific refraction appears to be independent of the iodine number, and is practically constant, namely, 0·51. The mean molecular refraction varies with the saponification number. The molecular refraction of itself is of but little value, but is useful when compared with other constants. It is shown that determinations of specific gravity by the pyknometer or by the hydrometer do not affect the value of the molecular refraction to any large extent, and that even a few degrees difference in temperature at which the determinations are made has only a small effect on the final value. J. J. S.

[Detection of Ferricyanides.] CARLO GASTALDI (*Gazzetta*, 1910, **40**, 481—482).—See this vol., i, 185.

Assay of Cinchona Bark. Estimation of Quinine and Total Alkaloids. VIGNERON (*J. Pharm. Chim.*, 1911, [vii], 3, 103—108).—The methods described are simplifications of the processes described in the French Codex, and are recommended as affording results which are accurate enough for practical purposes.

The bark is extracted with 0·01% hydrochloric acid, and the extract concentrated, so that 100 c.c. contains the alkaloids of 20 grams of bark. An aliquot portion of this concentrated extract is precipitated with a definite quantity of a solution of ammonia and sodium hydroxide, previously saturated with (1) the total alkaloids of the bark under examination, and (2) quinine, by a special process.

The precipitated alkaloids are washed slightly, dried below 45°, dissolved in a mixture of ether and chloroform, and the residue from this solution dried and weighed as the "total alkaloids." For the estimation of quinine, the precipitate of total alkaloids is dried, the quinine washed out with ether, dissolved in dilute sulphuric acid, and precipitated, dried, and weighed as the chromate. Full directions are given in the original as to the quantities of materials to be used and the precautions to be adopted in carrying out the prescribed operations.

T. A. H.

Precipitation of Cocaine Solutions with Platinum Chloride.

MAX NYMANN and RICH. BJÖRKSTEN (*Pharm. Zentr.-h.*, 1911, **52**, 71—74).—The cocaine solution (about 20 c.c.) is acidified with 2 c.c. of hydrochloric acid (D 1·125), a sufficiency of platinum chloride is added, and then treble the volume of alcohol. When fully deposited, the compound is collected on a weighed filter, washed with alcohol, dried at 105°, and weighed. As the salt is not absolutely insoluble, a correction should be made by adding 0·022 gram for each 100 c.c. of filtrate.

The compound has the composition $(C_{17}H_{21}O_4N)_2,H_2PtCl_6$. In the presence of atropine the method cannot be applied. Boric acid does not interfere to any extent, but in the presence of sodium chloride the precipitation is very incomplete.

L. DE K.

Saponin Reactions.

C. REICHARD (*Pharm. Zentr.-h.*, 1910, **51**, 1199—1204).—A large number of tests are given, of which the following are the most characteristic.

Sodium nitroprusside in aqueous solution is at once reduced on adding saponin, when a flesh-coloured liquid is formed, which dries up to a dark green residue. This reaction neatly distinguishes saponin from alkaloids.

Diphenylamine Test.—Solid diphenylamine is moistened with a few drops of colourless 25% nitric acid, and a few drops of sulphuric acid are added. The liquid is then divided into two parts, and to one of these is added a little saponin. After about half an hour, the reagent should be still colourless, or but very faintly green, whilst the saponin mixture has assumed a beautiful yellow colour.

Titanic Acid Test.—Pure titanic acid is heated with sulphuric acid until the liquid does not adhere obstinately to the glass. If now a little saponin is added, a violet coloration appears, but this soon fades.

Mercurammonium Chloride Test.—When a mixture of equal parts of white precipitate and saponin is moistened with water and allowed to dry, nothing takes place, but if now the mass is moistened with potassium hydroxide, the edges turn yellow, then grey, and after a few hours the mass has completely blackened.

L. DE K.

Estimation of Tannin by means of Casein. MAXIMILIAN NIERENSTEIN (*Chem. Zeit.*, 1911, 35, 31).—Fat-free casein may be employed in place of hide-powder for removing tannin from solutions containing the latter, together with gallic acid and sugars. One hundred c.c. of the solution are shaken for ten minutes with six grams of casein, a further quantity of three grams of casein is added, and the mixture is filtered. The estimation is then proceeded with in the usual way. W. P. S.

The Degree of Accuracy with which Proteins can be Estimated in Milk by Formaldehyde Titration. H. DROOP RICHMOND (*Analyst*, 1911, 36, 9—11).—The author has applied this process to a number of samples of fresh milk with the object of ascertaining the agreement between duplicate estimations and the constancy of the factor for calculating the proteins from the aldehyde figure obtained. As mentioned previously (Abstr., 1906, ii, 634), strontium hydroxide is preferred for use in the titration owing to the fact that when this substance is used, the acidity of formaldehyde does not increase with dilution. The method employed is as follows: To 10 c.c. of the milk are added 1 c.c. of a 0·5% phenolphthalein solution, and the milk is neutralised with $N/11$-strontium hydroxide solution; 2 c.c. of a 40% formaldehyde solution are then added, and the titration is continued until a pink coloration is obtained. After deducting the acidity of the formaldehyde solution, the latter titration represents the aldehyde figure. The proteins were also estimated by Kjeldahl's method, using the factor 6·38 to convert the nitrogen found into protein. From the results obtained, the factor 0·170 is calculated as the most probable figure to express the relation between the proteins and the aldehyde figure. The difference between the amounts of proteins found by the aldehyde method and by the Kjeldahl method varied from +0·20 to −0·13%. W. P. S.

Micro-chemical Detection of Albumin. THOMAS BOKORNY (*Chem. Zeit.*, 1911, 35, 69—70).—The true albumin in proteosomæ may be coagulated and recognised under the microscope by immersing them for half an hour in a solution containing 8% of acetic acid, 4% of sodium chloride, and 0·5% of caffeine. L. DE K.

The Estimation of the Enzymatic Activity of Nuclease by the Optical Method. GIACOMO PIGHINI (*Zeitsch. physiol. Chem.*, 1910, 70, 85—93).—The activity of nuclease in blood-serum and various tissue extracts may be investigated, not only by estimating the cleavage products chemically, but also by the polarimeter; nucleic acid is dextrorotatory; as it is broken up into its cleavage products, this power disappears, and the rate of fall in the dextrorotation measures the activity of the nuclease. The present research deals only with the nuclease of blood-serum. W. D. H.

General and Physical Chemistry.

Spectroscopy of Oxygen. HEINRICH KAYSER (*Ann. Physik*, 1911, [iv], 34, 498—504).—The author criticises statements made by Steubing (Abstr., 1910, ii, 913) relative to the constitution of banded spectra, and disputes the validity of the conclusions drawn from the observations on the fluorescence and band spectra of oxygen. In reference to the first ultra-violet spectrum, which has generally been attributed to water, but which Steubing supposes to be characteristic of oxygen, the author points out that this is not only exhibited by Geissler tubes containing oxygen, but also by tubes containing any other gas. Although it is not quite certain that this banded emission spectrum is due to water, available observations demonstrate positively that it cannot be ascribed to oxygen. H. M. D.

The Structure of Certain Spectral Lines and the Zeeman Effect in Weak Magnetic Fields. HARALD LUNELUND (*Ann. Physik*, 1911, [iv], 34, 505—542).—The utility of the Heraeus amalgam lamp as a means of producing line spectra, and the behaviour of some of the finest lines in weak magnetic fields, have been investigated. With a small current (3 amperes), good results are obtained for the mercury spectrum, and the strongest cadmium lines appear quite sharply, but the amalgam lamp cannot be recommended for the examination of the spectra of bismuth and lead. Of the various lines examined, the mercury line $\lambda = 4916$, the cadmium line $\lambda = 6439$, the zinc lines $\lambda = 6362$, 4810, 4722, and 4680, and the lead lines $\lambda = 5190$, 5006, 4168, 4062 and 4020 appear to be simple.

In a weak magnetic field, the components of the mercury lines $\lambda = 5750$, 5769, 5461, and 4359; of the cadmium lines $\lambda = 5086$ and 4800, and of the bismuth line $\lambda = 4722$ were found to undergo resolution. One of the components of the mercury line $\lambda = 5790$ undergoes a displacement which is proportional to the square of the strength of the applied field. In the case of the line $\lambda = 5461$, one of the components shows remarkable changes in the distribution of the intensity as the strength of the field is altered. H. M. D.

Absorption-Spectra. III. F. H. EYDMAN, jun. (*Chem. Weekblad*, 1911, 8, 123—131).—A criticism of the methods employed by Formánek and by Hartley in their experiments on absorption-spectra.
A. J. W.

Permeability to Light of Mixtures of Several Light-absorbing Substances [Spectroscopic Evidence for the Formation of New Compounds]. OTTO RUFF (*Zeitsch. physikal. Chem.*, 1911, 76, 21—57).—When to a solution of nitrogen sulphide (N_4S_4) in liquid ammonia increasing amounts of hydrogen sulphide are added, the absorbing power of the solution for light of a definite wave-length goes through a number of maxima and minima. The occurrence of such maxima and minima is ascribed to the formation of a series of new compounds, since it can be shown mathematically that if certain conditions hold, such maxima and minima must always be observed when two coloured substances, or a coloured and a colourless substance, interact in solution to form new substances; further, from the position of the maxima and minima certain conclusions can be drawn as to the composition of the new compounds.

The subject is treated mathematically on two separate experimental conditions: (1) when the concentration of one of the reacting substances is kept constant and that of the other is varied; (2) when both concentrations are varied, but the sum is always kept constant. The following types of reaction are discussed on both assumptions: (a) $nA+B \rightleftarrows C$; (b) $ab+cd \rightleftarrows ac+bd$; (c) the coupled reaction $nA+B \rightleftarrows C$ and $nA+C \rightleftarrows D$, and the results to be expected when one new compound is formed are deduced. If several new compounds may be formed, it is shown that the number of limiting values for the absorption cannot exceed the number of new compounds, but may be less. The position of the limiting values gives only approximate information as to the composition of the compounds.

The observations with mixtures of nitrogen and hydrogen sulphide indicate the presence in liquid ammonia of a number of compounds, $(NH_4)_2S_2$, $(NH_4)_2S_3$, $(NH_4)_2S_4$, $(NH_4)_2S_5$, and compounds containing still more sulphur.

Measurements with mixtures of cobalt and nickel chlorides and of methylene-blue and azobenzene showed no indication of chemical combination. Mixtures of helianthin and azobenzene and of methyl-orange and methylene-blue gave curves with one maximum or one minimum, indicating chemical interaction. Finally, no evidence of chemical combination was obtained in a highly diluted solution of bromine and iodine. G. S.

Duration of Phosphorescence of Uranyl Salts. JEAN BECQUEREL (*Compt. rend.*, 1911, **152**,, 511—513).—With the majority of phosphorescent substances the duration of phosphorescence increases as the temperature is lowered. This is also the case with certain uranium salts, especially those of organic acids, such as the acetate, tartrate, and oxalates, which show a much more prolonged phosphorescence at the temperature of liquid nitrogen than at the ordinary temperature. Uranyl nitrate, however, shows no difference in the duration or intensity of luminosity at $-190°$ and at the temperature at which the fused hydrated salt crystallises. The sulphates and double sulphates are perhaps slightly more luminous at low temperatures, but do not show more prolonged emission.

The observations agree with those already published (Abstr., 1906, ii, 630), and confirm the view that phosphorescence is localised in the uranyl radicle. W. O. W.

Actino-dielectric Action in the Phosphorescence of the Alkaline-earth Sulphides. C. RAMSAUER, W. HAUSSER, and ROBERT OEDER (*Ann. Physik*, 1911, [iv], **34**, 445—454).—The actino-dielectric action observed by Lenard and Saeland (Abstr., 1909, ii, 283) has been further examined under more favourable conditions in the case of calcium sulphide containing bismuth as metallic "impurity." When the phosphorescent substance is under the influence of an electric field, the photo-electric effects, which are observed on exposing to the exciting light for successive short intervals of time and on reversing the field of force, indicate that the actino-dielectric action is of the nature of a dielectric displacement.

The actino-dielectric effect increases with the time of exposure of the calcium sulphide to the exciting light, at first rapidly, and then more slowly, but even after an hour it has not attained a limiting value. It increases much less rapidly than the intensity of the exciting light, and approximates to a maximum as the light intensity is increased. The effect is also dependent on the wave-length of the light which falls on the substance. The curve which is obtained by plotting the actino-dielectric effect as a function of the wave-length exhibits a pronounced maximum at about $\lambda = 600\mu\mu$, a minimum at about $\lambda = 500\mu\mu$, and as the wave-length further diminishes the dielectric effect increases rapidly. H. M. D.

Optical Sensitisation. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1911, 9, 205—228).—By means of experiments with Eder's solution and with photographic plates, the author has examined the sensitising action of ferric chloride, eosin, erythrosin, acridine, and cyanine.

If an aqueous solution of ferric chloride, prepared in the dark, is added to Eder's solution, the resulting liquid can be kept for months in the dark without separation of mercurous chloride. On the other hand, if the ferric chloride solution is insolated for a very short interval before being added to the Eder's solution, reduction takes place and mercurous chloride is precipitated. From this it follows that pure aqueous solutions of ferric chloride (or sulphate) are photo-sensitive.

To ascertain the photo-chemically active constituents in the other cases examined, the substances concerned were subjected, either singly or in pairs, to a primary insolation before being brought together in the dark. Primary insolation of eosin, eosin + ammonium oxalate, and erythrosin + ammonium oxalate gave no result, whereas insolation of eosin + mercuric chloride and of erythrosin + mercuric chloride resulted in the precipitation of calomel. A very slight precipitate was also obtained after insolation of erythrosin alone.

From experiments carried out on these lines, it is found that the photo-chemically sensitive constituents are complex compounds formed by combination of the mercuric salt with the colouring matter.

Other observations show that a solution of acridine chloride is sensitised by the addition of ammonium oxalate, and that cyanine yields an extremely sensitive precipitate with mercuric chloride. In the case of the photographic plate, the sensitising influence of eosin and the development of the latent image by mercurous nitrate have been investigated. H. M. D.

The Theory of Colour Sensitiveness. CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1911, 9, 229—236).—A theoretical paper, in which the connexion between the nature of the photo-chemically active rays and that of the sensitive substance is discussed in reference to Grotthuss's theorem, according to which chemical action is brought about only by the absorbed rays.

In photo-chemical reactions in which oxidation and reduction occur, as in the action of light on Fehling's solution, the primary photo-chemical effect consists in the removal of an electron from a substance which is thereby oxidised. The free electron then enters into combination with a second substance, which undergoes reduction. According to this view, the colour sensitiveness of the active mixture or complex is determined by the absorption of the oxidisable substance. Examples of this are found in the oxidation of iodine, sulphur, and sulphite ions, and of pyrogallol, cuprous chloride, and ferrous salts.

It is further supposed that all oxidisable substances which exhibit selective absorption must be more or less photo-sensitive, and in this way the author draws the conclusion that the converse of Grotthuss's theorem holds good for photo-chemical changes in which oxidation is involved.

Since the action of the active light consists in setting free an electron, it follows that the photo-sensitiveness must be approximately proportional to the reduction potential of the oxidisable substance. If no reducible substance is present in the medium which is acted on by the light rays, the primary photo-action leads quickly to a stationary condition, which depends on the intensity of the light. When the light is removed, the system returns more or less quickly to its original condition. In presence of an oxidising agent, the progress of the complete photo-chemical change is determined by the relative rates at which the electrons are set free by the primary photo-action, and taken up by the oxidisable substance in the secondary action. It follows from this, that every photo-chemical oxidation-reduction reaction, in which the oxidisable substance is reduced more slowly than free oxygen, must be retarded by the presence of free oxygen.

On the basis of these views, the author describes a method of classifying different photo-chemical sensitisers. H. M. D.

Nitrification by Ultra-violet Light. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1911, **152**, 522—524. Compare Abstr., 1910, i, 349, 543; ii, 564, 606).—Although ultra-violet light does not bring about direct combination between oxygen and nitrogen, yet the rays are able to effect the nitrification of many organic compounds and ammonium salts, in this respect, as in others, showing a remarkable similarity to the action of natural ferments. In the experiments the substances were exposed in presence of air or oxygen to the light from a 110-volt lamp, at a distance of 3—6 cms., for three to nine hours at temperatures not exceeding 35—50°. Under these conditions a 4% solution of ammonia showed the reactions of a nitrite, but remained free from nitrate. Ammonium hydrogen carbonate, ammonium chloride and sulphate in aqueous solution underwent oxidation in the same way, as did also compounds, such as methylamine, ethylamine, ethylenediamine, guanidine, acetoxime, hydroxylamine, acetamide, acetonitrile, etc. The conversion of carbamide into ammonia under the action of the light (Abstr., 1910, ii, 814) is only the first stage in its oxidation to a nitrite.

As in the case of fermentation, nitrification is prevented by the presence of acids. Similarly, the process is a reversible one; thus a concentrated solution of ammonium nitrite is decomposed on exposure with liberation of nitrogen. Ammonium or potassium nitrate are first converted into the nitrites, oxygen being evolved. W. O. W.

Ultra-violet Radiations. ANTOINE GUNTZ and JULES MINGUIN (*Compt. rend.*, 1911, **152**, 372—373).—Using a 3·5 ampere, 220 volt, silica mercury lamp at distances from 15 to 6 cm., three classes of action on substances were observed. (1) Mechanical effects: *d*-Benzylidenecamphor, in good crystals, got warm, and after two hours exposure the crystal faces became dull, and showed under the microscope corrosion figures similar to those obtained with solvents, such as toluene. These actions are due to the rays, and not to heat. (2) Chemical effects: A crystal of sugar-candy warmed without melting, and rapidly turned dull and yellow, showing corrosion figures under the microscope. Seven grams gave with Fehling's solution 0·107 gram of a reducing substance, and dextrose was characterised by its osazone. (3) Changes of state: Anthracene in benzene solution deposited its polymeride, para-anthracene, melting at 275°, and indene was resinified. White phosphorus, alone, and in solution in carbon disulphide, was transformed into the red variety. A crystal of transparent sulphur became opaque, and powdered under slight pressure. Solutions of sulphur in benzene and carbon disulphide deposited the insoluble modification. F. S.

Photo-kinetics of Bromine Substitution. I. The Course of the Photo-reaction. LUDWIK BRUNER and S. CZARNECKI (*Bull. Acad. Sci. Cracow*, 1910, 516—559. Compare Abstr., 1909, i, 900; ii, 951).—Further investigation of the photo-bromination of toluene has shown that consistent results cannot be obtained in different experiments on account of the enormous influence exerted by traces of oxygen. In presence of small quantities of iodine (0·0004 to 0·003 mol. per litre), the disturbing effect of traces of oxygen is eliminated, and experiments have been made in these circumstances to determine the nature of the photo-bromination process. The rate of disappearance of bromine in a particular experiment is constant, and this is attributed to the increasing transparency of the solution towards the active light rays which counterbalances the effect of the diminishing bromine concentration. In experiments with different quantities of toluene in an inert solvent, the velocity is proportional to the concentration of the toluene. For variations in the amount of added iodine, the velocity diminishes as the amount of iodine increases.

Between 1° and 33°, the temperature-coefficient of the reaction is 1·85, which is much greater than for most photo-chemical reactions, although only about half as large as the coefficient of the side-chain substitution when this takes place in the dark.

The nature of the solvent in which the toluene is dissolved has also an influence on the rate of the photo-reaction.

In carbon tetrachloride and carbon disulphide the velocity is nearly the same, but is almost three times as great in benzene.

In an ionising solvent like nitrobenzene, the reaction proceeds much more slowly, and until the intensity of the light reaches a certain value it appears not to take place at all.

Comparative measurements of the velocity of the photo-reaction have also been made with the homologous and with various substitution products. The photo-sensitiveness of the hydrocarbons increases in the series: toluene, *m*-xylene, *o*-xylene, *p*-xylene, ethylbenzene, *iso*propylbenzene, cymene. On the other hand, nuclear-substituted halogen derivatives are much less photo-sensitive than toluene.

From experiments in which rays from a mercury arc lamp were used as exciting agent, it seems probable that each kind of light which is absorbed is equally effective in connexion with the photo-bromination process independent of its wave-length. H. M. D.

Photo-kinetics of Bromine Substitution. II. The Course of and the Factors which Influence the Photo-chemical After-effect. Ludwik Bruner and Z. Łahociński (*Bull. Acad. Sci. Cracow*, 1910, 560—593. Compare preceding abstract).—Experiments have been made to determine the nature of the after-effect which has been found to accompany the photo-bromination of toluene. These show that the presence of oxygen during the photo-bromination is necessary for the rapid subsequent reaction which is observed in the dark. This after-reaction is of the auto-catalytic type and is probably due to oxidation products of bromine, which are produced during the photo-bromination process in the presence of oxygen. When the partly photo-brominated toluene is heated for two hours at 100°, or is kept for fifteen to eighteen hours at the ordinary temperature, the catalyst is destroyed, for no after-effect is observed when more bromine is added. The addition of oxidisable substances, such as hydrogen bromide and iodine, to the solution, either before or after the photo-bromination, also brings about the disappearance of the after-reaction.

Certain observations relating to the bromination of toluene in the dark without previous insolation are supposed to be due to the presence of this catalytic agent. In very dilute solution, the bromine enters only the side-chain, and this reaction is auto-catalytically accelerated. If oxygen is excluded, or the solution is saturated with hydrogen bromide, or if a trace of iodine is added, the side-chain substitution reaction does not take place.

In agreement with this view, it has been found that the treatment of the toluene solutions with ozonised oxygen facilitates enormously substitution in the side-chain. The action of bromine on such solutions gives the side-chain substitution product even in the dark and in concentrated solutions, and the reaction proceeds with great rapidity. H. M. D.

Comparative Action of Ultra-violet Light on Straight Chain and Cyclic Organic Compounds. Mineral Salts in Aqueous Solution. Daniel Berthelot and Henry Gaudechon (*Compt. rend.*, 1911, **152**, 376—378. Compare this vol., ii, 86).—Cyclic compounds, so long as they are not completely saturated, are extremely stable towards ultra-violet light. Thus pyridine undergoes no change, whilst piperidine decomposes with liberation of hydrogen, under the action of the light. Cyclic compounds containing a side-chain, such as cinnamic acid, undergo slight decomposition, but to a much less extent than corresponding aliphatic compounds.

Ultra-violet light is, as a rule, without action on aqueous solutions of metallic salts. Ferrous sulphate solutions, however, at once give a rust-coloured precipitate, probably of a basic sulphate. Advantage may be taken of this reaction to purify salts of nickel and cobalt from small quantities of iron. Ferric sulphate gives no precipitate when pure, but if nickel or cobalt sulphates are present, a precipitate is formed. W. O. W.

Action of Ultra-violet Light on Diastases. H. AGULHON (*Compt. rend.*, 1911, **152**, 398—401. Compare Green, Abstr., 1896, i, 110; 1898, ii, 399; Cernovodeanu and Henri, Abstr., 1909, ii, 822; 1910, ii, 332).—The diastatic activity of yeast sucrase, commercial diastase, and pancreatin, emulsin, pepsin, rennet, and catalase (from the pig) is diminished to a greater or less extent by exposure to the light from a quartz-mercury lamp. Light of wave-length exceeding 3022 Ångstrom units has practically no action on the enzymes. When a 1% solution of emulsin is exposed to ultra-violet light, a flocculent precipitate appears; all the enzyme, however, remains in solution. The presence of proteins or colouring matter in the diastase preparations protects them to a certain extent from the action of the light. W. O. W.

Investigations on the Radium Contents of Rocks. II. ERNST H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 818—819. Compare Abstr., 1910, ii, 1025).—Measurements of the amount of radium in eleven specimens of sedimentary rocks of different geological periods (four of marble, six of limestone, and one of chalk) showed, with the exception of one carboniferous limestone containing three times the mean quantity of radium, very little individual differences from the mean quantity ($1{\cdot}4 \times 10^{-12}$ gram of radium per gram). This mean is in good agreement with the mean of the values found for limestone by other observers, but is much less than that from Joly's data (3·3). Excluding granites, which have a high radium content, and of which a particularly large number have been investigated, the mean for sedimentary rocks is somewhat higher than the mean for igneous rocks. F. S.

The Radium-content of Salts of Potassium. JOHN SATTERLY (*Proc. Camb. Phil. Soc.*, 1911, **16**, 67—70).—Previous determinations by the emanation test of the radium content of potassium salts having been made without boiling, the radium in a series of Campbell's specimens was measured by boiling the solutions to expel the emanation. The average amount found was 3×10^{-14} gram of radium per gram of salt, but the amount varied and bore no relation to the percentage of potassium present. This amount of radium is only one ten-thousandth part of what would be necessary to produce the observed radioactivity of the salts. F. S.

Action of Slight Rise of Temperature on the Induced Radioactivity. ÉDOUARD SARASIN and TH. TOMMASINA (*Compt. rend.*, 1911, 152, 434—436).—It is stated that the experiments described show that an elevation of 20° or 30° increases the radioactivity of a metal rendered radioactive by exposure to radium. Three concentric bells of metal gauze within a bell of sheet metal were placed inside an external bell containing a salt of radium for some weeks. The gauze and inner bells showed a feeble residual activity, whilst the external bell showed a very strong residual activity, which decayed to only three-fourths of its initial value in a day and then remained constant. Placing this bell on a radiator to increase its temperature 12° increased its activity strongly, but this returned to its initial value at the ordinary temperature. A new metal bell exposed directly to radium showed superimposed on the decay curve of its radioactivity the same increases of activity due to rise of temperature. All experiments with glass surfaces gave only null results. F. S.

Behaviour of Lead Chloride from Pitchblende towards Magnesium Phenyl Bromide. GEORG EBERT (*Chem. Zentr.*, 1910, ii, 1128; from *Ion*, 1910, 2, 277—283).—Determinations of the equivalent of the lead from active lead chloride which had been treated with magnesium phenyl bromide (Hofmann and Wölfe, Abstr., 1907, ii, 521), which effects a concentration of the active material, showed the presence of a substance with an equivalent less than that of lead. In order to concentrate the radium-*D* further, the sulphate was sublimed. The sublimate is distinguished from lead sulphate only by its volatility and by its lower equivalent. Its analytical reactions are those of lead. The α-activity is strong from the first, and after four weeks is unmeasurably strong. The β-activity is feeble at first, but after four weeks rises to 14 uranium units. No emanation could be detected after eight weeks. F. S.

Ionisation of Gases by Chemical Change. H. BRERETON BAKER (Reprint of Royal Institution Lecture delivered March 11, 1910).—The term "electromerism" is proposed instead of "ionisation" as used in connexion with the conduction of electricity through gases, in view of the fact that the nature of the ions is different in gases to those of liquid electrolytes. Radium bromide in an open silica tube sealed up with a mixture of very pure and dry hydrogen and oxygen causes no combination, although the combination of 1/5000th part could have been detected. Very dry air does undergo electromerism under the action of radium bromide. Carbon monoxide and oxygen, whether moist or dry, do not contract under the action of radium. Hydrogen and nitrous oxide, dried only by passage through phosphoric oxide, combine in a Jena tube with great uniformity when heated at 530°. When lime or thoria is present, the starting point of the reaction occurs at lower temperatures. When 2 mg. of radium bromide are heated in the mixture, the latter explodes when the combining temperature is reached.

Hydrogen sulphide and sulphur dioxide, dried only by calcium chloride, do not react at the ordinary temperature, but in presence of

liquid water decomposition into sulphur and water takes place. In presence of 2 mg. of dried radium bromide, after six hours, decomposition is complete, the whole of the water and sulphur condensing in the small tube containing the radium bromide. Ten mg. of radium bromide exposed to an atmosphere saturated with water-vapour at 0° for two days collected 1·5 mg. of water on its surface. Probably the water vapour condenses in liquid drops on the electromers (ions), and in these drops the chemical action occurs. If this deposition of liquid drops occurs with minute quantities of water, the influence of moisture on chemical change is explained according to Sir J. J. Thomson's theory, since the electromers are present in ordinary gases.
F. S.

The Mobility of the Positive Ion in Gases at Low Pressure. George W. Todd (*Proc. Camb. Phil. Soc.*, 1911, **16**, 21—25 *).—By means of a modification of Rutherford's alternating field method the mobilities of the positive ions in air, hydrogen, carbon dioxide, and ethyl bromide have been measured at varying pressures down to from 5 mm. to 1 mm. in the different cases. In all cases the product of the pressure of the gas and the mobility of the ion was constant, showing that the positive ion, unlike the negative ion, is inseparable from the gas molecules attached to it at higher pressure, at all pressures down to a few millimetres. F. S.

The Mobility of the Positive Flame Ion. S. G. Lusby (*Proc. Camb. Phil. Soc.*, 1911, **16**, 26—34).—The velocity of the positive ions produced by introducing a salt bead into a Bunsen flame has been measured by H. A. Wilson's method. Various salts of the metals of the alkali and alkaline-earth families of elements were investigated, and the same velocity was found for all, namely, 290 cm. per second, under a potential gradient of 1 volt per cm., at a temperature of 1450° A. Potassium permanganate was found to be an ideal salt for the measurements, the changes of its chemical composition by heat not affecting its ions, but a variety of salts were employed and all gave the same result. It is calculated that a positive ion of the same mass as the hydrogen atom should have a mobility very near to that found in the experiments, which points to the conclusion that the positive flame ion has the same mass as the hydrogen atom. The mobility should vary as the square-root of the absolute temperature, and this theoretical deduction is being tested.
F. S.

The Ionisation of Heavy Gases by X-Rays. R. T. Beatty (*Proc. Camb. Phil. Soc.*, 1911, **16**, 46—47).—The sudden increase in the ionisation produced in, and the absorption of X-rays by, heavy gases, such as nickel carbonyl, hydrogen arsenide, and hydrogen selenide, when the X-rays attain a certain degree of penetrating power is connected with the production of secondary X-rays characteristic of the heavy element, and of an increased production of β-rays which ionise the gas. The production of β-rays was put into evidence by plotting the curves connecting ionisation with the pressure of hydrogen selenide ionised by *X*-rays sufficiently penetrating to evoke the selenium secondary *X*-radiation. The curve at low pressures was convex to the axis of pressure, but by lining the ionisation chamber with selenium a linear curve was obtained. In the latter case, any β-rays striking the walls before using up all their energy in ionisation are balanced exactly by β-rays coming from the selenium. From similar curves when air was used in the ionisation chamber, it was found that the relative ionisation of hydrogen selenide was 30 for the secondary *X*-radiations of iron, nickel, copper, zinc, and selenium, but increased greatly for the rays of strontium, molybdenum, silver, tin, and iodine, attaining the maximum value of 286 for the last. Similar results were obtained with nickel carbonyl and hydrogen arsenide. F. S.

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* and *Le Radium*, 1911, **8**, 113—115.

The Discharge of Positive Electricity from Sodium Phosphate Heated in Different Gases. FRANK HORTON (*Proc. Camb. Phil. Soc.*, 1911, **16**, 89—101).—The leak of positive electricity from an anode consisting of a platinum strip coated with sodium phosphate and heated by a current in an apparatus carefully freed from all carbon by nitric and chromic acids was measured by a sensitive galvanometer in oxygen, carbon monoxide, and hydrogen at various pressures. The leak was greatest in hydrogen and least in oxygen, but in all cases varied with the time, on changing the gas in the apparatus, before coming to a steady value. On changing from hydrogen or carbon monoxide to oxygen, the leak decreased, whilst on changing to carbon monoxide the leak increased. The conclusion is drawn that the gas molecules diffuse into the anode and take an active part in carrying the current from its surface. F. S.

Observations on the Ions and Fog-nuclei which are Produced in Gases by Ultra-violet Light. STANISLAUS SACHS (*Ann. Physik*, 1911, [iv], **34**, 469—497).—Measurements of the potential differences required to produce saturation currents in dust-free air subjected to the action of ultra-violet light indicate that the velocities of the least mobile positive and negative ions are respectively 0·0022 and 0 0033 cm. per second for a fall of potential of one volt per cm.

In reference to the nature of the fog-nuclei which are simultaneously produced by the action of ultra-violet light, experiments have been made with several gases which were subjected to adiabatic expansion after saturation with the vapours of different liquids. These condensation nuclei are found in dry air, carbon dioxide, oxygen, and nitrogen, but not in hydrogen. The absence of the effect in hydrogen is due to the very small extent to which this gas absorbs the ultra-violet rays. Expansion experiments, in which the gases were passed over water, benzene, chloroform, and a 5% aqueous hydrochloric acid solution, gave similar results.

Other experiments with air show that the period of illumination is without appreciable influence on the formation of the condensation nuclei. These persist for a considerable time, and could be recognised at the end of an hour. Bubbling through distilled water or cooling to −80° has no effect on the nuclei, but they are found to be destroyed by heating above 180°.

From these observations, the author draws the conclusion that the formation of the nuclei cannot be due to chemical changes, as has been supposed by certain observers. On the other hand, the facts are consistent with the assumption that the action of the ultra-violet light consists in producing larger molecules of the gas by a process of polymerisation. H. M. D.

Electrical Conductivity of Non-aqueous Solutions. VIII. Aluminium Bromide and Nitrobenzene. WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1589—1596).—Conductivity measurements of solutions of aluminium bromide in nitrobenzene at 18° show that the specific conductivity at first rises rapidly with the concentration to reach a maximum at 19%, after which it falls, the conductivity curve being almost symmetrical.

The molecular conductivity increases continuously with the dilution. For the dilution $\phi = 1190$ (c.c.), μ is about 2·5 calculated for the molecule $AlBr_3$; μ_∞ is approximately 4·5. The conclusion is drawn that aluminium bromide is moderately highly ionised in nitrobenzene.

The molecular weight of aluminium bromide is only about half as large in nitrobenzene as in carbon disulphide.

The conductivity of these solutions is probably due to ionisation of the complex $Al_2Br_6,2C_6H_5{\cdot}NO_2$, the constitution of which is discussed.
T. H. P.

Electrical Conductivity of Solutions in Esters with Small Dielectric Constants. AL. N. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1910, 42, 1363—1370).—Walden's measurements of the conductivities of solutions of salts in liquids with relatively high dielectric constants (Abstr., 1906, ii, 149) indicated the dominating influence of the dielectric constant on the dissociating power of the solvent and the general independence of this power of the chemical nature of the solvent. With solvents having low dielectric constants, however, the author has shown that the dissociating power depends especially on their chemical nature (compare Abstr., 1910, ii, 1027).

The present paper gives the results of measurements of the conductivities of solutions of various salts in *iso*amyl acetate, methyl benzoate, and *iso*amyl benzoate, the respective dielectric constants of which are 4·79, 6·62, and 4·99. In all cases, the molecular conductivities are very small, so that the dissociating powers of the esters with low dielectric constants are inconsiderable, and are, indeed, much less than those of primary amines with identical dielectric constants. In a few cases the molecular conductivity increases slightly with increase of dilution, but more often it diminishes.

The conclusion is drawn that, in general, when the dielectric constant is low, the chemical character of the solvent is the most important factor in determining the dissociating power, the magnitude of the dielectric constant playing a secondary part. When, however, the dielectric constant is comparatively high, it exerts a dominating influence on the dissociating power, which is then only slightly affected by the chemical nature of the solvent. The Nernst-Thomson law is only valid for solvents with relatively high dielectric constants.
T. H. P.

The Theory of Electrolytic Dissociation, taking into Account the Electrical Energy of the Ions.

F. A. Kjellin (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 7, 1—23).—Taking the electrostatic repulsions and attractions between the ions in a solution as the basis, it is shown that the electrical energy of the ions diminishes with increasing dilution, finally attaining at infinite dilution a value which corresponds with the transference of electrons from atoms of the one sign to atoms of the opposite sign.

From a consideration of the variation of the electrical energy with change in volume, the total energy of the ions being independent of the volume, the conclusion is drawn that the kinetic energy of the ions varies with the volume of the solution. The application of the theorem that the gas pressure depends on the kinetic energy of the particles then leads to an equation of condition for the dissociation of a binary compound into univalent ions. From this equation of condition is deduced an expression for the dissociation equilibrium, which is found to give extremely good constants for the binary electrolytes, sodium chloride, potassium chloride, magnesium sulphate, zinc sulphate, and copper sulphate.

The equation of condition is $(p+a/\sqrt[3]{V^4})V=\frac{2}{3}C$, where V is the volume of solution containing 1 gram-ion, and C is a constant; p is the effective pressure of the ions, and is given by the relation $p=P+a/\sqrt[3]{V^4}$, where P is the pressure exerted by the ions on the walls of the containing vessel, according to the kinetic theory, and $a=1{\cdot}802K$, K being the unit pressure due to the repulsive force between the positive ions when there is 1 gram-ion per unit volume. When the dilution becomes infinitely great, $\frac{2}{3}C=p_\infty V_\infty$.

The equation for the dissociation equilibrium is :

$$\{(p_\infty V_\infty)/RT\}\log C_i-(4a/2{\cdot}3025RT)\sqrt[3]{C_i}-\log C_s=\log k,$$

where C_i is the concentration of the ions, C_s that of the undissociated salt, and k is a constant.

It is further shown that if it is assumed that in the combination of a metal with a non-metal there is a transference of electrons from the atoms of the metal to those of the non-metal, that is, that the forces holding the atoms together within the molecule are of an electrostatic nature, then, if the molecules are surrounded by a dielectric with a higher dielectric constant than that of a vacuum or of the ether, the electrostatic forces tend to force the solvent in between the atoms, thus causing electrolytic dissociation.

By the application of similar reasoning to the change of a metal into ions, a simple explanation is given for the influence of different media on the potential difference between a metal and a solution of its salt.

It is also shown how the equation of condition may be applied to calculate the value of the so-called electrolytic solution pressure.

T. S. P.

Electromotive Force Produced in Solutions by Centrifugal Action.

Richard C. Tolman (*J. Amer. Chem. Soc.*, 1911, 33, 121—147).—Colley has shown that when an electric current is passed through a solution of silver nitrate or cadmium iodide in a vertical tube with a silver electrode at each end, the existence of a difference of potential between the electrodes can be detected which is due to the effect of gravitation. Des Coudres carried out similar experiments in which centrifugal force was substituted for gravitation, and by this means obtained a much larger *E.M.F.*

It is now shown that it is possible to derive a relation connecting the *E.M.F.* produced by the action of gravity with the transference number of the electrolyte, both from thermodynamic and from kinetic considerations, and it is pointed out in connexion with the latter that the production of an *E.M.F.* by centrifugal force is a proof of the presence of free ions in a solution of an electrolyte or at least of a certain degree of polarisation in the molecules.

An account is given of a method for determining transference numbers by centrifugal experiments. It consists in the measurement of the *E.M.F.* between electrodes placed at the central and peripheral ends of a rotating tube containing the electrolyte. The apparatus is described with the aid of diagrams. An equation is given connecting the *E.M.F.* and the transference number of the salt with the rate of rotation, the density of the solution, and the molecular weight and "partial" specific volumes of the substances involved.

Measurements have been made of the *E.M.F.* produced by the rotation of molar solutions of the iodides of potassium, sodium, lithium, and hydrogen. The *E.M.F.* was found to increase in proportion to the square of the rate of rotation. The transference numbers were calculated, and were found to agree fairly closely with those obtained by other methods. E. G.

Experiments with Gas Cells Yielding Current at High Temperatures. A. Beutner (*Zeitsch. Elektrochem,* 1911, **17**, 91—93).—This is an attempt to construct a gas cell which will yield an appreciable current. The electrodes consisted of platinum tubes closed at one end by palladium foil. The closed ends were immersed in a fused mixture of sodium chloride and potassium fluoride, or of sodium and lithium chlorides, and one tube filled with hydrogen and the other with air. The *E.M.F.* at 760° was 0·95 volt, and this fell very rapidly when a current was taken from the cell, partly owing to the small permeability of palladium for oxygen, and partly to the depolarisation of the hydrogen electrode by atmospheric oxygen dissolved in the electrolyte. By passing a current of carbon dioxide through the electrolyte, the depolarisation of the hydrogen electrode is much diminished, and the *E.M.F.* falls much less rapidly. When nickel tubes were used as electrodes the results were similar, but quantitatively much worse. T. E.

Rate of Discharge of Galvanic Cells. I. D. Reichinstein (*Zeitsch. Elektrochem.,* 1911, **17**, 85—90).—The cells consist of a small electrode of copper, zinc, or nickel immersed in a suitable solution and a large lead peroxide accumulator plate in sulphuric acid; the solutions are separated by a porous pot, and that surrounding the metallic electrode is well stirred. The current taken from the cell is varied, and the corresponding potential of the metallic electrode is measured. With copper in *N*-copper sulphate the potential, with a current of 0·133 ampere per 5 sq. cm., was 0·817 volt less than on open circuit. Such a large difference cannot be ascribed to increased concentration of copper ions at the surface of the electrode. The addition of sulphuric acid to the copper sulphate solution diminishes the fall in a very marked way. Very similar results were obtained with zinc in normal and acid sodium sulphate solutions. Nickel in 20% sulphuric acid behaves qualitatively in the same way. The decrease of potential is, however, very much more rapid, and the nickel becomes passive with a very small current. If a chloride is added to the sulphuric acid, this does not occur. T. E.

Electrophoresis of Lampblack. ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1911, **25**, 81—85).—The first part of the paper consists of a reply to Spring (this vol., ii, 15). The second part contains an account of further experiments with slightly alkaline suspensions (*n*/410– *n*/1100) of lampblack, the preparation of which is described in detail. The apparatus used to investigate the electrophoresis of such suspensions was similar to that used by Coehn (Abstr., 1909, ii, 841), except that the upper portions of the U-tube were connected by a horizontal tube. The experiments were carried out in two ways. (1). The suspension filled the lower part of the U-tube to the height of the stopcocks. Above the stopcocks was a dilute solution of potassium hydroxide containing the electrodes, but not reaching to the level of the horizontal tube. The phenomenon then observed was one of anaphoresis. (2). The arrangement was similar to that in (1), except that the potassium hydroxide solution above the stopcocks also filled the horizontal tube. The effect was then cataphoretic.

These results may be explained as follows: During the electrolysis the migration of potassium hydroxide from the anode through the suspension to the cathode carries with it some of the water. In (1) the adjustment of level, by means of the hydrostatic pressure, forces the suspension towards the anode, without destroying the surfaces of separation. The phenomenon thus appears to be one of anaphoresis. In (2) the adjustment of level takes place through the horizontal tube, and the process becomes one of cataphoresis.

This explanation assumes that the lampblack is completely indifferent to the action of the current. There is reason to believe, however, that it is slightly acid in nature, so that in an alkaline medium the anaphoresis would be increased. T. S. P.

Value of Magneton, Deduced from the Coefficients of Magnetisation of Solutions of Iron Salts. PIERRE WEISS (*Compt. rend.*, 1911, **152**, 367—369. Compare this vol., ii, 91, 183).—From the data of Pascal and others, the author deduces the value 1122·1 for the magnetic saturation of magneton in magnetic substances.

W. O. W.

The Magnetisation of Ferro-magnetic Substances above the Curie Point. PIERRE WEISS and G. FOËX (*Arch. Sci. phys. nat.*, 1911, [iv], **31**, 89—117. Compare this vol., ii, 183).—Measurements of the magnetic susceptibility of iron, nickel, cobalt, magnetite, and nickel iron alloys have been made at high temperatures by means of the apparatus described previously. Magnetisation temperature curves are drawn which show the behaviour of the different substances. From the data for the various alloys at constant temperature, the conclusion is drawn that a definite compound of the composition Fe_2Ni is proved. At this point two magnetisation curves intersect, and it is supposed that these correspond with two series of solid solutions. H. M. D.

The Magnetic Susceptibilities of Certain Compounds. A. E. OXLEY (*Proc. Camb. Phil. Soc.*, 1911, **16**, [1], 102—111).—The magnetic susceptibilities of iron carbonyl, nickel carbonyl, potassium ferrocyanide and potassium ferricyanide were found to be respectively $-4{\cdot}00\times10^{-7}$, $-4{\cdot}81\times10^{-7}$, $-4{\cdot}23\times10^{-7}$, and $+93{\cdot}83\times10^{-7}$ at 19°. The great difference between the values for the ferrocyanide and the ferricyanide is attributed to the presence of the molecules of water of crystallisation in the crystals of the ferrocyanide. The low susceptibility of the two metals in the carbonyl compounds is also supposed to be connected with the high apparent valency. From measurements between $-60°$ and $+15°$, it has been found that the susceptibility of the carbonyls and of the ferrocyanide is nearly independent of the temperature, whereas that of the ferricyanide diminishes as the temperature rises. H. M. D.

Magnetic Constants of Feebly Magnetic Alloys. TULLIO GNESOTTO and MARIA BINGHINOTTO (*Nuovo Cim.*, 1910, [v], **20**, ii, 384—441).—The authors have measured the coefficient of magnetisation and the susceptibility of bismuth, tin, cadmium, and lead, and of the various alloys of each of the six different pairs of these metals. The susceptibility of those alloys which do not contain bismuth is a linear function of their composition, as was to be expected according to Curie's law. The magnetic properties of alloys containing bismuth may serve, however, to elucidate their constitution. Eight of the tin-bismuth alloys were examined; those containing much bismuth have a susceptibility much lower than that of pure bismuth, whilst those rich in tin are more paramagnetic than tin itself. The alloy containing 10% of bismuth is amagnetic. The cadmium-bismuth alloys (of which twelve were investigated) all have a lower susceptibility than would be the case if the variation were linear. The two lead-bismuth alloys examined had susceptibilities far lower than they would have if the variation were a linear function. R. V. S.

Use of the Magnetic Field as a means of Determining Constitution in Organic Chemistry. VII. PAUL PASCAL (*Bull. Soc. chim.*, 1911, [iv], **9**, 134—139). Compare Abstr., 1910, ii, 100, 179, 580; this vol., ii, 91, 183).—In this part the influence of oxygenated functions on molecular magnetic susceptibility is discussed. This influence depends on (*a*) the mode of saturation of the oxygen valencies, (*b*) the structure of the rest of the molecule. The values assigned to the various effects included under (*a*) have been given already (Abstr., 1909, ii, 859; 1910, ii, 100), and they apply both to saturated, normal, aliphatic substances and to polymethylenes, free from side-chains. As regards effects included under (*b*) it is found that a branched-chain compound has always a higher magnetic susceptibility than the normal isomeride. The presence of a tertiary carbon atom in position α, γ, δ, or ϵ, with respect to the oxygen atom, raises the susceptibility by $-13{\cdot}5\times10^{-7}$; in position β the effect is $-5{\cdot}0\times10^{-7}$; in ζ or η it is $-8{\cdot}0\times10^{-7}$, and in θ it is *nil*. The corresponding values for a quaternary atom are -16×10^{-7}, -5×10^{-7}, -10×10^{-7}, and *nil*. These results can be extended to closed-chain compounds, with the convention that a cyclic carbon is regarded as tertiary if it carries no side-chain and as quaternary if it does. The influence of the nucleus is confined to that of the carbon atom joined directly to the oxygen, and other side-chains produce no effect. The study of magnetic susceptibility throws very little light on the internal structure of oxygenated aromatic compounds, since the results are the same for diagonal linkings as for alternate single and double linkings.

The application of these rules is illustrated in the original in the case of *as*-diphenylpentadienone, where the calculated value is -1469×10^{-7}, and the value found is -1462×10^{-7}. The magnetic susceptibility of furfuraldehyde is -492×10^{-7}, whilst that calculated on the assumption that there are two diagonal linkings is $-496{\cdot}5\times10^{-7}$. This view of its structure is in harmony with the results of Marquis's nitration experiments (Abstr., 1901, i, 222; 1903, i, 50; 1905, i, 224).

T. A. H.

Use of the Magnetic Field in Determining Constitution in Organic Chemistry. VIII. PAUL PASCAL (*Bull. Soc. chim.*, 1911, [iv], **9**, 177—182).—The discussion of the influence of oxygenated functions on magnetic susceptibility (preceding abstract) is continued.

Investigation of *iso*amyl ether, phenyl ether, benzophenone, xanthone, and similar symmetrical substances shows that in these cases the disturbing influence of tertiary and quaternary carbon atoms on magnetic susceptibility is eliminated, whence the following rule is deduced: when an open-chain compound contains an oxygen atom joining two identical groups, or when a carbonyl group unites two identical radicles, the influences of tertiary or quaternary carbon atoms in the radicles mutually destroy each other.

The magnetic susceptibility of anthraquinone is best explained by referring this substance to anthracene, and supposing it to contain four binuclear and eight uninuclear carbon atoms, which is tantamount to accepting the representation of this compound, and also that of phenanthraquinone, by diagonal linkings.

The influence of a methoxyl group is equal to $+5\times10^{-7}$.

A long list of calculated and experimental values for the magnetic susceptibility of oxygenated compounds is given, showing good agreement between the two sets of values.

T. A. H.

Modification of the Reichert Thermoregulator. E. FONTAINE (*Ann. Chim. anal.*, 1911, **16**, 52—53).—In the Reichert thermoregulator the level of the mercury is altered by means of a screw at the end of a horizontal side-tube. In the present modification the outer half of the side-tube in bent upwards parallel with the main tube of the regulator, and contains a cylinder of wood which does not touch the walls. The position of the cylinder in the mercury, and therefore the level of the mercury in the main tube, can be altered by means of the screw. G. S.

Conduction of Heat Through Rarefied Gases. II. FREDERICK SODDY and ARTHUR JOHN BERRY (*Proc. Roy. Soc.*, 1911, *A*, **84**, 576—585. Compare Abstr., 1910, ii, 180).—Measurements of the conduction of heat in argon, helium, and hydrogen at very low pressure from an electrically heated platinum strip stretched through a long exhausted tube have been continued at various temperatures of the strip and the surrounding bath in order to test the theory that for the light gases the interchange of energy is imperfect after a single impact with the surface. The experiments were performed with the temperature of the bath from − 185° to 187°, and of the strip from − 120° to 264°. In an addendum a correction is made in the results owing to the pressure measured in the guage not being the same as the real pressure in the tube containing the heated strip, on account of the difference of temperature between them (Knudsen). The theoretical values for the conductivity calculated from the kinetic theory are also multiplied by a correcting numerical factor (Smoluchowski). The corrected results for the ratio of the observed to the calculated conductivity show that in helium and hydrogen the ratio is highest at the lowest temperature, and decreases with rise of temperature. For argon the influence of temperature is small and irregular. Hydrogen showed the same value of the conductivity whether the heated surface was of palladium or platinum. The reason why the heat conductivity of gases, especially of the lighter gases, is less than that calculated from the kinetic theory remains undecided. F. S.

Specific Heats of Barytes, Witherite, Fused Lime, Quartz, and Chalcedony at High Temperatures. P. N. LASCHTSCHENKO (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1604—1614).—The specific heat of barytes increases practically linearly with rise of temperature from 0·1137 at 150° to 0·1486 at 1050°, this result being in agreement with the absence of any indication of polymorphism in barium sulphate.

In the case of witherite, the specific heat rises from 0·1158 at 250° to about 0·13 at 615°, then remains almost constant up to 800°, becomes 0·1429 at 810°, again increases slowly to about 0·16 at 910°, and falls from 0·1620 at 1030° to 0·1500 at 1060°. These results indicate a molecular transformation of witherite at 800°; the heat of transformation is found to be 1·76 Cal. per 1 gram.-mol.

With lime fused in a Moissan electric furnace, the specific heat is 0·172 at 190°, 0·181 at 375° and 400°, 0·190 at 415°, after which it increases gradually to 0·193 at 590° and 680°. Fused lime hence undergoes transformation at 400—415°, the heat of transformation being 0·28 Cal. per gram.-mol.

The specific heat of chalcedony increases from 0·1930 at 139° to

0·2039 at 224°, 0·2484 at 230°, 0·2485 at 247°, and 0·2530 at 442°. The heat of the transformation, which occurs at 224—230°, is 0·523 Cal. per 1 gram.-mol. of silica.

With quartz, the specific heat increases slowly from 0·2250 at 200° to 0·2350 at 580°. At 600° it becomes 0·2400, the heat of the transformation at 580—600° being 0·181 Cal. per gram.-mol. of silica. The specific heat then rises to 0·2480 at 650°, and beyond 700° diminishes slightly. T. H. P.

Convenient Attachments for a Melting-point Apparatus. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1911, **33**, 83—84).—A new form of melting-point apparatus has recently been described by Menge (*Bull.* No. 70, *Hyg. Lab. U.S.P.H. and M.H. Serv.*). The bath requires to be stirred continuously during a determination, and the heat must be so applied that the temperature rises at a certain constant rate before the m. p. is reached, and at a slower constant rate whilst the compound is melting. In order to facilitate these operations, a simple attachment, driven by a small water-motor, has been constructed to move the stirrer automatically, and an arrangement has been devised to ensure constant heating by the Bunsen burner. The latter device consists of a piece of wire gauze fixed in a horizontal position about an inch above the burner, and an ordinary lantern chimney to surround the flame. The upper end of the chimney is nearly closed with a piece of asbestos board provided with a hole, through which the bath of the melting-point apparatus passes. E. G.

Laws of Distillation of Liquid Binary Mixtures. C. MARILLER (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 473—490, 537—559).—A mixture of two mutually insoluble liquids boils when the sum of the vapour pressures ($P_1 + P_2$) equals the external pressure, that is, at a temperature which may be lower than the boiling point of both liquids separately. The distillate contains the two liquids in the constant proportion $M_1P_1 : M_2P_2$, where M_1 and M_2 are the molecular weights of the two liquids. This formula, established by Regnault and by Gernez, holds very closely for mixtures of carbon disulphide and water. Any substance, such as water, with a product MP which is small, appears in a mixed distillate in relatively small amount. The proportions in a distillate can be varied at will by distilling under increased or diminished pressure, a fact which finds technical application in the distillation of brandy where a high pressure leads to increased bouquet. The proportions are also altered by the presence of dissolved solids which diminish the vapour pressure of their solvents.

In the case of completely miscible liquids, such as water and alcohol, Duclaux established that $da/dw = Ka/(a+w)$, where da, a are the proportions of alcohol, and dw, w the proportions of water in vapour and liquid phases respectively. In ascending the series from methyl to octyl alcohol, K increases, that is, methyl alcohol is the most difficult alcohol to dehydrate by distillation. The ratio da/a diminishes to a value very near 1 as the strength of ethyl alcohol approaches 95%, so that the last traces of water are difficult to remove by distillation.

If the volumes A, w, of the vapours of alcohol and water are considered instead of da, dw, the constant K must be multiplied by a factor to take account of the various densities. The modified constant has a value about 4·8 for the first three, soluble, alcohols and 8·0 for the next three, partly soluble, alcohols in the aliphatic series. The author deduces theoretically that in the range of concentrations for which Duclaux' equation holds, the vapour tension of the water is the same as the tension of pure water, and the boiling point of all these water–alcohol mixtures must be below that of water. The tension of the alcohol, however, is approximately proportional to its concentration. The volumes of each substance in the vapour phase are strictly proportional to the vapour pressures, so that by determining the composition of the distillate the vapour pressures in the original mixture can be deduced. Experimental data for ethyl alcohol show that, in fact, the vapour pressure of the water is not affected until the proportion of alcohol exceeds 20% by volume. Further addition of alcohol increases the vapour tension of the water, a maximum increase of 6% being attained at 40% alcohol, after which a progressive decrease occurs.

In rectifying alcohol the depth of liquid in the retort appears to have no influence on the strength of the distillate, but rapid evaporation or evaporation from a small surface or under reduced pressure gives a distillate richer in water than slow evaporation or evaporation in a current of air. Violent ebullition by radiant heat was avoided in the author's experiments. Sodium hydroxide, copper sulphate, potassium carbonate, potassium alum, or potassium sodium tartrate may bring about a separation into two phases. So long as two phases exist the distillate is of constant composition, but single phase mixtures containing salts may yield a distillate which is richer or poorer than the residue according to the various concentrations.

Methyl alcohol behaves similarly to ethyl alcohol, but is generally more difficult to dehydrate by distillation. Propyl alcohol–water mixtures resemble hydrogen chloride, giving a certain constant boiling mixture for each pressure. At 760 mm. this mixture contains 77% of propyl alcohol. All other mixtures tend to attain this composition on boiling. The higher alcohols behave normally up to the limit of their solubility, but when two phases are present a distillate of constant composition is obtained.

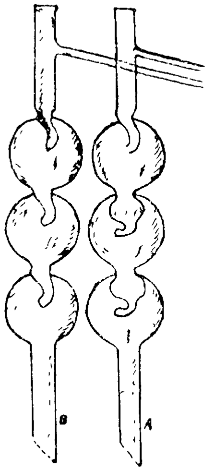
Formic and acetic acids are concentrated by evaporation, whereas propionic and butyric acids give constant boiling mixtures with water, above which strength the pure acids become tail products of the distillation.

The usual evaporation formula does not hold for dilute solutions of acetic acid, which is supposed to be partly polymerised in the gaseous phase.

Mixtures of ethyl alcohol with benzene or ether and of benzene with acetic acid behave similarly to ethyl alcohol–water mixtures. Ethyl alcohol with carbon disulphide or acetonitrile and methyl alcohol with acetonitrile behave like propyl alcohol–water mixtures, there being in each case a constant boiling mixture. R. J. C

Composition and Vapour Pressure of Solutions. IV. Change in Composition of Mixtures of Constant Boiling Point. M. S. VREVSKY (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1349—1355).—The author extends his previous theoretical considerations (Abstr., 1910, ii, 1038) to the cases of binary liquid mixtures forming constant-boiling mixtures possessing (1) a maximum, and (2) a minimum vapour pressure. It is shown that, if, on raising the temperature, the proportion of the component *A* in the vapour increases, then in case (1) the proportion of this component, and in case (2) that of the other component, increases in the mixture cf constant boiling point.

By means of the results of Roscoe's measurements of the compositions of aqueous hydrochloric, hydrobromic, hydriodic, and formic acids having constant boiling points (*Annalen*, 1860, **116**, 203; 1863, **125**, 321), and of Thomsen's values for the heats of dilution of these acids with water (*Thermochemische Untersuchungen*), the following general conclusions are attained. Rise of temperature of a solution having a maximum (minimum) vapour pressure produces, in the mixture of constant boiling point, an increase in the proportion of that component the evaporation of which involves the greater (less) expenditure of energy. T. H. P.



New Rectification Tubes. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 501).—The laboratory still-heads shown in the annexed illustration are self-explanatory. The form *A* is more efficient than *B* for the same number of bulbs. R. J. C.

An Electrically Heated Vacuum Fractionation Apparatus. H. S. BAILEY (*J. Amer. Chem. Soc.*, 1911, **33**, 447—450).—A special apparatus for the fractional distillations of essential oils is described. The bottom of the flask is made as narrow as possible, so that on working with 50 c.c. portions all but the last 5 c.c. may be distilled. The heater is a coil of German silver or nichrome wire sealed into the narrow portion of the flask.

The apparatus is so designed that the successive fractions may be collected without releasing the vacuum. T. S. P.

"Simple" and Complex "Systems" of Thermodynamical Chemistry. JOHANNES J. VAN LAAR (*Zeitsch. physikal. Chem.*, 1911, **76**, 67—74).—The "simple" system of thermodynamic chemistry recently put forward by Washburn (Abstr., 1910, ii, 391) possesses no substantial advantage over the other methods depending on cyclical processes, and in the author's opinion is much inferior to the method based on thermodynamic potential. Some details of Washburn's paper are also adversely criticised. G. S.

The Heat of Solution of Fused Mixtures of Potassium and Sodium Nitrate. JAN VON ZAWIDZKI and A. SCHAGGER (*Chem. Zentr.*, 1910, ii, 1025; from *Kosmos*, 1910, 35, *Radziszewski Festband*, 498—505).—The heats of solution in water of mechanical and of fused solidified mixtures of potassium and sodium nitrate have been measured. In both cases the observed heats of solution are in agreement with those calculated from the values for the pure substances according to the mixture rule. Since the two nitrates form a complete series of mixed crystals, it follows that the heat of formation of the mixed crystals must be extremely small. H. M. D.

Relations between the Density, Temperature, and Pressure of Substances. RICHARD D. KLEEMAN (*Phil. Mag.*, 1911, [vi], 21, 325—341. Compare Abstr., 1910, ii, 22, 492, 600, 932; this vol., ii, 34, 97).—Further relationships between the pressure, volume, temperature, and the latent heat of vaporisation are deduced from the assumed law of molecular attraction. It is also shown that this law leads to the theory of corresponding states, and that the equation corresponding with this theory must apply to all states of matter. H. M. D.

Dilatometric Investigations of Hydrolytic Decompositions. GINO GALEOTTI (*Zeitsch. physikal. Chem.*, 1911, 76, 105—126).—The hydrolytic decomposition of sucrose, ethyl acetate, starch, peptone, and proteins is accompanied by a diminution of volume, independent of whether the change is effected by acids or by enzymes. The rate of change of volume proceeds parallel to the rate of the reaction, and in certain cases (hydrolysis of sucrose and of ethyl acetate) it has been found possible to determine the rate of reaction by measuring the volume change.

The diminution of volume takes place independently of whether pressure accelerates or retards the reaction. From the results the conclusion must be drawn that water occupies a smaller volume in the combined state than when it forms part of the solvent. G. S.

Viscosity of the Liquids used for the Mechanical Separation of Minerals. ENRICO CLERICI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 45—50).—The author has determined the viscosity of sixteen liquids used for this purpose, including the solutions of barium mercuribromide, thallium formate, thallium malonate, and the mixture of the two last proposed by him. R. V. S.

The Turbulence Viscosity of Different Liquids. EMIL BOSE and MARGRETE BOSE (*Physikal. Zeitsch.*, 1911, 12, 126—135).—The observations of Bose and Rauert (Abstr., 1909, ii, 645) relating to the viscosities of liquids when in a condition of "hydraulic" flow are subjected to analysis. For the same liquid, the times (z) required for the discharge of a given volume through the same tube at different pressures can be represented by

$$\log. 1/z = A + B \log. p + C(\log. p)^2 + D(\log. p)^3.$$

The connexion between the density, the Poiseuille coefficient of viscosity, and the "critical" time of discharge is found to be the same for the other liquids examined as for water. H. M. D.

Van der Waals' Theory of the Liquid State from the Standpoint of Viscosity Phenomena. MARYAN SMOLUCHOWSKI (*Chem. Zentr.*, 1910, ii, 1015; from *Kosmos*, 1910, **35**, *Radziszewski Festband*, 543—549).—The theory of van der Waals is examined with reference to the viscosity of liquids. It is shown that the theory of corresponding states offers no explanation of the relationships between the viscosities of different liquids. From the measurements of Warburg and Sachs of the increase in viscosity with increase in pressure, the author calculates the change in viscosity with the temperature at constant volume in the case of benzene and ethyl ether. This is not in agreement with the requirements of the generalised van der Waals' theory. H. M. D.

Measurements of Surface-Tension. R. MAGINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 30—37. Compare Abstr., 1910, ii, 932).—The author's measurements of the surface-tension of water by the method of maximum pressure of small bubbles show that the surface-tension when the water is first brought into contact with air is 73·692 dynes per cm. at 18°, whilst after complete aeration it has decreased to 73·065 dynes per cm., at which value it remains constant; the difference exceeds the limit of experimental error of the method. This water of constant surface-tension serves as a control of the accuracy of the experimental method.

Equimolecular solutions of maleic and fumaric acids affect equally the surface-tension of ethyl alcohol (95%).

The surface-tension of absolute ethyl alcohol is 23·33 dynes per cm. at 15°, and is a linear function of the temperature down to the m. p. R. V. S.

Observations on the Surface-Tension of Liquid Sulphur. W. A. DOUGLAS RUDGE (*Proc. Camb. Phil. Soc.*, 1911, **16**, [i], 55—63).—Measurements of the angle of contact between glass and drops of liquid sulphur have been made at different temperatures. The angle of contact changes when the temperature reaches 185°, and again at 256°, the observed angles at 130°, 190°, and 260° being 60°, 43·4°, and 26·6°.

From the rise of the liquid in a capillary tube at 133°, the surface-tension was found to be 11·56 dynes per cm. At higher temperatures the capillary behaviour is somewhat anomalous, but there appears to be no sudden change at the temperatures at which the angle of contact of the liquid drops exhibits variations. H. M. D.

Adhesiveness. MAURICE HANRIOT (*Compt. rend.*, 1911, **152**, 369—372. Compare this vol., ii, 118).—When two plates of brown gold are heated below the temperature at which they rapidly pass into ordinary gold, and then brought into contact, strong adhesion takes place between them. The phenomenon is not due to electric or magnetic action, and it appears to be possible for it to occur only during the actual transformation of one variety of gold into the other. W. O. W.

Adsorption from Solution. ROBERT MARC (*Zeitsch. physikal. Chem.*, 1911, **76**, 58—66).—Remarks on the recent paper on this subject by Schmidt (Abstr. 1910, ii, 1041). The author agrees with Schmidt that there is an upper limit of adsorption, but points out that the greater part of the experimental curve obtained by Schmidt is represented at least as well by the usual logarithmic adsorption formula as by that of Schmidt, whereas the latter is quite inapplicable for slight adsorption. It is suggested that the adsorption curve obtained by plotting amounts adsorbed as ordinates against concentrations as abscissæ is discontinuous; above a certain concentration it becomes practically horizontal, and can therefore not be represented by a single formula. G. S.

The Adsorption of Sugar in Aqueous Solution. Georg Wiegner and Frerik Burmeister (*Zeitsch. Chem. Ind. Kolloide,* 1911, **8**, 126—133).—Experimental data are recorded which show that sucrose and lactose are removed from aqueous solutions of different concentrations by animal charcoal in accordance with an exponential adsorption formula. The magnitude of the adsorption is approximately the same for the two sugars. The adsorption is probably due to a reduction of the surface-tension at the surface of contact between the charcoal and the solution, and although the sugars increase the surface-tension of water at the air contact surface, this is not the case for other contact surfaces, as is shown by reference to data for the surface-tension of solutions in contact with mercury.

Lactose is also absorbed by animal charcoal from milk, but to a smaller extent than from pure aqueous solutions. This is attributed to the emulsoid character of milk which brings other surface contact factors into play. H. M. D.

Solid Solutions in the Dissociation Oxides. Lothar Wohler (*Zeitsch. Elektrochem.,* 1911, **17**, 98—103).—The author maintains that the changes in the dissociation pressure of an oxide at constant temperature are due to the formation of solid solutions, and not as Allmand (Trans., 1910, **97**, 618) has supposed, to changes in the size of the molecules. T. E.

Methods of Investigation of Capillary Chemical Problems. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide,* 1911, **8**, 133—138). —Polemical against Pawloff (Abstr., 1910, ii, 1043). The author maintains the correctness of his views relative to the nature of the surface layers of crystalline substances, and points out that these are in agreement with all experimental observations. H. M. D.

Capillary Analysis of Colloidal Solutions. Fritz Fichter and Naima Sahlbom (*Chem. Zentr.,* 1910, ii, 1088—1089; from *Verh. Naturf. Ges. in Basel,* 1910, **21**, 1—24).—Most of the results have been published previously (compare this vol., ii, 100). The positive colloids which have been found to be precipitated in the capillary rise of solutions through strips of unsized paper are ferric, chromic, aluminium, ceric, cupric, and ruthenic oxides, and zirconium and thorium dioxides. The phenomenon varies with the kind of paper used, and, in the case of thin sheets, it is only observable if evaporation of the water is prevented. The following negative colloids are not precipitated:

Prussian-blue, cupric ferrocyanide, uranyl ferrocyanide, arsenic trisulphide, antimony trisulphide, selenium, gold, silver, and vanadic acid.

The potential difference which causes precipitation of the positive colloids has been measured for ferric oxide solutions and found to diminish as the concentration diminishes. The potential difference, calculated from measurements of the limiting diameter of glass tubes which show the precipitation effect, is in moderate agreement with the observed values.

The capillary precipitation phenomena may be utilised for testing the progress of dialysis, for comparing different kinds of paper, and for the investigation of the degree of hydrolysis of salt solutions.

H. M. D.

Mixtures of Acetic Acid with Normal Liquids. L GAY (*Compt. rend.*, 1911, **152**, 518—519. Compare Abstr., 1910, ii, 935, 1043).—The conclusion previously arrived at on theoretical grounds, that for two fluid phases in osmotic equilibrium with a common constituent at infinite dilution, the variations in volume should be equal at the same temperature and pressure, has now been experimentally verified for mixtures of acetic acid with toluene, ethylene dibromide and propylene dibromide. On the other hand, mixtures of acetic acid with chloro- and bromo-benzene, ethylene dichloride, and ethyl nitrate show an increase in volume smaller than that observed on making the preceding mixtures. Acetic acid and ether show marked contraction on mixing. W. O. W.

Diffusion [of Dissolved Substances]. BARTOLO L. VANZETTI (*Nuovo Cim.*, 1910, [v], **20**, ii, 442—444).—Polemical. A reply to the criticisms of Scarpa (Abstr., 1910, ii, 1044). Factors of importance in the author's experiments are not allowed for by the formulæ used by Scarpa. The observed deviations cannot be due solely to false equilibrium, because that does not explain the behaviour of the lithium and sodium salts, and the fact that the deviations do not accord with theoretical expectations does not necessarily invalidate the author's method. R. V. S.

A New Dialysor. RICHARD ZSIGMONDY and R. HEYER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 123—126).—A new form of dialysor is described in which the dialysing membrane, consisting of a thin sheet of collodion, forms the ceiling of a shallow compartment into which water enters at the centre and is made to flow rapidly towards the circumference. The flow of water is maintained by the aid of strips of blotting paper which are supported at the periphery of each radial section. With this apparatus, it was found that the solution, prepared by mixing 200 c.c. of water glass and 40 c.c. of concentrated hydrochloric acid, was practically free from chlorine after dialysis had proceeded for twenty hours. Comparative experiments in which the "star" dialysor was filled with a collodion and a parchment membrane showed that the former acts much more rapidly than the latter.

H. M. D.

Solubility Studies. Walter Herz (*Zeitsch. anorg. Chem.*, 1911, **70**, 70—72. Compare Abstr., 1910, ii, 192).—The solubility of succinic acid in water is lessened by the addition of hydrogen chloride or bromide, the effect being greater than that produced by alkali salts, with the exception of lithium chloride. The two halogen acids are equal in their influence.

The solubility of boric acid in water is increased to an equal extent by tartaric and racemic acids. C. H. D.

Pseudo-solutions or Apparent Solutions According to Francesco Selmi. Icilio Guareschi (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 113—123).—Quotations are given from various papers published by F. Selmi which show that this author was probably the first to recognise the special characteristics of colloidal solutions, and already in 1846–1847 applied the term pseudo-solutions to those solutions which are now distinguished as colloidal disperse systems.
H. M. D.

The "Precipitation Coefficient" of P. P. von Weimarn. P. N. Pawloff (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 138—141; *J Russ. Phys. Chem. Soc.*, 1910, **42**, 1650).—According to von Weimarn the size of the particles of a precipitated substance is determined by a coefficient $N = P/L$, where P is the rate of formation of the crystalline substance, and L the concentration of the solution from which precipitation takes place. This conception of a precipitation coefficient is criticised, and a simpler method of deducing the connexion between the degree of dispersity of a precipitate and the properties of the mother solution is indicated. According to this view, the degree of dispersity of a precipitate at a given temperature is determined by (1) the free energy at the surface of contact with the solution, (2) the molecular weight of the dissolved substance, (3) the concentration of the solution in contact with the actual precipitate, and (4) the concentration of the solution in contact with the macro-crystalline substance. H. M. D.

The "Precipitation Coefficient." P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 141—143).—A reply to Pawloff (compare preceding abstract), in which the outlines of the author's views are again brought forward. H. M. D.

Mechanical Stimulus to Crystallisation in Supercooled Liquids. Stewart W. Young (*J. Amer. Chem. Soc.*, 1911, **33**, 148—162).—Ostwald has stated that when a liquid is cooled below its m. p., it remains through a certain range of temperature in the metastable state, in which it cannot crystallise spontaneously, even under the influence of stirring, but that, as the supercooling is increased, the substance passes out of the metastable into the labile state, in which the conditions are entirely changed, and crystallisation must occur spontaneously sooner or later. Numerous attempts have been made to determine the temperature at which a given substance passes from the metastable into the labile condition, but without much success. De

Coppet (Abstr., 1901, ii, 384) made a study of the spontaneous crystallisation of sodium sulphate and other substances, as a result of which he was led to the conclusion that a definite metastable limit does not exist, but that the transition from the metastable to the labile condition is very gradual.

In a series of cryoscopic experiments with water with the ordinary Beckmann apparatus, it was found that much less supercooling was possible when a platinum or copper stirrer was employed than when a glass one was used. The simplest explanation of this seemed to be that crystallisation was promoted by the friction between the stirrer and the thermometer, and that this varied with different stirrers.

Experiments were next made in which friction was generated between a movable rod and a fixed ring, the liquid being stirred meanwhile by means of bubbles of pure hydrogen. Both rod and ring were made of various substances, and the results showed that the effect of the friction was greater between rough than between smooth surfaces.

In another series of experiments, friction was produced by the rotation of a rod with a conical tip, which moved in a similarly formed conical bearing, and the conclusion was reached that the factor which stimulated crystallisation was not pure friction, but consisted of a succession of small impacts between points on the surfaces.

Experiments were therefore carried out in which an apparatus on the principle of a stamp mill was employed, which was worked by means of a small motor. The stamp consisted of a steel rod, which carried a bit at the end, and was allowed to drop through a guide and strike upon an anvil on which was cemented a flat disk. Both bit and disk could be changed in order to permit of experiments being made with any desired materials. Measurements were made with water, benzene, and a concentrated solution of calcium chloride hexahydrate, and the relations between the number of degrees of supercooling and the impact values are shown by means of curves.

The results show that it is no longer justifiable to assume the existence of a metastable limit, since the whole unstable field is labile, and crystallisation may be brought about in any portion of it by the production of sufficient mechanical shock.

Interesting results were obtained with a solution of sodium sulphate, this being a case in which the supercooled liquid can yield more than one phase. E. G.

Habit of Crystals of Artificial Barytes. HILDA GERHART (*Tsch. Min. Mitt.*, 1910, **29**, 185—191).—The experiments were made with the idea of determining the influence of various salts in solution on the habit of the resulting crystals (compare Abstr., 1910, ii, 276). The salts employed were barium chloride and one or other of the sulphates of iron, sodium, magnesium, or ammonium, or potash-alum, either alone or with the addition of potassium nitrate. An excess of one salt (in some experiments the chloride, and in others the sulphate) was placed in the solid form at the bottom of a reagent-glass, and covered with a thick layer of silica jelly; a solution of the other salt was placed over the separating layer, and the whole kept at an equable temperature for some months. Crystals of barytes, measuring up to 0·1 mm. across, were formed mostly in the upper portion of the silica jelly; these have the form of plates, *a*(100), with irregular outlines, or of boat-shaped forms flattened parallel to *b*(010). The greatest influence in the form of the crystals is produced by the presence of potash-alum and potassium nitrate. The presence of sodium sulphate favours the growth of skeletal forms. L. J. S.

Crystallisation, Dissolution, and Regeneration Polyhedra of Potassium- and Ammonium-aluminium Alums in Aqueous Solutions containing Hydrochloric and Nitric Acid. ZYGMUNT WEYBERG (*Chem. Zentr.*, 1910, ii, 1026; from *Kosmos*, 1910, **35**, *Radziszewski Festband*, 487—494).—Small quantities of hydrochloric acid have no influence on the crystalline form of the alums. When the acid concentration amounts to 6 grams per 100 grams of water, the surfaces (211) and (201) appear on the crystals. With increasing concentration, the surfaces (211) and (110) disappear and (201) becomes more developed. In solutions which contain more than 25 grams of acid per litre, crystals are formed which exhibit the surfaces (100), (111), and (211).

Similar observations relating to the dissolution and regeneration of crystals indicate that in all cases the same modifications of the exposed form are determined by a given concentration of hydrochloric acid. Nitric acid has a similar action, but more concentrated solutions are required to produce the same effects. H. M. D.

Confirmations of the New Theory of the Phenomenon of Allotropy. ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 822—829).—Observations relating to differences in the behaviour of white phosphorus at its melting point are interpreted in terms of the theory that the liquid and solid consist of allotropic forms which are in dynamic equilibrium (compare Abstr., 1910, ii, 195, 400).

A method of purifying white phosphorus is described, in which the element is distilled and subjected to a series of fractional crystallisation processes in a highly exhausted apparatus. By this means a perfectly colourless, coarsely crystalline product is obtained, which on immersion of the melting-point vessel in a thermostat, the temperature of which varied slowly, was found to melt at 44·0° within a range of 0·02°. This is regarded as the unary melting point.

When the pure phosphorus is maintained in the liquid condition for some time, the unary temperature is no longer found on solidification. The actual behaviour depends on the heat treatment and on the rate of cooling, and the cooling and heating curves which have been obtained for white phosphorus under different conditions are considered to indicate a partial conversion of white phosphorus into an allotropic modification. H. M. D.

Condensed Disperse Systems. P. N. PAWLOFF (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1631—1649).—A mathematical paper, in which the author deals with surface energy, the degree of dispersion of the phase in the condition of most stable equilibrium, formation of disperse precipitates in solutions, the equilibrium of the system drops + vapour, monotropic and enantiotropic substances, position of the stable region of highly disperse crystalline condition among substances in other states, and the surface energy of crystalline substances. T. H. P.

The Determination of Three-Phase Pressures in the System: Hydrogen Sulphide and Water. F. E. C. Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 829—837).—Pressure measurements at different temperatures have been made for the three-phase systems (*SLV*), (*SL′V*), and (*LL′V*), where *S* represents a solid compound, *L* and *L′* liquid phases, and *V* the coexisting vapour. The data show the existence of a quadruple point at 29·5° and 22·1 atmospheres. A comparison of the pressure-temperature curves for the systems (*SLV*) and (*LL′V*) with that representing the vapour pressure of pure hydrogen sulphide indicates that they are nearly identical. H. M. D.

The Equilibrium between Nitric Acid, Nitrous Acid, and Nitric Oxide. Gilbert N. Lewis and Arthur Edgar (*J. Amer. Chem. Soc.*, 1911, **33**, 292—299).—The results obtained by Saposchnikoff (Abstr., 1902, ii, 16) for the equilibrium constants in the reaction: $3HNO_2 = HNO_3 + 2NO + H_2O$ and with acid concentrations ranging from 0·05*N* to 3·0*N* not being entirely concordant, the authors have re-investigated the matter.

The method employed consisted in passing a stream of nitric oxide through a tenth-normal solution of nitric acid at 25° in a vessel which permits the measurement of the electrical conductivity of the solution. The conductivity is measured from time to time until it attains a constant value. Since the conductivity of the nitrous acid produced is almost negligible in the presence of the nitric acid, and can readily be allowed for, the change in conductivity is very nearly proportional to the amount of nitric acid decomposed.

The reaction is complete after about fifty hours, and in five different experiments very concordant results were obtained. The value of the constant $K = (HNO_3)^3/(H^{\cdot})(NO_3')$ is found to be 0·0267 at 25°. The value obtained by Saposchnikoff, starting with nitric acid of the same concentration, was 0·0175. If, however, his results are re-calculated, using the same value for the degree of dissociation of the nitric acid as that used by the authors, the value becomes 0·0208.

Some experiments made with 0·2*N*-nitric acid seem to indicate a change in the equilibrium constant with the concentration.

T. S. P.

A New Method for the Analysis of Some Binary Compounds, Based on the Law of Mass Action. Otto Ruff (*Ber.*, 1911, **44**, 548).—A claim of priority over Ostromisslensky (this vol., ii, 195). C. S.

Chemical Formulæ of Certain Eutectics and Transition Points. Alex. Gorboff (*J. Russ. Phys. Chem. Soc.*, 1910, **42**, 1517—1529).—The author applies the views previously expressed

(Abstr., 1910, ii, 111) to the data published for a large number of eutectic mixtures by various authors, and derives formulæ for the compounds which the components of the eutectics form with one another. For the details of his conclusions the original must be consulted. T. H. P.

Application of the Phase Rule to Stereoisomeric Compounds and the Recognition of Racemic Compounds. Albert Ladenburg (*Ber.*, 1911, **44**, 676—680. Compare Abstr., 1910, i, 696, 769, also Roozeboom, Abstr., 1899, ii, 732).—To determine whether a given substance is a racemic or an inactive mixture a saturated solution is prepared which is optically inactive, and a small quantity of one of the optically active components is then added. If a mixture is present the solution remains inactive, but if the racemic compound is present the solution becomes optically active (compare Ladenburg, Trans., 1899, **75**, 465; Abstr., 1899, ii, 551).

The phase rule only applies to stereoisomerides in the case of liquids if the various forms are taken as representing one component.

Measurements of the vapour pressure and refractive index of various mixtures of racemic and *d*-pipecoline show for liquids how closely the properties of the racemate approximate to those of its components. There is no doubt that liquid racemates exist. E. F. A.

Velocity of Crystallisation and Dissolution. Carl L. Wagner (*Zeitsch. Elektrochem.*, 1911, **17**, 125—134); Robert Marc (*ibid.*, 134—139).—Wagner thinks that Marc's experimental results are not sufficiently accurate to decide whether the rate of crystallisation is of the first or second order. Marc replies that if the whole of the results are taken into account there can be no doubt that his interpretation of them is correct (Abstr., 1910, ii, 834; also 1908, ii, 160; 1909, ii, 798, 983). T. E.

Velocities of Reactions in Gas-Liquid Systems. J. Boselli (*Compt. rend.*, 1911, **152**, 374—375, 602—603. Compare this vol., ii, 196).—Experiments on the rate of dissolution of oxygen and carbon monoxide have been made, and the results found to confirm the conclusions arrived at in a previous paper. Two classes of reaction have also been studied. Of the first, the oxidation of, and fixation of, carbon monoxide by hæmoglobin or the oxidation of potassiumpyrogallol and of ferrous oxalate may be taken as examples. The velocity of reaction in such cases is practically independent of the volume of liquid, but varies considerably with the rate of agitation. The oxidation of dextrose in alkaline solution and of ferrous sulphate, with and without a catalyst, have been examined as instances of the second class of reaction. In this group the velocities are proportional to the volume of liquid and independent of the speed of agitation.

The rate of absorption of oxygen by hæmoglobin is the same for warm-blooded vertebrates whether the substance is present in blood, suspended as corpuscles in physiological salt solution, or dissolved in water. It is independent of the reaction of the medium, and is practically uninfluenced by temperature. The speed increases less rapidly than the pressure of oxygen above the liquid, and is proportional to the square-root of the rate of agitation. The same remarks apply to the oxidation of pyrogallol and ferrous oxalate.

The velocity of reaction between ferrous sulphate solutions and oxygen follows Arrhenius' law. Copper salts act as positive catalysts, dextrose and sulphuric acid as negative ones. The rate of oxidation of dextrose in alkaline solution is approximately proportional to the cube-root of the concentration of alkali; ferric potassium tartrate acts as an accelerating catalyst up to a certain concentration.

W. O. W.

Velocity of Decomposition of Dissolved Dithionic Acid. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1911, [iv], **9**, 183—185).—It has been shown previously (Abstr., 1910, ii, 154) that iodine acts slowly on sodium dithionate in presence of acid, in accordance with the equation $Na_2S_2O_6 + I_2 + 2H_2O = 2NaHSO_4 + 2HI$. Investigation of this reaction shows that it is unimolecular in type, whence it must be supposed that three successive reactions occur: (*a*) liberation of dithionic acid, (*b*) decomposition of the latter into sulphurous and sulphuric acids, (*c*) action of iodine on sulphurous acid. The time required for reactions (*a*) and (*c*) is negligible in comparison with that required for (*b*), so that the velocity of (*b*) only is measured. At 51·3° the constant of velocity of decomposition of dithionic acid is 0·00836, under the conditions of these experiments. T. A. H.

Catalysis in a Homogeneous System. JOSEPH A. MULLER (*Bull. Soc. chim.*, 1911, [iv], **9**, 185—188).—Investigation of the influence of (*a*) change of temperature and (*b*) concentration of acid on the velocity of decomposition of dithionic acid by iodine (compare preceding abstract) shows that the velocity of decomposition increases (1) with increasing concentration of acid, and (2) with rise of temperature. Further, investigation of the states of ionisation of acid solutions of the same strengths and at the same temperatures as those used in these experiments shows that there is no relationship between the concentration of hydrogen or chlorine ions and the velocity of decomposition. The conclusion is drawn, therefore, that the decomposition is due to the action of the non-ionised acid. The value of k as a function of the absolute temperature of the system is approximately given by the equation: $k = n(a^{\gamma T} - 1)/(b^T - 1)$, where $n = 4{\cdot}6 \times 10^{-22}$, $a = 1{\cdot}0023$, $b = 1{\cdot}1458$. T. A. H.

Kinetics of the Transformation of Chloroalkylamines into Heterocyclic Compounds. HERBERT FREUNDLICH and A. KRESTOVNIKOFF (*Zeitsch. physikal. Chem.*, 1911, **76**, 79—104).—The rate of transformation of δ-chlorobutylamine into pyrrolidine hydrochloride, $Cl{\cdot}[CH_2]_4{\cdot}NH_2 \longrightarrow C_4NH_9,HCl$, and of ε-chloroamylamine into the isomeric piperidine hydrochloride, $Cl{\cdot}[CH_2]_5{\cdot}NH_2 \longrightarrow C_5NH_{11},HCl$, has been investigated, the change being followed by titrating the ionised chlorine with silver nitrate. The reactions proceed quantitatively according to the above equations in alkaline solution. In acid or neutral solution no change occurs.

With excess of alkali the reactions are unimolecular, and are only very slightly accelerated by greatly increasing the alkali concentration. If to ε-chloroamylamine hydrochloride an equivalent of alkali is added, the reaction proceeds as if only the non-ionised amine is undergoing change, the hydrochloric acid distributing itself between amine and piperidine according to the law of mass action. The slower change when ammonia is used instead of alkali can be interpreted on the same lines. Neutral salts increase the rate of reaction somewhat; alcohol retards it. The temperature-coefficient for 10° between 0° and 10° is 3·9 for the amylamine, 3·6 for the butylamine. The rate of ring formation is about seventy times faster for the butylamine than for the amylamine, a result in accordance with Baeyer's tension theory.

The general question of the transformation of labile bases into their isomerides is considered, and it is shown that when the base in question is strong, the OH′-ion concentration of the base added should have a considerable influence, and the reaction must be bimolecular, whilst for weak bases the OH′-ion concentration should have comparatively little influence, and the reaction must therefore be unimolecular. This is in entire accord with the results of previous observers, who have used strong bases, and of the present investigation, as the amines in question are weak bases. The dissociation constant of ε-chloroamylamine at 0° is about $3 \cdot 10^{-4}$. G. S.

The Development of the Atomic Theory. II. The Various Accounts of the Origin of Dalton's Theory. III. Newton's Theory, and its Influence in the Eighteenth Century. ANDREW N. MELDRUM (*Mem. Manchester Phil. Soc.*, 1911, **55**, No. III, 1—12; No. IV, 1—15).—Historical.

Practical Method for Preparing Semi-permeable Membranes, Applicable to the Determination of Molecular Weights. EUGÈNE FOUARD (*Compt. rend.*, 1911, **152**, 519—521).—A collodion cell, prepared according to the method of Roux and Salimbeni, is filled with a solution of tannic acid and immersed in a gelatin solution. After this treatment it is impermeable to dissolved molecules, but remains pervious to water. To avoid distension of the fragile membrane under pressure, it is deposited on a cylinder of metallic gauze terminating in metal sockets, one of which is fitted with a stopper and manometer. Such a cell is superior to de Vries' apparatus, and may be used to determine molecular weights by comparison of isotonic solutions. The pressure indicated by the manometer with non-isotonic solutions is always lower than the calculated value, van't Hoff's constant for substances of known molecular weight being about 20% less than the theoretical number. W. O. W.

Universal Chemical Language. WILHELM OSTWALD (*Zeitsch. physikal. Chem.*, 1911, **76**, 1—20).—The author makes suggestions for the translation of chemical literature into the universal language Ido, a modified form of Esperanto. The most suitable equivalents in Ido for the names of the elements and of inorganic and organic compounds are discussed in detail. G. S.

Modified Boltwood Pump. Allan F. Odell (*J. Amer. Chem. Soc.*, 1911, **33**, 56).—A diagram is given of a modification of Boltwood's automatic Sprengel pump (Abstr., 1897, ii, 205), which is just as efficient as the larger forms, although occupying only one-third of the space, and requiring only 100 grams of mercury for successful working.

In the manufactured forms of the Boltwood pump, the internal diameter of the dropping tube often deviates considerably from that prescribed (2·5 mm.). It has been observed that low vacua cannot be obtained with tubes slightly wider than 2·5 mm., whilst tubes of smaller diameter than 2 mm. work very slowly. E. G.

New Gas Wash-bottles. Fritz Friedrichs (*Zeitsch. anal. Chem.*, 1911, **50**, 175—176).—The gas inlet tube of the apparatus is expanded into a screw-like form nearly touching the sides of the cylindrical containing vessel, so that there is formed a spiral channel about 125 cm. long, through which the gas bubbles have to pass. Four different forms of this wash-bottle are described and figured.

L. de K.

Simple Device for Use in Fitting Up a Series of Absorption Flasks, etc. Hans Reckleben (*Chem. Zeit.*, 1911, **35**, 279).—The device consists of a wooden lath or rod and a number of short lengths of wire; the absorption flasks, wash-bottles, or U-tubes used for purifying gases are bound to the lath by means of the wires, a couple of turns of the wire being sufficient for the purpose. The lath may be fixed in a clamp-stand so that the series of flasks, etc., attached to it can be arranged at any desired height. W. P. S.

The Efficiency of Calcium Bromide, Zinc Bromide, and Zinc Chloride as Drying Agents. Gregory P. Baxter and R. D. Warren (*J. Amer. Chem. Soc.*, 1911, **33**, 340—344).—Since hydrogen chloride cannot be dried with phosphoric oxide, owing to the formation of volatile phosphorus compounds, it is probable that this will also be the case with hydrogen bromide. It is therefore necessary to investigate the action of various anhydrous bromides as drying agents.

The method used was as follows: A measured amount of moist air was passed through a tube containing a layer of crushed fused bromide, and then through a weighed phosphoric oxide tube. From the gain in weight of the latter and known volume of air passed over the bromide, the pressure of the aqueous vapour in the air which was in equilibrium with the fused bromide could be determined.

Similar experiments were made with zinc chloride in order to compare it with sulphuric acid and calcium chloride as a drying agent for hydrogen chloride.

As shown in the following tables, the first hydrate of zinc bromide has an aqueous vapour pressure six times as great as that of calcium bromide at the ordinary temperature, so that calcium bromide is a much better drying agent than zinc bromide. Zinc chloride is less well suited for drying hydrogen chloride than sulphuric acid, but more so than calcium chloride.

Vapour pressures, in mm. of mercury, of the lower hydrates of:

	0°.	25°.	50°.
$CaBr_2$	0·09	0·18	0·19
$ZnBr_2$	0·28	1·16	6·34
$ZnCl_2$	—	0·85	2·19

The weights, in grams, of residual water in one litre of gas dried at 25° by these salts and by calcium chloride and sulphuric acid are: calcium bromide, 0·0002; zinc bromide, 0·0011; zinc chloride, 0 0008; calcium chloride, 0·0021; sulphuric acid, 0·000003. T. S. P.

Dehydration of Substances by means of Ether. VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm*, 1911, 35, 311—315).—The substance to be dehydrated, which should be insoluble in ether, is spread, in as fine a state of division as possible, on a gauze sheet, which is immersed in ether in a large closed vessel with a capacity of 2—3 litres. The gauze rests on a wire basket, filled with sticks of sodium hydroxide, which is supported by a porcelain dish resting on the bottom of the vessel. The ether dissolves water from the substance, becoming denser thereby and sinking, so that it comes in contact with the sodium hydroxide and is dehydrated again. Circulation is continuous, and as the sodium hydroxide dissolves, the lye falls to the bottom of the vessel; 52 grams of mashed beet containing 78% of water were dehydrated by this means in twenty-four to thirty-six hours. When the substance is partly soluble in ether, it is preferable to use an apparatus in which ether distilled from a flask is condensed, rises through sticks of sodium hydroxide to dehydrate it, and then flows down over the substance back to the distillation flask. E. F. A.

Good Substitute for the Platinum Triangle. RAYMOND C. BENNER (*J. Amer. Chem. Soc.*, 1911, 33, 189—190).—Wire composed of an alloy of nickel and chromium is recommended as a substitute for platinum for making triangles. The alloy is specially adapted for the purpose owing to its resistance to oxidation at high temperatures, and to its being unaffected by the ordinary fumes of the laboratory. Platinum crucibles placed on such triangles were ignited side by side with others on platinum or pipe-clay triangles, and all the crucibles showed the same loss of weight. E. G.

Laboratory Muffle Furnace. M. EMMANUEL POZZI-ESCOT (*Bull. Assoc. chim. Sucr. Dist.*, 1911, 28, 501—502).—A small muffle furnace made of sheet metal is supported on the tube of a single Bunsen burner. The arrangement gives temperatures up to 400°, and is suitable for determining ash in plants, etc. R. J. C.

Lecture Experiment for Demonstrating Chemical Luminescence. ARNOLD HECZKO (*Chem. Zeit.*, 1911, 35, 199.)—A very distinct green luminescence is produced when moist air is allowed to come in contact with a solution of magnesium phenyl bromide in anhydrous ether. The latter solution is most conveniently contained in a round-bottomed stoppered flask, and the luminescence may be caused to appear by removing the stopper and breathing into the flask; when the solution comes into contact with the moist side of the flask, a green light is produced, which fades away after a time. It may be reproduced by the introduction of a further quantity of moist air. Magnesium phenyl iodide exhibits a similar, but less intense, luminescence. W. P. S.

Lecture Apparatus. [Action of Acids on Pure and Impure Zinc.] FRITZ CASPARI (*Chem. Zeit.*, 1911, **35**, 183).—The apparatus described is intended for use in demonstrating the fact that dilute acids attack pure zinc but slightly, if at all, whilst zinc containing traces of other metals is readily attacked. It consists of a U-tube, one limb of which is shorter than the other; a tap is placed on the shorter limb at about one-half its height, and the whole tube except the portion above the tap is filled with dilute sulphuric acid. A rod of pure zinc, one end of which has been immersed in a solution of copper sulphate, is placed in the shorter limb of the tube above the tap, the end of the rod coated with copper being uppermost. When the tap is opened slightly, the acid comes into contact with the zinc, but no evolution of hydrogen takes place until the acid rises sufficiently high to reach the end of the rod which is coated with copper; hydrogen is then evolved rapidly. W. P. S.

Inorganic Chemistry.

Dehydration of Salts. P. E. LECOQ DE BOISBAUDRAN (*Compt. rend.* 1911, **152**, 356—358).—The author takes exception to a statement of Rosenstiehl to the effect that no salts lose only $1H_2O$, except those which contain only 1 mol. Earlier observations are cited (*Compt. rend.*, 1867, **64**, 1249; **65**, 111; *Ann. Chim. Phys.*, 1869, [iv], **18**).

W. O. W.

Polymerised Water and Water of Crystallisation. AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1911, **152**, 598—601).—The observations of Lecoq de Boisbaudran (preceding abstract) are not incompatible with the author's conclusions, since the latter refer to the elimination or fixation of several molecules of water, whereas the experiments of the former observer showed the influence of isomorphism on the addition or removal of one molecule only.

A statistical study of one hundred and seventy-nine salts containing water of crystallisation appears to show that the water may be present as H_2O, or as the groups $(H_2O)_2$ and $(H_2O)_3$, or else as a mixture of the two latter. Thus salts containing 4, 7, and 10 molecules behave on partial dehydration as if the water was combined as $1+3$, $1+6$, and $1+9$ molecules respectively. The complex $(H_2O)_3$ is the one of most frequent occurrence. On dehydrating salts, such groups may be split off without themselves undergoing disruption. W. O. W.

Determination of the Ratio between Chlorine and Bromine and Sodium. JACOB S. GOLDBAUM (*J. Amer. Chem. Soc.*, 1911, **33**, 35—50).—This investigation was undertaken primarily as a test of the applicability of electrolytic methods to work demanding extreme accuracy rather than with the object of revising the atomic weights of chlorine and bromine.

Experiments were carried out in which aqueous solutions of sodium chloride and sodium bromide respectively were electrolysed with a rotating, silver-plated platinum gauze anode and a mercury cathode. The halogen combines with the silver, and the increase in the weight of the anode thus represents the amount of halogen in the salt, corrections being made by means of the nephelometer for the quantity of silver halide dissolved in the liquid in the inner cup. A full description is given of the mode of preparing the anode, and the methods of purifying the materials and conducting the experiments.

The average of the results of a preliminary series of eight experiments with sodium chloride gave the atomic weight of chlorine $35{\cdot}456 \pm 0{\cdot}0037$ ($Na = 23{\cdot}00$), whilst that of a final series of eleven experiments gave the value $35{\cdot}462 \pm 0{\cdot}0005$, or a value for the atomic weight of sodium $22{\cdot}997 \pm 0{\cdot}0003$ ($Cl = 35{\cdot}458$).

The average of the results of eight experiments with sodium bromide gave the atomic weight of bromine $79{\cdot}927 \pm 0{\cdot}0014$ ($Na = 23{\cdot}00$), or of sodium, $22{\cdot}998 \pm 0{\cdot}0003$ ($Br = 79{\cdot}920$). E. G.

Solubility of Oxygen in Sea-Water. GEORGE C. WHIPPLE and MELVILLE C. WHIPPLE (*J. Amer. Chem. Soc.*, 1911, **33**, 362—365). —The authors were engaged in determining the solubility of dissolved oxygen in sea-water of known chlorine content at temperatures of 0°, 10°, 20°, and 30° when Fox's paper on the same subject was published (Abstr., 1910, ii, 29). As far as they had gone their results are in agreement with those of Fox. For convenience of reference they have re-calculated Fox's results in terms of the solubility of oxygen in parts per million of sea-water exposed to an atmosphere containing 20·9% of oxygen. T. S. P.

The Nature of the Uppermost Layers of the Atmosphere. ALFRED WEGENER (*Physikal. Zeitsch.*, 1911, **12**, 170—178).—A theoretical paper in which various geophysical phenomena attributed to the influence of the earth's atmosphere are examined, and from which conclusions are drawn relative to the constitution of the gaseous envelope. According to these, there is a comparatively sudden change in the character of the envelope at a height of about 70 kilometres, and a further similar change at about 200 kilometres. The chief constituent of the outermost layer is a gas lighter than hydrogen, to which the name *geocoronium* is given. The spectrum of this gas is supposed to be responsible for the polar light line at 557 $\mu\mu$. By making certain assumptions, the percentages of nitrogen, oxygen, argon, helium, hydrogen, and geocoronium at different heights are

calculated. These show that hydrogen is the chief constituent of the atmosphere in the intermediate layer between 70 and 200 kilometres.
H. M. D.

A Simple Hydrogen Sulphide Generator. J. I. D. Hinds (*J. Amer. Chem. Soc.*, 1911, **33**, 384—385).—The apparatus consists essentially of a cylindrical vessel containing the ferrous sulphide, the bottom of which ends in a goose-neck tube. The top of the vessel is fitted with a tap-funnel for containing the acid, and a tube with a stopcock for the delivery of the hydrogen sulphide. The goose-neck tube is of such dimensions that a sufficient head of pressure is maintained for the delivery of the gas for ordinary purposes.

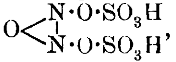
The apparatus possesses the advantages that if the acid is added drop by drop and not in large excess, it will be practically exhausted before it passes out through the goose-neck, and when the stopcock is closed the pressure of the hydrogen sulphide generated automatically expels the waste acid.
T. S. P.

Chemistry of the Lead Chamber Process. Fritz Raschig (*J. Soc. Chem. Ind.*, 1911, **30**, 166—172. Compare Abstr., 1905, ii, 700).—A résumé of our present knowledge of the chemistry of the lead chamber process for the manufacture of sulphuric acid. Some of the conclusions drawn are: (1) Nitrosulphonic acid (nitrosyl sulphate) cannot be an intermediate product in the chamber process, as it is completely destroyed by sulphuric acid concentrations such as those present in the chamber and Glover tower. (2) Nitrosisulphonic acid, H_2NSO_5. is probably the true intermediate product; this is formed by the reaction of sulphur dioxide with nitrous acid, $2HNO_2 + SO_2 = H_2NSO_5 + NO$, and decomposes into sulphuric acid and nitric oxide.

The relations between nitrosisulphonic acid, nitrilosulphonic acid, hydroxylamino-mono- and -di-sulphonic acids, nitrososulphonic acid and their oxidation products are discussed. The conclusion is drawn that a purple or blue colour is due to the presence of a quadrivalent nitrogen atom, and hence the nitrosisulphonic acid should contain quadrivalent nitrogen. As this acid appears to be formed by the oxidation of hydroxylaminosulphonic acid, and on further oxidation yields nitrosulphonic acid, the formula $O{:}N(OH){\cdot}SO_3H$ is suggested. The reaction between nitrous acid and sulphur dioxide leads to the formation of nitrososulphonic acid, $O{:}N{\cdot}SO_3H$, and this with a further quantity of nitrous acid yields nitric oxide and nitrosisulphonic acid, which dissociates into nitric oxide and sulphuric acid.

The purple acid sometimes formed in the Gay-Lussac tower is regarded as nitrosisulphonic acid, and as it continually undergoes decomposition, yielding nitric oxide, its formation produces appreciable loss of nitre. This loss can be avoided by allowing the nitric acid, which is usually supplied to the Glover tower, to trickle down the Gay-Lussac tower, when it oxidises the nitrosi-acid to nitrosulphonic acid and loss of nitric oxide is avoided.

The nitrous oxide which is met with in the exit gases from the leaden chambers (Inglis, *J. Soc. Chem. Ind.*, 1904, **25**, 149) is probably due to the reaction of the nitrososulphonic acid with water instead of with nitrous acid. The formation of this oxide is got over by blowing dilute sulphuric acid instead of water into the leaden chambers. Hydroxylamine and ammonia may also be formed in the chamber, and these with nitrous acid would yield nitrous oxide and nitrogen. When excess of nitrous acid is absent, ammonia can be detected in the chamber acid. J. J. S.

Theory of the Lead Chamber Process. O. WENTZKI (*Zeitsch. angew. Chem.*, 1911, **24**, 392—400. Compare *ibid*, 1910, **23**, 1707; Lunge and Berl, Abstr., 1906, ii, 438; Manchot, Abstr., 1910, ii, 1055).—Mainly a reply to Raschig and Berl (*ibid.*, 1910, **23**, 2241; compare also preceding abstract). Raschig's blue nitrosisulphonic acid is regarded as  $O<\begin{matrix}N\cdot O\cdot SO_3H\\ | \\ N\cdot O\cdot SO_3H\end{matrix}$, and is termed *nitrosylous sulphuric acid*. The objection is raised that Raschig's acid should be a feeble acid, whereas it is capable of displacing sulphuric acid from copper sulphate. Raschig considers that nascent hydrogen combines with the nitrosulphonic to form nitrosisulphonic acid, whereas no hydrogen is formed by the action of mercury on sulphuric acid; the reduction consists in the removal of oxygen from the nitro-acid, and the characteristic deep blue copper salt is represented as $CuO_9N_2S_2$ (compare Manchot, this vol., ii, 107). The author agrees with Raschig and Berl that sulphurous acid does not reduce the blue copper compound.

The view that nitrosisulphonic acid is an important intermediate product in the leaden chamber process is not accepted. The formation of this compound under the conditions prevailing in the chambers is considered impossible, and nitrogen peroxide is considered to be the most probable catalyst.

Sulphuric acid of 50° B contains its oxides of nitrogen in the form of free oxides (N_2O_3), and only with stronger acid, for example, 53—60° B, is nitrosulphonic acid (nitrosylsulphuric acid) formed, and it is only nitro-acids of the higher concentrations which give a blue colour with sulphurous acid. With more concentrated acids, for example, 88%, the nitrosulphonic acid does not appear to be reduced by sulphur dioxide.

The existence of nitrososulphonic acid is questioned. J. J. S.

Hydroxynitrosylsulphuric Acid. EVERARDO SCANDOLA (*Chem. Zentr.*, 1910, ii, 543. Reprint from *Bol. Soc. med.-chirurg.*, *Pavia*, 1910, 11 pp.).—The acid, $OH\cdot NO\cdot SO_3H$, termed hydroxynitrosylsulphuric acid, described by Lunge, Fremy, Raschig, and others as nitrosylsulphuric acid [nitrosisulphonic acid], is also obtained by the careful decomposition of sulphuric acid, solutions of alkyl nitrates or nitrites, best when concentrated sulphuric acid is mixed with a few drops of nitric acid and some drops of the alcohol, and then added to a cold concentrated solution of copper sulphate, the mixture being heated. Methyl, ethyl, propyl, *iso*butyl, and *iso*amyl alcohols give positive reactions; octyl alcohol gives an uncertain reaction, but at a higher temperature a blue coloration is formed, whilst cetyl alcohol does not react. *iso*Propyl and *sec.*-butyl alcohols both give the reaction, but menthyl alcohol forms a resin. *tert.*-Butyl and *tert*-amyl alcohols react easily at the ordinary temperature without the formation of blue compounds, which seem to appear on heating the alcohols with amyl alcohol at 140 – 150°.

Glycerol, mannitol, erythritol, and many carbohydrates give the reaction; allyl alcohol forms only a brown resin. Lactic, malic, and tartaric acids react easily, citric acid with difficulty, whilst benzyl and cinnamyl alcohols become resinous. Nitro-ethane and -butane give a positive, nitromethane a negative, result; in the same way nitrobenzene, nitrotoluene, and trinitrophenol do not react.

The ethers behave like the alcohols; of the aldehydes only formaldehyde gives the reaction; others become resinous without turning blue. Chloral neither gets resinous nor gives the reaction; acetone immediately gives a brown resin; the results were negative in the case of benzaldehyde and salicylaldehyde, also with formic, acetic, oxalic, benzoic, and cinnamic acids, but positive with the esters of the acids. Carbamide and uric acid give no reaction; phenol gives a reddish-brown to a bluish-green coloration, which is a different from the lustrous colour of copper hydroxynitrosylsulphonate. Anisic acid gives the reaction. The mechanism of the formation of nitrosisulphonic acid by the decomposition of alkylnitrates and nitrites can be explained by a reaction between the ester and the acid which leads to the formation of alkyl sulphuric acids, which form addition or condensation products of nitric acid with the sulphonic acid. N. C.

The Action of Sulphur Dioxide on Ammonia. FRITZ EPHRAIM and HENRYK PIOTROWSKI (*Ber.*, 1911, **44**, 379—386. Compare Divers and Ogawa, Trans., 1901, **79**, 1102).—Depending on the conditions of experiment, three different compounds are formed by the interaction of sulphur dioxide and ammonia. With excess of sulphur dioxide, amidosulphinic acid, $NH_2\cdot SO_2H$, is always formed, but with excess of ammonia, either white ammonium amidosulphite, $NH_2\cdot SO_2\cdot NH_4$, is obtained, or a red compound (Abstr., 1900, ii, 271) of the same percentage composition as the amidosulphite, but with double the molecular weight, $2SO_2,4NH_3$. This red compound is *triammonium imidodisulphinate*, $NH_4\cdot N{:}(SO_2\cdot NH_4)_2$; it must contain four nitrogen atoms, since one quarter of the nitrogen is differently linked from the other three quarters. This is shown by the preparation of a *silver* salt, $AgN{:}(SO_2Ag)_2$, which is also red in colour, such coloured salts being often obtained when metals are directly combined with nitrogen.

The above explanation of the reactions between ammonia and sulphur dioxide has been arrived at chiefly from a study of the reactions between thionyl chloride and ammonia. When thionyl chloride is added drop by drop to liquid ammonia, the liquid assumes the same intense red colour as that possessed by the product formed from sulphur dioxide and excess of ammonia. On evaporation, a cinnabar-red residue is left, contaminated with ammonium chloride and other products. On digestion with absolute alcohol at – 5°, a deep red solution is obtained, which, on evaporation in a vacuum, gives a residue consisting of amorphous, red flakes, easily soluble in water, and mixed with a small quantity of stable, golden-yellow crystals (not enough to analyse completely), which are only slightly soluble in water. The red flakes consist of the above-mentioned triammonium imidosulphinate (no analyses are given), which gradually decomposes with loss of colour. The freshly prepared aqueous solution, when added to ammoniacal silver nitrate, gives a purple-red precipitate of the silver salt, $AgN\colon(SO_2Ag)$, which was analysed. The same silver salt can be obtained from the red product from the interaction of sulphur dioxide and ammonia. It is not very stable, gradually losing nitrogen.

The reactions taking place are: $2SOCl_2 + 7NH_3 = 4NH_4Cl + HN\colon(SO\cdot NH_2)_2$. This diamide is readily hydrolysed by water, giving $NH(SO_2\cdot NH_4)_2$, from which the silver salt is obtained by precipitation. The solution of the diamide in liquid ammonia is red, probably containing the compound $NH_4N\colon(SO\cdot NH_2)_2$; although not stated in the text there is presumably enough water in the liquid ammonia to convert this amide into the above-mentioned triammonium imidosulphinate on evaporation.

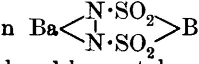
In the preparation of imidodisulphinic acid by Divers and Ogawa (*loc. cit.*), a by-product was obtained having the composition $N_4H_{12}O_{10}S_5$. Its formula and properties are readily explained by the constitution: $SO_2H\cdot[NH\cdot SO]_3\cdot NH\cdot SO_2H$ (compare Abstr., 1909, ii, 994).

An investigation of the precipitate obtained by the interaction of silver nitrate and amidosulphinic acid led to no satisfactory results.

T. S. P.

Action of Sulphur and of Compounds Containing Sulphur on Hydrazine.

FRITZ EPHRAIM and HENRYK PIOTROWSKI (*Ber.*, 1911, **44**, 386—394).—When sulphur dioxide is slowly passed into a cooled solution of hydrazine in absolute alcohol, a white, crystalline precipitate of the *hydrazine* salt of *hydrazinedisulphinic acid* is produced, namely, $N_2H_2(SO_2\cdot N_2H_5)_2$. It sinters at 50°, and then gives a cloudy liquid which at 70—80° decomposes with evolution of gas. The aqueous solution is weakly acid, smelling slightly of sulphur dioxide, and gives precipitates with solutions of barium, calcium, lead, and silver salts, sulphur dioxide being evolved at the same time. The *barium* salt has the composition



$Ba<\begin{matrix}N\cdot SO_2\\ | \\ N\cdot SO_2\end{matrix}>Ba$, the hydrogens of the hydrazine residue being replaced by metal as well as those in the sulphinic radicle. The salt gradually decomposes with loss of nitrogen. The silver salt could not be obtained pure.

Sulphur readily dissolves both in hydrazine and hydrazine hydrate, giving a dark brown solution, which on pouring into water deposits sulphur. At the ordinary temperature anhydrous hydrazine dissolves about 60% of its weight of sulphur. After a short time a reaction occurs according to the equation: $N_2H_4 + 2S = N_2 + 2H_2S$, nitrogen being evolved and an unstable hydrazine hydrosulphide remaining in solution. This equation was supported by quantitative measurements.

Hydrogen sulphide readily dissolves in hydrazine hydrate, but no solid is obtained. With anhydrous hydrazine, however, a crystalline compound is obtained in the form of long needles. More hydrogen sulphide is absorbed than corresponds with the formula $2N_2H_4,H_2S$, but not enough for the formula N_2H_4,H_2S. It is probable that the latter compound is formed, and by surrounding part of the hydrazine prevents further absorption of hydrogen sulphide. The compound readily loses hydrogen sulphide on exposure to the atmosphere, becoming liquid because of the liberation of hydrazine. Its vapour tension was determined approximately and found to be 760 mm. at about 35°.

Sulphur trioxide is immediately reduced by hydrazine under all conditions, sulphur sesquioxide, S_2O_3, being formed.

The behaviour of hydrazine towards thionyl chloride depends on the concentration of its solution. With a concentrated solution of hydrazine, sulphur is produced, which then reacts with the excess of hydrazine in the way mentioned above. In dilute solution an hydrazide of sulphurous acid is probably formed, but so far the authors have not been able to isolate it. T. S. P.

Nitrosulphamide and Sulphohydrazide. FRITZ EPHRAIM and EDUARD LASOCKI (*Ber.*, 1911, **44**, 395—403).—Sulphamide (Abstr., 1910, ii, 198) readily dissolves in cold concentrated nitric acid ($D = 1{\cdot}48$) without being decomposed or nitrated. Nitration takes place immediately, however, if concentrated sulphuric acid is added to the solution, the nitro-compound thus formed precipitating in the solid form. It is necessary to avoid any rise in temperature during the reaction and to work with small quantities only, since the *nitrosulphamide* formed very readily decomposes with explosive violence when present in large quantity. When dry, it is much more stable than when moist. As so prepared, it is fairly pure, and it may be further purified from ether. When heated carefully, it decomposes quietly at 95—96°, but ordinarily it decomposes with a slight puff, but without detonation, white vapours being evolved. The composition corresponds with the formula $NH_2{\cdot}SO_2{\cdot}NH{\cdot}NO_2$, and this formula is further confirmed by analysis of the *silver* salt, $NHAg{\cdot}SO_2{\cdot}NAg{\cdot}NO_2$, which is obtained as a flocculent, white precipitate when silver nitrate is added to the aqueous solution of the nitrosulphamide, and then ammonia until the precipitate no longer increases in volume.

Hydrogen is evolved when zinc dust is added to the aqueous solution of nitrosulphamide, the zinc salt being formed. If the solution is then acidified with sulphuric acid, complete reduction to *hydrazinesulphonamide*, $NH_2{\cdot}SO_2{\cdot}NH{\cdot}NH_2$, occurs. The reaction does not stop at this point, but proceeds further with the formation of aminosulphonic acid and *hydrazinesulphonic acid*, or their zinc salts. The zinc salt of the latter is much more soluble in alcohol than that of the former compound, but the quantity of substance obtained was too small to admit of complete separation and identification.

If the nitric acid solution of sulphamide is well cooled there is at times a deposition of a white substance on the addition of the first few drops of sulphuric acid. In contradistinction to nitrosulphamide this substance is deliquescent, and cannot be dried by spreading on a porous plate. It is probably a salt of sulphamide and nitric acid.

Attempts to nitrate amidosulphonic acid, $NH_2{\cdot}SO_3H$, were unsuccessful, owing to its insolubility in both nitric and sulphuric acids. The *methyl* ester, $NH_2{\cdot}SO_2{\cdot}OMe$, was obtained from the silver salt and methyl iodide in the form of microscopic rhombohedra, which sinter at

170° and have m. p. about 198° (decomp.). The ester cannot be nitrated, but by treatment with liquid ammonia, sulphamide can be obtained from it.

Sulphuryl chloride reacts with hydrazinecarboxylic acid, or preferably with hydrazine hydrazinecarboxylate (Abstr., 1905, i, 28), according to the equation:
$SO_2Cl_2 + 2NH_2{\cdot}NH{\cdot}CO_2H,N_2H_4 = SO_2(NH{\cdot}NH_2)_2 + 2N_2H_4,HCl + 2CO_2$ *sulphohydrazide*, $SO_2(NH{\cdot}NH_2)_2$, being formed. The hydrazine hydrazinecarboxylate is suspended in light petroleum or carbon tetrachloride, and the sulphuryl chloride gradually added, the mass obtained being well kneaded in order for the reaction to become complete. It was not found possible to obtain the pure sulphohydrazide, owing to the difficulty of separation from the accompanying hydrazine hydrochloride, but the *hydrazine* salt,

$$SO_2[N(N_2H_5){\cdot}NH_2]_2,$$

was obtained from the reaction product as follows: The reaction product was dissolved in water, and the solution digested at 50° with freshly precipitated and washed lead hydroxide for several hours. The suspension of lead hydroxide is alkaline enough to prevent the decomposition of the sulphohydrazide, which is very sensitive towards acids. On evaporating the filtrate in a vacuum an uncrystallisable syrup was obtained, which proved to be the above-mentioned hydrazine salt, analysis giving the required ratio of 8·1 for the nitrogen and sulphur. The compound is stable in neutral or alkaline solution, but readily decomposes in the presence of acids. It gives no precipitate with the salts of the heavy metals, except mercury. When the solution is evaporated with lead nitrate ($\frac{1}{2}$ mol.) a syrupy residue is left, from which hydrazine nitrate may be crystallised out by inoculation, leaving an oil corresponding with the formula of lead hydrazine sulphohydrazide, $Pb[N(NH_2){\cdot}SO_2{\cdot}N(N_2H_5){\cdot}NH_2]_2$. A crystalline benzoyl derivative, sodium dibenzoylsulphohydrazide,

$$SO_2(NNa{\cdot}NHBz)_2,$$

was obtained by the action of benzoyl chloride on the alkaline solution of hydrazine sulphohydrazide. T. S. P.

Sulphammonium and its Relation to Nitrogen Sulphide.

Otto Ruff and Leopold Hecht (*Zeitsch. anorg. Chem.*, 1911, **70**, 49—69. Compare Ruff and Geisel, Abstr., 1905, ii, 699).—The freezing-point curve of solutions of sulphur in liquid ammonia has been determined. The curve falls from the freezing point of ammonia, −77·34°, to a eutectic point at −79·7° and 16·3% S; it then rises to a maximum at −78·3° and 24% S, corresponding with the compound $S(NH_3)_6$, and falls to −84·6° at the composition corresponding with $S(NH_3)_3$, the existence of this compound being indicated by the solubility curve. Both compounds are associated, at least to double molecules, in solution. Moissan's sulphammonium, $S(NH_3)_2$, is not present in such solutions.

An examination of the absorption of light of six different wavelengths by solutions of hydrogen sulphide and nitrogen sulphide in liquid ammonia shows that several compounds must exist. The results are complicated, and it is not yet possible to fix the formulæ of these compounds. Only dilute solutions can be used on account of their high absorbing power. The apparatus used for their preparation and examination is described. C. H. D.

The Preparation of Pure Hyposulphites and the System Hyposulphite-Water.

Karl Jellinek (*Zeitsch anorg. Chem*, 1911, 70, 93—134).—The preparation and analysis of hyposulphites must be conducted in absence of air. Purified carbon dioxide or nitrogen is used, with water previously distilled in a stream of nitrogen. An apparatus in which the analytical operations are conducted is described in detail. The titration is carried out by adding an excess of ammoniacal copper sulphate, and titrating back with a standard solution of sodium hyposulphite, using indigotin as an indicator. The presence of sulphites is without influence. Sulphates are estimated by precipitation after boiling with hydrochloric acid and removing separated sulphur, and thiosulphates by oxidation with iodine, when sulphites and hyposulphites are converted into sulphates and thiosulphate into tetrathionate. The latter is estimated by reduction with aluminium and hydrochloric acid, followed by addition of iodine and titration with thiosulphate: $Na_2S_4O_6 + 6Al + 20HCl = 2NaCl + 3Al_2Cl_6 + 6H_2O + 4H_2S$; $4H_2S + 8I = 8HI + 4S$. Sulphites may be estimated by difference, after oxidising the whole of the sulphur by means of ammoniacal hydrogen peroxide and precipitating as barium sulphate, or directly. For this purpose, the solution is oxidised with an excess of ammoniacal copper solution, the cuprous salt re-converted into cupric salt by exposure to air, and then treated with mercuric chloride and hydrochloric acid, when thiosulphates are decomposed according to the equation: $Na_2S_2O_3 + HgCl_2 + H_2O = Na_2SO_4 + HgS + 2HCl$, whilst sulphur dioxide is evolved from the sulphite, and is absorbed in bulbs containing iodine and estimated in the usual manner.

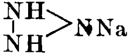
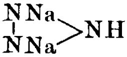
Sodium hyposulphite is purified by salting out with sodium chloride, the quantity added being such that precipitation is instantaneous. The salt, $Na_2S_2O_4,2H_2O$, is unstable, and must be dehydrated. The best results are obtained by adding solid salt to a concentrated solution of the commercial hyposulphite, filtering by means of a vacuum filter, and pressing the residue until as much mother liquor as possible is removed. It is then several times stirred with saturated salt solution and filtered, finally leaving a paste of the hydrate. This is stirred, and the temperature is gradually raised. Dehydration takes place at 60°. If the mass is too dry, partial decomposition takes place. After filtering rapidly, the crystals are washed successively with hot 50% alcohol and hot and cold absolute alcohol. Dehydration by means of alcohol is not successful. The anhydrous salt, dried at 60° in a vacuum, remains stable for months.

Freezing-point determinations with the purified salt show that the eutectic point of its aqueous solutions lies at $-4{\cdot}58°$ and 19·0 grams $Na_2S_2O_4$ per 100 grams water (1·93 molecular % $Na_2S_2O_4$). The freezing-point measurements confirm the formula $Na_2S_2O_4$.

The hydrated salt is best prepared by cooling the concentrated solution, and then forms glassy prisms, up to 1·5 cm. in length. The solubility curve has been determined up to and slightly beyond the transition point, anhydrous salt ⇄ hydrate, which lies at 52° and 2·8 molecular % $Na_2S_2O_4$. C. H. D.

New Anhydrous Selenites. R. L. Espil (*Compt. rend.*, 1911, **152**, 378—380).—Anhydrous selenites can be prepared in the amorphous state by passing the vapour of selenium oxide over a heated metallic oxide, or by heating the oxides together in a sealed tube. By using excess of selenium oxide in the latter method crystalline selenites are obtained. Copper selenite, $CuSeO_3$, forms green rods. The nickel salt is yellow, and the cobalt salt crystallises in long, violet prisms. Ceric selenite is an insoluble, yellow powder. The selenites of praseodymium, lanthanum, and samarium are colourless, whilst the neodymium salt is rose-coloured; the solubility of these substances in aqueous selenious acid furnishes a method for separating the metals from cerium and thorium.

Thorium oxide is unchanged by boiling with selenious acid, whilst cerium oxide, under these conditions, readily forms the selenite. As the latter is easily decomposed by heat, this reaction may be used to estimate the two metals in mixtures of their oxides. W. O. W.

The Action of Metallic Sodium on Hydrazine Hydrate. Everardo Scandola (*Chem. Zentr.*, 1910, ii, 544; Reprint from *Boll. Soc. med.-chirurg., Pavia*, 1910, 8 pp.).—By the action of sodium on hydrazine hydrate, Lobry de Bruyn (*Rec. trav. chim.*, 1896, **15**, 174) obtained a crystalline substance to which he assigned the formula $N_2H_5{\cdot}ONa$, ammonia and hydrogen being evolved. Under somewhat different conditions, hydrazine hydrate was added, drop by drop, to fine granulated sodium suspended in ether, the mixture being heated for some time on a water-bath in a reflux apparatus. In this way a white substance was obtained, which exploded by simply drying it in air, but on leaving it longer in contact with the ether it lost this property. It decomposes at 58°, and burns on platinum foil with a slight explosion. The solution reduces ammoniacal silver nitrate and Fehling's solution. The gases which are given off in the reaction are ammonia and hydrogen. The dry white compound which has been suspended longer in ether liquefies, and shows no action with ammoniacal silver nitrate. Contrary to the view of Lobry de Bruyn, the substance is regarded as having the formula  $\begin{matrix}NH\\ |\\ NH\end{matrix}\!>NNa$ or  $\begin{matrix}NNa\\ |\\ NNa\end{matrix}\!>NH$; in accordance with its cyclic nature, it easily decomposes. N. C.

Two New Methods for the Preparation of Hydrogen Borides. Josef Hoffmann (*Chem. Zeit.*, 1911, **35**, 265).—When ordinary commercial iron boride is dissolved in dilute sulphuric acid a gas is evolved consisting of a mixture of boron hydride and hydrogen. An undissolved residue remains, which contains solid hydrogen borides; on heating, a mixture of hydrogen and boron hydride is evolved.

Similar results are obtained with manganese boride.

Borides prepared by Goldschmidt's method always contain some solid hydrogen boride. T. S. P.

Chlorobromides and Chloroiodides of Silicon. ADOLPHE BESSON and L. FOURNIER (*Compt. rend.*, 1911, **152**, 603—605. Compare this vol., ii, 38).—Silicon chlorobromides can be obtained by the action of hydrogen and bromine on silicon tetrachloride under the influence of the silent electric discharge. The compounds $SiClBr_3$, $SiCl_2Br_2$, $SiCl_3Br$ can readily be isolated by fractionating the product. The dibromide is the chief constituent of the mixture, and when this is submitted in the presence of hydrogen to the further action of the discharge, it undergoes decomposition in accordance with the equation $2SiCl_2Br_2 = SiCl_3Br + SiClBr_3$. If a mixture of the three chlorobromides is treated in the same way, derivatives of the type Si_2X_6 appear to be formed, but their separation has not been satisfactorily accomplished.

Chloroiodides are formed under the same conditions as chlorobromides. W. O. W.

The Ratio of Argon to Nitrogen in Gases from Springs. B. WALTER (*Physikal. Zeitsch.*, 1911, **12**, 178—179).—The data obtained by Moureu and by Biquard in the analysis of the gases collected from twenty-eight spring waters show that, whereas the helium content varies between very wide limits, the proportion of argon varies to only a small extent. By taking the ratio of argon to nitrogen, it is found that this varies from 0·009 to 0·0183. The approximate constancy of the ratio indicates that the argon present in the spring waters has been derived from the atmosphere. On the other hand, the enormous variations in the helium content show that it is mainly derived from radio-active constituents of the particular geological formations. H. M. D.

Lithiumimide. OTTO RUFF and HANS GOERGES (*Ber*, 1911, **44**, 502—506).—Dafert and Miklauz (this vol., ii, 38) have obtained a substance which they designate as trilithium ammonium, Li_3NH_4. Its properties and appearance, however, are in accordance with its being a mixture, or it may be a solid solution, of 1 mol. lithiumamide and 2 mols. lithium hydride. It is formed from lithium nitride by the addition of hydrogen (*loc. cit.*), and, according to the present authors, the reactions which take place are as follows: Lithiumamide and hydride are first formed, according to the equation: $Li_3N + 2H_2 = LiNH_2 + 2LiH$. The resulting mixture of amide and hydride at 340—480° gives lithiumimide and ammonia, from the decomposition of the amide, and the ammonia immediately combines with the hydride, forming imide and hydrogen, so that the total reaction is given by the equation: $2LiNH_2 + 4LiH = 2Li_2NH + 2LiH + 2H_2$. This explanation is supported by the fact that lithiumamide does decompose into the imide and ammonia at 240—450°, and that at a slightly higher temperature lithium hydride reacts with ammonia with the formation of lithiumamide.

Lithiumamide, $LiNH_2$, was prepared by the interaction of lithium and liquid ammonia in a sealed tube at the ordinary temperature for two weeks. It forms white, shining crystals, consisting of regular hexahedra mixed with octahedra and tetrakishexahedra. In sealed tubes it has m. p. 373—375°, and may be sublimed under pressure of ammonia, $D^{17.5}$ 1·178.

Lithiumimide, Li_2NH, was obtained by heating the amide in a silver dish at 360° until most of the ammonia had been expelled, and finally at 450°. It forms a white, partly sintered mass, which does not melt at 600°, but assumes a yellow colour, becoming white again on cooling. At higher temperatures it decomposes, giving the blue lithium ammonia compound and a white powder, probably lithium nitride. It has D^{19} 1·303. T. S. P.

Alloys of Silver and Cadmium. G. J. PETRENKO and A. S. FEDOROFF (*Zeitsch. anorg. Chem.*, 1911, **70**, 157—169).—In the preparation of alloys of silver and cadmium, silver is lost by volatilisation as well as cadmium, so that it is necessary to analyse each alloy. The freezing-point curve shows that six types of crystals are formed, α, β, γ, δ, ϵ, and η, all of which are solid solutions, the principal gap being from 7 to 19% Ag. At 200°, the α and γ crystals react to form the compound AgCd on cooling. The existence of the compounds $AgCd_4$ and $AgCd_3$ is probable, whilst the γ-crystals appear to contain a compound, Ag_2Cd_3. Another compound, Ag_2Cd, is possible. There is no eutectic point, the freezing point of cadmium being raised by silver. The diagram obtained differs from that of Bruni and Quercigh (Abstr., 1910, ii, 953) in the interval from 19 to 100% Ag, these authors having observed an unbroken series of solid solutions throughout this range. C. H. D.

Ternary System Silver–Tin–Lead. NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 170—172).—In the present paper the author reproduces and discusses the diagram obtained by the thermal and micrographic study of the above ternary system, which belongs to the same type as the system copper–antimony–bismuth previously investigated (Parravano and Viviani, Abstr., 1910, ii, 1068).

R. V. S.

Constitution of Photo-halides. A. P. H. TRIVELLI (*Chem. Weekblad*, 1911, **8**, 101—115. Compare Reinders, this vol., ii, 39).—The author criticises the theory that the photo-halides are absorption compounds of colloidal silver and normal halides. He considers that they are sub-halides. A. J. W.

Decomposition of Silver Nitrite by Heat. MARCEL OSWALD (*Compt. rend.*, 1911, **152**, 381—384).—Divers (Trans., 1871, **9**, 85) and Shimidzu (Trans., 1885, **47**, 630) have shown that the decomposition of silver nitrite by heat proceeds in accordance with the equation $AgNO_2 = Ag + NO_2$, this action being accompanied by another: $Ag + N_2O_4 = AgNO_3 + NO$. It is now shown that a second subsidiary reaction occurs, represented as $AgNO_2 + NO_2 = AgNO_3 + NO$.

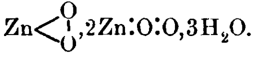
W. O. W.

Normal Barium Orthothioarsenate, $Ba_3As_2O_8,6H_2O$. EMANUEL GLATZEL (*Zeitsch. anorg. Chem.*, 1911, **70**, 86—92).—Barium orthothioarsenate, $Ba_3As_2O_8$, was obtained by Berzelius by a dry process, and in a hydrated form by Nilson from barium hydrogen sulphide and arsenic pentasulphide, being regarded by the latter author as a double arsenate-arsenite.

Arsenic pentasulphide, prepared by the action of a rapid stream of hydrogen sulphide in excess on a solution of arsenic acid and hydrochloric acid (McCay, Abstr., 1902, ii, 135), reacts with a freshly prepared solution of barium hydrogen sulphide according to the equation: $3Ba(SH)_2 + As_2O_5 = Ba_3As_2O_8 + 3H_2S$. After evaporation, transparent, pale yellow needles of $Ba_3As_2O_8,6H_2O$ separate, sometimes 5—10 mm. in length. It is partly decomposed by water, and is darkened by heating, burning in air. C. H. D.

Action of Potassium Hydrogen Carbonate on Magnesium Chloride and on Soluble Magnesium Salts in General. NANTY (*Compt. rend.*, 1911, **152**, 605—607. Compare this vol., ii, 103).—On mixing aqueous solutions of potassium hydrogen carbonate and magnesium chloride at the ordinary temperature, a precipitate is formed consisting of the double salt, $MgCO_3,KHCO_3,4H_2O$, or of $MgCO_3,3H_2O$, or of a mixture of the two. The composition of the precipitate depends solely on the concentration of the original salts. The limits for the formation of each substance have been experimentally determined, and the results are shown graphically by Gibb's method for ternary mixtures. W. O. W.

Zinc Peroxide. P. KAZANECKY (*J. Russ. Phys. Chem. Soc*, 1910, **42**, 1452—1458).—The action of 30% hydrogen peroxide solution on potassium, sodium, or ammonium zincoxide results in the formation of a white, microcrystalline precipitate, which is found to consist of a zinc peroxide, ZnO_2,H_2O, containing an admixture of zinc carbonate, the presence of the latter being due to the strong alkalinity of the solution in which the reaction takes place. When the peroxide is heated, explosive evolution of oxygen and water occurs at 178°. When treated with dilute sulphuric acid, it yields hydrogen peroxide, whilst, with concentrated hydrochloric acid, chlorine is evolved. The peroxide must, indeed, be regarded as consisting of three molecules of ZnO_2, one of which is the dioxide corresponding with an acid anhydride, the other two representing true zinc peroxide:



$$\mathrm{Zn}{<}\begin{matrix}\mathrm{O}\\ | \\ \mathrm{O}\end{matrix},2\mathrm{Zn}{:}\mathrm{O}{:}\mathrm{O},3\mathrm{H_2O}.$$

The three molecules form a salt-like compound. Those zinc peroxides which have been described previously by various authors consist either of mixtures of zinc peroxide and oxide or of compounds of the two oxides. T. H. P.

Nature of the Peroxides of Zinc. ORESTE CARRASCO (*Gazzetta*, 1911, **41**, i, 16—20. Compare Abstr., 1909, ii, 808, and de Forcrand, Abstr., 1902, ii, 606).—Pure zinc oxide reacts with an ethereal solution of hydrogen peroxide, yielding under all conditions (provided that sufficient hydrogen peroxide is present) the same compound, which, after drying at 60—70°, always has the composition $Zn_4O_7,2H_2O$. The substance is stable at 70—80°, and is not further oxidised even by 50% ethereal solutions of hydrogen peroxide. It is unaffected by cold water, but, when heated with water at 100°, it loses oxygen and the compound Zn_3O_5,H_2O, is formed, which is stable even under those conditions. The two peroxides are reddish-yellow powders, which explode at 212—216°, although the first-mentioned compound shows signs of decomposition at about 150°. It follows that these two substances are true compounds, of which higher hydrates were obtained by de Forcrand. They are hydrated peroxides, not additive compounds of condensed hydrates of zinc oxide with hydrogen peroxide, because they contain less water molecules than active oxygen atoms. In structure they differ from the peroxides of other metals, and are to be considered as *perzincic acids* of the following probable constitutions: HO·Zn·O·O·Zn·O·O·Zn·O·O·Zn·OH and HO·Zn·O·O·Zn·O·O·Zn·OH. R. V. S.

The Influence of Lime on the Sulphur Content of Roasted Blendes. EUGÈNE PROST (*Bull. Soc. chim. Belg.*, 1911, **25**, 103—115).—It is generally admitted that the lime contained in zinc blende is converted into sulphate during the roasting, but some metallurgists have maintained that during the operation the sulphate thus formed is decomposed for the most part, and that the sulphate existing in the roasted blende is present as zinc sulphate. The latter view is contrary to what would be expected from a knowledge of the behaviour of the sulphates of calcium and zinc at different temperatures, but it is impossible to disprove it by analysis of the roasted ore, since on extraction with water any zinc sulphate which may be present would react with the lime forming calcium sulphate. The author has therefore carried out a series of experiments with a pure Transvaal blende containing only 0·74% of lime.

Two experiments were generally carried out side by side, the one consisting of roasting the pure ore, the other of roasting the ore mixed with a certain proportion of pure lime, or of lime mixed with known quantities of silica, lead oxide, or iron oxide. From the analyses of the resulting products conclusions could be drawn as to the amount of calcium sulphate present.

In the first set of experiments the roasting was done in a muffle at a temperature of 1025—1050°, that is, 100—250° higher than the temperature in a zinc furnace. The results show that at least 71—85% of the lime is present as sulphate. Similar results were obtained in a second series of experiments, in which the mixtures were heated in a Delplace zinc furnace.

Attempts to find a method for analysing a mixture of lime and zinc sulphate were unsuccessful. T. S. P.

Zinc Chromates. MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1911, **70**, 135—144).—By shaking zinc oxide with chromic acid solution in different quantities for several days in a thermostat, filtering through asbestos at constant temperature, and estimating the zinc and chromium in the filtrate and in the precipitate, the nature of the phases in equilibrium may be determined. Chromic acid is estimated iodometrically, and zinc by weighing the ignited residue, consisting of Cr_2O_3 and ZnO. Mixtures rich in chromic acid lose a portion of this by volatilisation, and it is, therefore, necessary to add a weighed quantity of zinc oxide before ignition.

Whilst the composition of the solution varies continuously, that of the solid phase shows discontinuities, the following five salts being assumed to be present: $4ZnO,CrO_3,3H_2O$; $3ZnO,CrO_3,2H_2O$; $4ZnO,2CrO_3,3H_2O$; $3ZnO,2CrO_3,H_2O$; ZnO,CrO_3,H_2O. All of these are crystalline except the fourth. The solutions contain zinc dichromate together with some zinc monochromate.

The monochromate, ZnO,CrO_3,H_2O, does not lose its water at 125°. It has not been found possible to convert it into the anhydrous insoluble salt (Schulze, Abstr., 1896, ii, 24; Briggs, Abstr., 1908, ii, 113). C. H. D.

Double Salts of Lead Fluoride and the Other Halides of the Same Metal. Carlo Sandonnini (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 172—176).—The present paper deals with the thermal study of the system $PbCl_2$–PbF_2. The melting points of the four lead halides employed in the work were determined from their cooling curves with the aid of a platinum platinum-rhodium thermoelement, and were found to be: lead fluoride, 824°; lead chloride, 495°; lead bromide, 366°; lead iodide, 400°. This last value differs from those of previous investigators. The thermal diagram of the system $PbCl_2$–PbF_2 exhibits the following facts. From the m. p. of the pure chloride the curve descends to an eutectic point at 454°, the concentration being about 10 mol. % of fluoride. It then rises to a maximum at 601°, which corresponds to 50 mol. % of fluoride, and it afterwards descends again to another eutectic point at 554° (composition 75 mol. % of fluoride). When the concentration of fluoride is further raised, the curve rises slowly to 570° (composition 80 mol. %), where an evident pause occurs. Finally, the curve ascends rapidly to the m. p. of pure fluoride. The existence of a *compound*, $PbCl_2,PbF_2$, melting without decomposition is thus established, whilst the pause at 570° shows the existence of a *compound*, $PbCl_2,4PbF_2$, which decomposes on fusion. R. V. S.

Oxidation of Lead Oxide in Presence of Light and Air. Georg Kassner (*Arch. Pharm.*, 1911, **249**, 22—30).—In a previous paper (Abstr., 1904, ii, 124) the author stated that dry lead monoxide underwent oxidation on exposure to light and dry air. On repeating this experiment with well dried lead monoxide sealed in a glass tube with air kept dry by means of phosphoric oxide, no oxidation of the lead monoxide took place even after seven years' exposure to sunlight. The oxidation previously noted must therefore have been occasioned by the presence of a trace of moisture, which probably facilitated indirect autoxidation. It is suggested that in presence of a trace of moisture, lead hydroxide is formed, which under the influence of light undergoes dissociation, whereon a molecule of oxygen is taken up by the liberated lead atom or the water which is formed, thus giving rise directly or indirectly to lead dioxide.

T. A. H.

Reactions of Mercurous Chloride. Walter Herz (*Zeitsch. anorg. Chem.*, 1911, **70**, 170—172. Compare Abstr., 1910, ii, 945).—The reaction $Hg_2Cl_2 + 2KOH \rightleftharpoons Hg_2O + H_2O + 2KCl$ has been studied. A constant is found for the ratio k, $= [KOH]/[KCl]$, and also for the constant $k = [Na_2CO_3]/[NaCl]^2$ for the reaction $Hg_2Cl_2 + Na_2CO_3 = Hg_2CO_3 + 2NaCl$.

C. H. D.

The Hydrazinates of Some Metallic Salts. II. Hartwig Franzen and Hubert L. Lucking (*Zeitsch. anorg. Chem.*, 1911, **70**, 145—156. Compare Franzen and Mayer, Abstr., 1909, ii, 40).—The hydrazinate of mercuric nitrate (Hofmann and Marburg, Abstr., 1899, i, 486) is exceptional in being formed in acid solution, whilst most hydrazinates are decomposed by very dilute acid. It may be assumed that a double salt, $Hg(NO_3)_2,N_2H_5NO_3$, is first formed, which then undergoes hydrolysis, the insoluble hydrazinate being precipitated Similar compounds have now been prepared.

Cobalt iodide dihydrazine, $CoI_2(N_2H_4)_2$, from cobalt iodide and hydrazine iodide or hydrate, forms a pink, sparingly soluble powder; the *nickel* compound, $NiI_2(N_2H_4)_2$, is yellow.

The following hydrazine compounds of cyanides have been obtained: *cadmium*, $Cd(CN)_2(N_2H_4)_2$; *zinc*, $Zn(CN)_2(N_2H_4)_2$; *silver*, $AgCN,N_2H_4$; *copper*, $Cu(CN)_2,N_2H_4$; *mercury*, $Hg(CN)_2,N_2H_4$; *nickel*, $Ni(CN)_2,(N_2H_4)_3$.

Cobalt cyanide forms a complex *compound*, $(N_2H_4)_4Co(CN)_6$.

The chlorides and bromides of cobalt and nickel do not yield hydrazinates, but double salts: $CoBr_2(N_2H_4,HBr)_2,4H_2O$; $CoCl_2(N_2H_4,HCl)_2,2H_2O$; $NiBr_2(N_2H_4,HBr)_2,4H_2O$; $NiCl_2(N_2H_4,HCl)_3,H_2O$.

C. H. D.

Fractionation of the Yttrium Earths by means of the Succinates. Raymond C. Benner (*J. Amer. Chem. Soc.*, 1911, **33**, 50—56).—It has been stated by Lenher (Abstr., 1908, ii, 385) that a separation of the earths of the yttrium group, obtained from samarskite, can be effected by fractionally precipitating a solution of the nitrates with sodium succinate. The method has now been applied to yttrium earths extracted from several minerals of widely different character. The results show that a satisfactory separation can be obtained, provided that the concentration of the earths does not exceed 2—3%, by adding sodium succinate solution drop by drop to a nearly neutral, boiling solution of the nitrates.

Yttrium succinate, $Yt_2(C_4H_4O_4)_3,2\frac{1}{2}H_2O$, is a white, crystalline salt, which is slightly hygroscopic and is soluble in boiling water to the extent of 0·1435 gram per litre.

E. G

The Atomic Weight of Neodymium. I. Analysis of Neodymium Chloride. Gregory P. Baxter and Harold Canning Chapin (*Zeitsch. anorg. Chem.*, 1911, **70**, 1—33; *J. Amer. Chem. Soc.*, 1911, **33**, 1—28).—A quantity of 3·5 kilograms of neodymium ammonium nitrate was fractionally crystallised from dilute nitric acid, samarium being removed in the more soluble fractions and praseodymium in the less soluble. The atomic weights of the last fractions were determined by titrating the oxalates with permanganate. Samarium was easily eliminated, praseodymium only with great difficulty. Crystallisation from concentrated nitric acid removed all impurities except traces of praseodymium, after a long series of fractionations. The absorption spectra of the purest fractions of neodymium were examined and tabulated.

In order to determine the atomic weight, the neodymium was precipitated as oxalate, ignited to oxide, and dissolved in hydrochloric acid. The chloride was then crystallised three times and precipitated by hydrogen chloride at 0°, dried in a vacuum, and finally heated in hydrogen chloride just below its melting point. It was then converted into silver chloride by means of silver nitrate prepared from pure silver. A small correction was made for the trace of moisture retained by the neodymium chloride.

The result obtained is Nd 144·27 for Ag 107·88. Neodymium chloride has D_4^{20} 4·134. C. H. D.

Holmium. Otto Holmberg (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 2, 1—8).—Twenty-nine kilos. of finely powdered euxenite were decomposed in small portions at a time with hot concentrated sulphuric acid, the excess of acid being finally expelled. After cooling, the resulting mass was powdered and gradually added to cold water, whereby the ytterbium earths, oxides of cerium, iron, uranium, and some of the acid oxides were dissolved. The solution was completely precipitated with ammonia, the washed precipitate dissolved in concentrated nitric acid, and the solution heated to boiling; the filtrate from the precipitate so formed was precipitated with oxalic acid, and the oxalate collected and ignited. The resulting oxide amounted to 5·5 kilos., and contained the holmium present in the original euxenite. The oxide was transformed into oxalate and separated into two fractions by repeated treatment with a hot saturated solution of ammonium oxalate, the oxalates of scandium, thorium, and of the ytterbium earths with the highest atomic weights being much more soluble than the oxalates of yttrium, terbium, etc. The lesser soluble oxalates gave 4773 grams of oxides, and were treated for holmium as follows: The oxides were converted into the *m*-nitrobenzenesulphonates (compare Abstr., 1907, ii, 90) and submitted to a long series of fractional crystallisations. The five least soluble fractions consisted of a mixture of yttrium, erbium, holmium, dysprosium, terbium, gadolinium, europium, and samarium; they were converted into the nitrates and fractionally crystallised in the presence of bismuth nitrate (Bodman and Urbain's method), whereby gadolinium is eliminated. The fourteen chief fractions consisted chiefly of holmium, dysprosium, terbium, and yttrium, but europium, samarium, and erbium were also present. The holmium in these fractions was further concentrated by the ammonium oxalate method; the nitrate solution of the three most soluble fractions (= 14·2 grams) showed a strong holmium spectrum, but also a weak erbium and dysprosium spectrum. The oxide was yellow in colour, showing the presence of terbium, and the atomic weight (= 144) indicated a considerable content of yttrium. It was converted into the nitrate and again submitted to a long series of fractionations (160), and the fractions richest in holmium submitted to spectral examination; they were found to be practically free from erbium, but contained a trace of terbium, a small quantity of dysprosium, and some yttrium (about 19%), the atomic-weight determination giving the value 150.

Further experiments are being made to separate the yttrium, depending on the great difference in basicity between this element and holmium. Two partial precipitations with aniline raised the atomic weight from 150 to 156. T. S. P.

The Ovifak Iron, a Natural Carbon Steel. Carl Benedicks (*Metallurgie*, 1911, 8, 65—68).—The mass of iron, weighing twenty-five tons, from Ovifak in Greenland, was regarded by Nordenskiold as a meteorite, but has been considered by others to be derived from basalt by reduction. A micrographic examination has now been performed in order to decide its character.

The iron is principally composed of pearlite and free cementite, thus resembling a high-carbon steel. Analysis shows 1·64% of carbon. The fine grain of the pearlite shows that the iron must have cooled rapidly from 700°. Thus the slowly cooled meteoric irons, even when containing much carbon, do not exhibit pearlite, the carbide having completely segregated.

Portions of the iron contain oxide, arranged in a lamellar form alternating with cementite. The name "oxide-pearlite" is proposed for this structure. Its arrangement in dendritic forms indicates a primary crystallisation of a constituent containing both oxide and carbide, which would only be possible under pressure. Iron sulphide (troilite) is present in the usual segregated masses. C. H. D.

A Revision of the Atomic Weight of Iron III. Gregory P. Baxter, Thorbergur Thorvaldson, and Victor Cobb (*J. Amer. Chem. Soc.*, 1911, 33, 319—337).—The change in the atomic weight of silver from 107·93 to 107·88 having destroyed the agreement between the atomic weights of iron determined by the reduction of ferric oxide (Abstr., 1900, ii, 407) and analysis of ferrous bromide (Abstr., 1904, ii, 177) respectively, it has been found necessary to redetermine the atomic weight of the latter metal.

The various reagents used, such as silver, hydrobromic acid, nitric acid, etc., were purified according to methods previously described. Three different samples of pure iron were prepared. Sample *A* was obtained by dissolving a pure ribbon iron in redistilled nitric acid, and recrystallising the ferric nitrate three times. The nitrate was dried and partly decomposed by heating in a platinum dish, and the resulting mixture of oxide and basic nitrate reduced to metal by means of ammonia. Sample *B* was prepared from another pure iron by conversion into the nitrate, recrystallising five times, converting into the oxide, and reducing the oxide with hydrogen. Sample *C* was obtained by dissolving iron in hydrochloric acid and precipitating the insoluble sulphides with hydrogen sulphide. The filtrate was oxidised with nitric acid, and the iron precipitated as hydroxide several times in order to remove nickel and cobalt, experiments having shown that this method is satisfactory when only traces of these latter metals are present. The ferric hydroxide was dissolved in sulphuric acid, and the ferric sulphate reduced electrolytically to ferrous sulphate, using a platinum dish as the cathode. Iron was then deposited electrically from the ferrous sulphate so obtained, using an ammonium oxalate electrolyte, thus removing aluminium, chromium, alkali metals, and silica. This iron was then treated as described for sample *B*.

Ferrous bromide was made by dissolving the iron in freshly distilled hydrobromic acid in a quartz dish. The solution so obtained was evaporated to crystallisation either in a large desiccator filled with hydrogen or in the air, any ferric bromide thus formed being removed by the subsequent treatment. The ferrous bromide was recrystallised several times. The anhydrous salt was prepared by fusion in a current of nitrogen and hydrogen bromide gases, and the bromine in a weighed quantity of the bromide precipitated as silver bromide, according to the method used in similar determinations of atomic weight. Before the precipitation was carried out, however, 99% of the ferrous salt was oxidised to the ferric condition by means of potassium dichromate and sulphuric acid, in order to prevent the action of the ferrous salt on the silver nitrate. The precipitated silver bromide was collected and dried at 170°, allowance being made for any remaining in solution by measurements with the nephelometer.

As a result of twenty-one determinations, the value obtained for the atomic weight of iron is 55·838 (Ag = 107·880). T. S. P.

A Revision of the Atomic Weight of Iron. IV. The Atomic Weight of Meteoric Iron. GREGORY P. BAXTER and THORBERGUR THORVALDSON (*J. Amer. Chem. Soc.*, 1911, 33, 337—340). —In order to ascertain if there is any difference between terrestrial and meteoric iron, the atomic weight of iron contained in a meteorite from Cumpas, Sonora, Mexico, has been determined.

Some of the meteorite was dissolved in hydrochloric acid, and any precipitate formed by passing hydrogen sulphide into the acid solution and into the solution after neutralisation with ammonia collected. The filtrate was made alkaline with ammonia, and saturated with hydrogen sulphide until there was no further precipitate formed. The collected sulphides were treated with 4% hydrochloric acid to dissolve the iron, leaving the greater part of the cobalt and nickel sulphides undissolved. This process was repeated, and then the ferrous chloride solution was oxidised with nitric acid and the iron precipitated with ammonium hydroxide in order to remove the nickel and cobalt. The precipitate was again dissolved in nitric acid and the iron reprecipitated, this process being repeated nine times before all the nickel and cobalt was removed. The resulting ferric hydroxide was then dissolved in sulphuric acid, and ferrous bromide prepared as described in the previous abstract.

Atomic-weight determinations with the ferrous bromide thus obtained gave the values 55·837 and 55·835 respectively, as the means in two series of experiments. In taking these means, the results where 98% only of the ferrous salt was oxidised with dichromate before addition of silver nitrate have been neglected, since they give slightly lower values, probably because of the action of the unoxidised ferrous salt on the silver precipitate.

There thus seems to be no evidence of dissimilarity between this specimen of meteoric iron and the ordinary metal. T. S. P.

Formation of Graphite in Iron Alloys. K. A. Jeriomin (*Zeitsch. Elektrochem.*, 1911, **17**, 93—98).—A discussion of Goerens' view that graphite is always produced by the decomposition of cementite. The literature of the subject is reviewed, and the hypothesis found to be in accordance with existing experimental evidence.

T. E.

The Formation of Iron Disulphide in Solutions, and Some Reactions of Thionates. Walter Feld (*Zeitsch. angew. Chem.*, 1911, **24**, 290—294).—The formation of iron disulphide from ferrous thiosulphate and hydrogen sulphide had been observed in 1900 by Carpenter and Linder, the reaction being then assumed to be complete. In cold solutions, however, the reaction may be arrested at an earlier stage.

Ferrous thiosulphate, free from sodium salts, is prepared by passing hydrogen sulphide into a cold solution of ferrous sulphate and sodium thiosulphate. The precipitate of ferrous sulphide and sulphur is collected, washed with cold boiled water, suspended in water, and added slowly to water through which sulphur dioxide, diluted with hydrogen, is passed, the mixture of gases being made more dilute as the operation proceeds. The reactions occurring are: (1) $2FeS + 3SO_2 = 2FeS_2O_3 + S$; (2) $FeS + 3SO_2 = FeS_4O_6$; (3) $FeS + 3SO_2 = FeS_3O_6 + S$. A further quantity of the sulphide is then added to remove excess of sulphur dioxide, the polythionates being reduced at the same time: (4) $FeS_4O_6 + FeS = 2FeS_2O_3 + S$; (5) $FeS_3O_6 + FeS = 2FeS_2O_3$.

In order to analyse such a solution, ammonium chloride is added, and the solution is titrated, first with *N*/10-iodine, and then with *N*/10-sodium hydroxide, using methyl-orange as indicator. The quantity of alkali required gives the free sulphur dioxide, and one-half of this figure, subtracted from the quantity of iodine, gives the quantity of thiosulphate. Polythionates may be estimated as follows. The solution is added to an excess of cold saturated mercuric chloride solution. Polythionates set free twice as much acid as thiosulphates:

$$Na_2S_2O_3 + 2HgCl_2 + H_2O = Na_2SO_4 + Hg_2Cl_2 + 2HCl + S;$$
$$Na_2S_3O_6 + 2HgCl_2 + 2H_2O = Na_2SO_4 + Hg_2Cl_2 + H_2SO_4 + 2HCl + S;$$
$$Na_2S_4O_6 + 2HgCl_2 + 2H_2O = Na_2SO_4 + Hg_2Cl_2 + H_2SO_4 + 2HCl + 2S.$$

After heating, an excess of ammonium chloride is added, and the solution is titrated with sodium hydroxide. The difference between the result obtained and that found by the iodine titration gives the polythionates.

Polythionate, if present, may be removed by hydrogen sulphide, and, after removing sulphur by filtration, a solution of ferrous thiosulphate is obtained. In the preparation of this salt from barium thiosulphate and ferrous sulphate, tetrathionate is always obtained as an impurity, owing to the presence of ferric sulphate. C. H. D.

The Ferronitrosulphides and Their Relation to the Nitroprussides. III. J. O. ROSENBERG (*Arkiv. Kem. Min. Geol.*, 1911, **4**, No. 3, 1—76).—The author brings forward various objections to the constitutional formulæ proposed by Bellucci and Cesaris (Abstr., 1908, ii, 593) and others for the ferronitrosulphides, or Roussin's salts. Further fresh observations are recorded.

In a former communication (*Arkiv. Kem. Min. Geol.*, **2**, No. 1), the preparation of a dark brown, insoluble compound of iron, sulphur, and nitric oxide, which is considered to be the parent substance of Roussin's salts, has been described. To this compound has been given the name *ferronitrososulphide.* Further investigation has shown that this substance is best prepared by the addition at − 2° of an *N*/10-solution of sodium trisulphide to a 2/5*N*-solution of ferrous chloride saturated with nitric oxide ; sodium disulphide and sodium sulphide do not give such good results as the trisulphide.

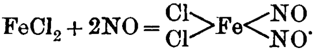
Ferronitrososulphide can only be preserved under water ; even in the moist condition it decomposes on exposure to the air. Under the action of a *N*/25-solution of potassium sulphide, the black Roussin's salt is formed ; the red salt is formed primarily, and this is then converted into the black salt by the excess of ferronitrososulphide. With *N*-potassium sulphide the red salt is formed, and is stable in the presence of excess of the alkali sulphide. Ferronitrososulphide is also decomposed by a hot normal solution of potassium hydroxide, the red Roussin salt being formed, together with ferric hydroxide, potassium thiosulphate, and evolution of nitrogen. This is a new method for the preparation of the red salt.

The transformation of the black Roussin's salt into the red salt under the influence of alkali hydroxide, and the reverse transformation under the influence of carbon dioxide, dilute acids, or ferrous chloride, were studied, but the results were not such as to lead to a definite rational formula for these compounds. A redetermination of the water of crystallisation of the red potassium salt gave $4H_2O$, agreeing with the formula $Fe_2(NO)_4S_2K_2,4H_2O$.

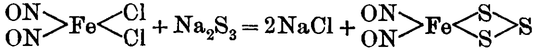
Further experiments showed that when ferronitrososulphide is acted on by a solution of sodium sulphide in such a way that the time of reaction is reduced to a minimum, a solution of the red Roussin's salt is obtained, sulphur being left behind. By evaporation in a vacuum, the pure red salt was obtained as crystals.

Analysis of the ferronitrososulphide was attended with great difficulties, and the results depended largely on the method of preparation ; they point to the formula $Fe(NO)_2S_3$ or $Fe(NO)_2S_4$.

From the above results it is concluded that the following reactions take place in the formation of Roussin's salts :

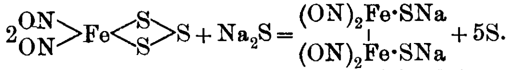
(1) 

$$\mathrm{FeCl_2 + 2NO = \substack{Cl\\Cl}{>}Fe{<}\substack{NO\\NO}}.$$

(2)  (ferronitroso-sulphide).

$$\mathrm{\substack{ON\\ON}{>}Fe{<}\substack{Cl\\Cl} + Na_2S_3 = 2NaCl + \substack{ON\\ON}{>}Fe{<}\substack{S\\S}{>}S}$$

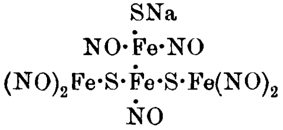
(3) The formation of the red salt from the ferronitrososulphide :



$$2\begin{matrix}ON\\ON\end{matrix}\!>\!Fe\!<\!\begin{matrix}S\\S\end{matrix}\!>\!S+Na_2S=\begin{matrix}(ON)_2Fe{\cdot}SNa\\ |\\ (ON)_2Fe{\cdot}SNa\end{matrix}+5S.$$

(Red Roussin's salt.)

(4) Change from the red salt into the black salt: $2Fe(NO)_2S_3+Fe_2(NO)_4S_2Na_2+H_2O=Fe_4(NO)_7S_3Na+NaNO_2+H_2S+4S$; (Black salt.) the black salt having the annexed constitution.



$$\begin{matrix}SNa\\ NO{\cdot}\dot{F}e{\cdot}NO\\ (NO)_2Fe{\cdot}S{\cdot}\dot{F}e{\cdot}S{\cdot}Fe(NO)_2\\ \dot{N}O\end{matrix}$$

The relation of these compounds with the nitroprussides is reserved for a future communication.

T. S. P.

Complex Molybdates of the Rare Earths. Giuseppe A. Barbieri (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 18—21. Compare Abstr, 1908, ii, 595).—The ammonium ceromolybdate formerly described is not monoclinic, but triclinic [$a:b:c=0{\cdot}3523:1:0{\cdot}3409$; $\alpha=102°22'$, $\beta=54°30'$, $\gamma=103°4'$]. The ammonium lanthanomolybdate also mentioned (*loc. cit.*) forms crystals which show holosymmetry of the triclinic system [$a:b:c=0{\cdot}3502:1:0{\cdot}3416$; $\alpha=102°29'$, $\beta=54°18'$, $\gamma=103°10'$]. The two compounds readily form mixed crystals. The following salts were prepared in the same way as the foregoing, and belong to the same class of symmetry:

Ammonium neodymomolybdate, $(NH_4)_3NdMo_7O_{24},12H_2O$; triclinic [$a:b:c=0{\cdot}3492:1:0{\cdot}3385$; $\alpha=102°15'$, $\beta=54°8'$, $\gamma=103°29'$].

Ammonium praseodymomolybdate, $(NH_4)_3PrMo_7O_{24},12H_2O$, forms a microcrystalline powder; triclinic [$a:b:c=0{\cdot}3514:1:0{\cdot}3461$; $\alpha=102°11'$, $\beta=54°15'$, $\gamma=103°44'30''$].

Ammonium samaromolybdate, $(NH_4)_3SmMo_7O_{24},12H_2O$,; triclinic [$a:b:c=0{\cdot}3611:1:0{\cdot}3330$; $\alpha=54°45'$, $\beta=54°45'$, $\gamma=102°36'30''$].

The crystallographic measurements are by E. Billows. R. V. S.

Vanadium Chlorides. Otto Ruff and Herbert Lickfett (*Ber.*, 1911, **44**, 506—521).—Of the various vanadium chlorides, the easiest to prepare is the vanadyl trichloride, $VOCl_3$. In addition to the various methods which have hitherto been used for its preparation, the authors give the following three methods: (1) Chlorine is passed over vanadium pentoxide heated to a dull red heat; oxygen is evolved, and the yield of vanadyl trichloride, which is thus obtained pure, is quantitative. (2) A mixture of vanadium pentoxide and sulphur is chlorinated at the ordinary temperature; the reaction takes place vigorously, with marked development of heat. (3) Vanadium trichloride when heated in a current of oxygen is converted quantitatively into the vanadyl trichloride.

Vanadium tetrachloride, VCl_4, is readily obtained by the action of chlorine on finely-powdered vanadium carbide. The reaction commences at the ordinary temperature. It is best prepared, however, by heating vanadium trichloride in a stream of chlorine.

Vanadium trichloride, VCl_3, is most easily obtained from vanadyl trichloride or vanadium tetrachloride, or from a mixture of both, by heating with sulphur under reflux, and then distilling off the excess of sulphur from the trichloride in a stream of nitrogen. This method is quicker and better than those hitherto used.

On heating vanadium trichloride in a current of nitrogen to a dark red heat, it is decomposed into vanadium tetrachloride, which distils off, and into vanadium dichloride, which remains behind. The quantity of vanadium tetrachloride, which is formed according to the equation: $2VCl_3 = VCl_4 + VCl_2$, is determined for each temperature by the partial pressure of the chlorine, since together with the above reaction a second occurs, namely, $2VCl_4 = 2VCl_3 + Cl_2$.

For the first reaction the relation $(VCl_4)/(VCl_3)^2 = k_1$ holds, since the vapour pressure of the VCl_2 in the presence of the solid is constant; for the second reaction the relation $(VCl_3)^2(Cl_2)/(VCl_4)^2 = k_2$ holds. Both these equilibria exist at the same time, and by multiplication we have $(Cl_2)/(VCl_4) = k_1k_2$, that is, the quantity of vanadium tetrachloride formed by heating the trichloride is determined by the partial pressure of the chlorine over the trichloride. It is consequently an easy matter to transform vanadium trichloride completely into the tetrachloride by heating in a current of chlorine which is free from oxygen.

Similar phenomena are observed when vanadium trichloride is heated at a dull red heat in a current of carbon dioxide instead of nitrogen. Green vanadium dichloride, VCl_2, is formed according to the equation $2VCl_3 \rightleftarrows VCl_4 + VCl_2$. If the heating is carried out at a bright red heat the carbon dioxide is reduced by the vanadium dichloride, with the result that vanadyl chloride, VOCl, and carbon monoxide are formed, as shown by the equation: $3VCl_2 + 2CO_2 = 2VOCl + VCl_4 + 2CO$. On still stronger heating the reaction goes further, according to the equation: $4VCl_2 + 3CO_2 = V_2O_3 + 2VCl_4 + 3CO$, and pure vanadium sesquioxide is left behind. Thus it is quite unnecessary to reduce vanadium trichloride in a current of hydrogen in order to obtain the dichloride.

Full descriptions of the various processes are given.

Vanadium tetrachloride has b. p. 153·7°/768 mm. Vanadium dichloride is stable in the air at first, but gradually deliquesces to a brown solution, water and oxygen being absorbed. This is in contradistinction to the statements of Roscoe. T. S. P.

Mineralogical Chemistry.

Gases Enclosed in Tektites. RICHARD BECK (*Jahrb. Min.*, 1911, i, Ref. 39; from *Monatsber. Deutsch. geol. Ges.*, 1910, No. 3, 240—245). —Billitonite from Déndang, Billiton, when heated in a vacuum at 900° yields per kilo. of material: NH_4Cl, 5 mg.; (Na,K)Cl, 60 mg.;

CO_2, 98·0 c.c.; CO, 100·4 c.c.; H, 14·2 c.c.; SO_2, 0·4 c.c.; N, trace; H_2S, O, not present. Moldavite from Moldauthein, Bohemia, gave from 20 grams: CO_2, 0·6 c.c.; CO, 2·2 c.c.; N + H, 0·7 c.c. A comparison of tektites with obsidian shows that the former are characterised by the presence of much carbon dioxide and carbon monoxide, and by the absence of free chlorine and hydrochloric acid.

L. J. S.

Bismuth Ochres from San Diego Co., California. WALDEMAR T. SCHALLER (*J. Amer. Chem. Soc.*, 1911, **33**, 162—166).—Analyses have been made of one grey and two yellow, amorphous bismuth ochres from the mines at Pala, San Diego Co. One of the yellow specimens consisted of a mixture of bismuth vanadate, $BiVO_4$, and hydroxide, $Bi(OH)_3$ (anal. I), whilst the composition of the other agreed with that of pucherite, $BiVO_4$ (anal. II). There does not appear to be any previous record either of the occurrence of pucherite in the United States, or of the existence of this mineral in an amorphous form. The grey sample consisted mainly of bismuth hydroxide, $Bi(OH)_3$ (anal. III). The author has shown previously (Abstr., 1910, ii, 220) that the crystalline form of the bismite of the Goldfield district of Nevada differs from that of artificial crystals of bismuth trioxide. The additional evidence now obtained tends to confirm the view that natural bismite is a bismuth hydroxide and not the trioxide.

			Gangue					
	Bi_2O_3.	V_2O_5.	Sol. in HNO_3.	Insol. in HNO_3.	H_2O at 107°.	H_2O at 240°.	H_2O, ignition.	Total.
I.	64·43	12·11	2·27	17·63	0·32	0·24	3·43	100·43
II.	66·14	25·80	—	7·37	0·21	0·32	0·84	100·68
III.	64·9	0·8	9·5	13·5	0·4	0·3	11·4	100·8

E. G.

Mixed Crystals of Sodium Chloride and Silver Chloride (Huantajayite). W. BOTTA (*Centr. Min.*, 1911, 138—139).—By adding sodium chloride to fused silver chloride there is obtained, on cooling, a brittle, crystalline mass, which under the microscope appears to be homogeneous. Those crystals containing but little silver chloride (as in the natural huantajayite, 3—11% AgCl) dissolve in water, leaving a curdy residue. The solidification points of mixtures in various proportions vary continuously from that of pure silver chloride (460°) to that of pure sodium chloride (792°), proving that the two salts form an unbroken series of mixed salts.

L. J. S.

Iron-salts in the Potash-salt Deposits. HENDRIK E. BOEKE (*Jahrb. Min.*, 1911, i, 48—76).—The iron compounds found in the Prussian potash-salt deposits include rinneite, ferric chloride, hæmatite, magnetite, iron-pyrites, and iron-boracite. Ferrous chloride may also be present in carnallite to a small extent in isomorphous mixture with the magnesium chloride. The red colour of some specimens of carnallite is due to the presence of enclosed hæmatite.

The crystallisation of mixed solutions of ferrous chloride and magnesium chloride, of ferrous chloride and potassium chloride, and of all three chlorides together, was studied and the equilibrium diagrams deduced. The tetrahydrate of ferrous chloride ($FeCl_2,4H_2O$) in contact with the saturated solution passes into the dihydrate at 72·6°; but in a saturated solution of ferrous magnesium chloride the dihydrate forms at the lower temperature of 43·2°. A new crystallised (triclinic) double salt, $FeCl_2,MgCl_2,8H_2O$, separates at 22·8°. The double salt, $FeCl_2,KCl,2H_2O$, separates at 38·3°, whilst below this temperature potassium chloride and $FeCl_2,4H_2O$ are deposited separately from the mixed solution. The observation of Schabus (1850) of the salt $FeCl_2,2KCl,2H_2O$ is not confirmed. L. J. S.

Origin of Dolomite. GOTTLOB LINCK (*Jahrb. Min.*, 1911, i, Ref. 18—20; from *Zeitsch. Deutsch. geol. Ges.*, 1909, **61**, 230—241).—A review is given of the occurrence and paragenesis of dolomite-rocks, and of previous results in the artificial production of dolomite. A solution of magnesium chloride (1 mol. = 2·4 grams) and magnesium sulphate (1 mol. in 50 c.c. of water) when mixed with a solution of ammonium sesquicarbonate ($1\frac{1}{2}$ mols. in 150 c.c. of water) remains clear; but on the addition of a solution of calcium chloride (1 mol. in 100 c.c. of water) and shaking, a thick, gelatinous precipitate appears. On warming the solution this precipitate appears more quickly and becomes crystalline. This material consists of minute spherules with practically the composition of dolomite; it is, however, optically positive and only feebly birefringent, D 2·6—2·7, and is slowly but completely soluble in cold dilute acetic acid. This is regarded as a mixed salt of calcium and magnesium carbonates. When it is heated with the solution in a sealed tube for several hours at 40—50°, the crystalline precipitate changes in character; the spherules being then optically negative with strong birefringence, D$>$2·72, almost insoluble in acetic acid, and containing $MgCO_3$ 44·8, $CaCO_3$ 49·5%. From more dilute solutions rhombohedra with all the characters of dolomite were obtained. The composition of the precipitate varies with the amounts of calcium and other salts (ammonium carbonate or sodium chloride) in the solution. The conditions of equilibrium are discussed, and it is held that dolomite is formed as a result of the chemical equilibrium between the solution and the precipitated material. L. J. S.

Mineralogy of the Mine of Calabona (Alghero). AURELIO SERRA (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 129—132).—The minerals found in this locality include smithsonite, pyrolusite, calcite, quartz, pyrites, chalcedony, jasper, igneous stone, and clay.

The smithsonite is usually white, but some specimens are yellow or green, the latter colour being due to copper. Analysis of the white variety gave:

ZnO.	CaO.	CO_2.	Total.
63·13	2·22	34·65	100·00

so that the mineral contains an unusual quantity of calcium carbonate in isomorphous mixture.

The pyrolusite gave on analysis:

MnO.	FeO.	O (by diff.).	H_2O.	Total.
73·20	5·38	19·19	2·23	100·00

R. V. S.

Red Glauberite and Polyhalite from Varangéville, near Nancy. V. DÜRRFELD (*Mitt. geol. Landesanstalt Elsass-Lothringen*, 1911, **7**, 345—348).—Nodules of brick-red glauberite and polyhalite have long been known from the beds of rock-salt at Vic, in Lorraine, and at Varangéville, near Nancy, but they have frequently been mistaken the one for the other. The glauberite is of a darker brick-red colour with a bright greasy lustre; it forms an aggregate of irregularly intergrown crystals with a distinct cleavage parallel to the basal plane. The polyhalite is paler in colour and dull; it forms compact masses without any distinct cleavage. Both minerals enclose iron hydroxide (which remains as flakes when the material is dissolved in water) and small quartz crystals; and the polyhalite encloses abundant lamellæ and specks of anhydrite. Analyses of material from Varangéville gave I. for the polyhalite, agreeing with the formula $K_2SO_4,MgSO_4,2CaSO_4,2\frac{1}{2}H_2O$ (the slight excess of water over $2H_2O$, as in the usual formula, being due to the hygroscopic nature of the powder and to the fact that the material analysed was not quite fresh); and II. for the glauberite, agreeing with the usual formula $Na_2SO_4,CaSO_4$:

	CaO.	MgO.	K_2O.	Na_2O.	SO_3.	Cl.	Fe_2O_3.	SiO_2.	H_2O.	Total.
I.	18·33	6·48	14·76	0·72	52·25	0·15	0·13	0·18	7·31	100·31
II.	20·13	0·43	1·63	20·49	57·50	0·11	0·46	0·22	—	100·97

L. J. S.

Comparison of Anhydride, Celestine, Barytes, and Anglesite in Respect to the Change of their Geometrical and Optical Characters with Temperature. R. KOLB (*Zeitsch. Kryst. Min.*, 1911, **49**, 14—61).—Numerous observations were made of the interfacial angles, refractive indices, and optic axial angles at various temperatures ranging from $-60°$ to $+570°$. The appreciable, although relatively slight, variations are plotted on curves. For example, for barytes:

	$a:b:c$	Prism angle $(111):(1\bar{1}0)$.	α.	β.	γ.
At $-60°$*	0·8161 : 1 : 1·3121	78°26·2′	1·6369	1·6383	1·6496
At $+570°$†	0·8124 : 1 : 1·3047	78°11′	1·6252	1·6283	1·6345

* $-53°$ to $-50°$ for α, β, γ; † $+550°$ for β.

L. J. S.

Two Uraniferous Columbo-titanates from Madagascar. ALFRED LACROIX (*Bull. Soc. franç. Min.*, 1910, **33**, 321—323).—The two minerals, euxenite and blomstrandite (of G. Lindström, 1874; not the blomstrandine of W. C. Brögger, 1906), were found in decomposed pegmatite at Ambolotara, near Betafo. The euxenite as masses without form, or rarely as indistinct crystals, with a greasy lustre and a brownish-black colour. It weathers to an earthy-yellow substance on the exterior. Thin slices are translucent, and the mineral is optically isotropic. D 4·862. The composition (anal. I. by Pisani) is very near to that of the euxenite from Arendal, in Norway.

	Cb_2O_5.	TiO_2.	ThO_2.	UO_2.	Y_2O_3.	Ce_2O_3.	Al_2O_3.	FeO.	CaO.	Loss on ignition.	Total.
I.	33·70	19·10	1·54	16·40	18·38	2·44	1·30	1·10	2·27	4·00	100·23

The blomstrandite is represented by a single massive specimen with a greasy lustre and greenish-brown colour; D 4·07—4·17. The mineral is attacked by hydrochloric acid. Anal. II. by Pisani.

Cb_2O_5.	TiO_2.	SnO_2.	ThO_2.	U_2O_3.	Al_2O_3.	Fe_2O_3.	Ce_2O_3	Y_2O_3.	MgO.	CaO.	H_2O.	Total.
34·80	18·30	0·30	1·30	26·60	2·10	2·87	0·60	0·90	0·40	3·45	7·60	99·22

L. J. S.

Radioactive Minerals from Madagascar. ALFRED LACROIX (*Compt. rend.*, 1911, **152**, 559—564. Compare Abstr., 1908, ii, 705; 1909, ii, 58, 813; 1910, ii, 46, 307; and preceding abstract).—A description of hatchettolite, blomstrandite, euxenite, and fergusonite has already been given. Microlite occurs in small crystals associated with triphane and rhodizite. Samarskite, from Antanamataza, black to yellowish-brown (analysis by Pisani):

Cb_2O_3.	Ta_2O_5.	TiO_2.	ThO_2.	UO_2.	$(Y.Er)_2O_3$.	$(Ce\ La,Di)_2O_3$.	Al_2O_3.	FeO.	CaO.	H_2O.	Total.	D.
43·60	11·15	1·42	1·05	8·70	9·50	4·05	0·80	5·40	2·43	11·14	99·24	4·20

Autunite, apparently of recent, secondary origin, is met with in pegmatites. It is suggested that this has been formed by the action of phosphoric acid from organic sources on soluble calcium and uranium salts. W. O. W.

Molengraaffite, a New Mineral in Lujaurite from the Transvaal. H. A. BROUWER (*Centr. Min.*, 1911, 129—132).—This mineral occurs, together with microcline, nepheline, ægirite, pseudomorphs of catapleiite after an eucolite mineral, etc, as a constituent of lujaurite (a rock of the nepheline-syenite group) in the Pilandsberg, north of Rustenburg, in the Transvaal. It forms small, yellowish-brown prisms with perfect cleavage parallel to the orthopinacoid, and resembles astrophyllite in appearance. The refraction and birefringence are high ($\alpha = 1·735$, $\gamma = 1·770$). The optical characters and the lamellar twinning on the orthopinacoid point to the monoclinic system. Analysis by F. Pisani gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
28·90	27·70	3·75	0·95	2·07	2·72	19·00	2·38	10·30	0·60	1·00	99·37

This is compared with analyses of astrophyllite, yttrotitanite, eucolite-titanite, and wöhlerite, from which it differs especially in the high percentage of sodium. The mineral fuses easily to a brown enamel, and is decomposed by hydrochloric acid. Titanite results by its alteration. L. J. S.

The Pegmatite of Ytterby, Sweden. IVAR NORDENSKJÖLD (*Jahrb. Min.*, 1911, i, Ref. 33—35; from *Bull. Geol. Inst. Univ. Upsala*, 1910, **9**, 183—227).—A general account is given of the history of the minerals, including the several rare-earth minerals, and the felspar quarries of this well-known locality. The following analyses are given of felspars: I and II of potash-felspar, corresponding with the formula $Or_3(Ab,An)_1$, and III—X of plagioclase, these being mostly oligoclase with the formula $Ab_{3·5}An_1$ to $Ab_{5·1}An_1$. Of the potash-felspars, microcline predominates, but orthoclase also occurs. The oligoclase is found rarely as crystals:

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Loss on ignition.	Total.*
I.	64·32	19·41	0·14	—	0·35	12·90	2·10	0·57	99·79
II.	64·40	19·30	0·30	0·40	—	12·56	2·68	—	99·64
III.	61·55	23·80	—	3 18	0·80	0·38	9·67	—	99·38
IV.	64·23	23·57	—	2·81	—	0·81	8·47	—	99 09
V.	63·19	23·52	—	4·81	—	—	9·01	—	100·53
VI.	62·81	23·21	0·10	3·81	0·18	0·58	8 18	0 81	99·68
VII.	63·66	23·45	—	3·53	0·05	1·59	7·91	—	100·19
VIII.	64·81	22·99	—	3·15	—	0·82	8·89	—	100·66
IX.	63·38	22·98	—	3·63	—	0·55	9·10	0 37	100·00
X.	63·00	23·00	0·30	2·60	0·03	0·38	10·84	—	100·13

The micas present in the pegmatite include biotite and muscovite, the former being frequently altered to chlorite. Analysis XI is of the fresh biotite, and XII of altered biotite:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Moisture.	F.	Y_2O_3.	$(Cb,Ta)_2O_5$.	Total* (less O for F).
XI.	32·23	15·97	7·87	28·06	0·23	2·75	7·93	1·91	2·80	0·31	—	—	—	100·18
XII.	27·68	15·48	14·25	19·39	3·48	6·38	0·57	1·69	7·51	—	0·14	1·54	1·36	100 05

* Several of these totals are incorrect.

L. J. S.

The Scapolite Group. ALFRED HIMMELBAUER (*Jahrb. Min.*, 1911, i, Ref. 22—28; from *Sitzungsber. Akad. Wiss. Wien*, 1910, **119** (1), 65 pp).—The chemical and physical characters were determined in detail for the following members of the scapolite group. Within the errors of observation, due to imperfections in the material, the results indicate that these minerals form an isomorphous series of mixed crystals of which the end-members are:

meionite (Me) .... $2CaAl_2Si_2O_8 + Ca_2Al_2Si_2O_9$

and marialite (Ma)............ $2NaAlSi_3O_8 + NaAlSi_3ClO_8$.

I. Scapolite from Malsjö, Sweden. II. Scapolite from Arendal, Norway. III. Scapolite from Gouverneur, New York. IV. Meionite from Vesuvius. V. Scapolite from Grasse Lake, New York. VI. Scapolite from Bolton, Massachusetts. VII. Scapolite from Gulsjö, Sweden. VIII. Couzeranite from Ariège. IX. Marialite from Pianura, near Naples.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	Cl.	SO_3.	CO_2.	H_2O.	Total.	Sp.gr.
I.	52·48	25·56	0·39	12·44	—	6·52	0·79	0 70	0·58	0·14	0·61	100·21	2·675
II	52·57	24·24	0·26	11·57	—	7·19	0·42	1·63	0·90	0·39	0·69	99·86	2·676
III.	52·65	25·32	0·11	11·30	0·23	6·64	1·58	2·14	0·14	—	0·42	100·53	2·660
IV.	41·42	—	—	—	—	—	—	—	—	—	—	—	—
V.	47·30	25·99	0·32	17·34	0·15	—	—	—	—	—	—	—	2·713
VI.	47·09	25·39	0·10	16·62	0·20	—	—	—	—	—	—	—	2 736
VII.	51·09	23·86	0·16	12·40	0·02	—	—	—	—	—	—	—	2·668
VIII.	56·67	19·47	0·20	7·08	0·23	—	—	—	—	—	—	—	2·625
IX.	59 29	22·66	—	2·74	—	—	—	—	—	—	—	—	—

As determined from the plotted curves, the sp. gr. of pure meionite should be 2·815, and of pure marialite, 2·560. A selection of the physical constants of the materials analysed is:

	Ma%.	$a:c$.	ω (yellow).	ϵ (yellow).	$\omega-\epsilon$.	T_1.*	T_2.*
IV.	4	1 : 0·4394	1·58526	1·55436	0·03090	1138°	1178°
V.	31	1 : 0·4407	1·58284	1·55120	0·03164	1125	1198
II.	54	1 : 0·4410	1·56645	1·54642	0·02003	1150	1238
IX.	85	1 : 0·4460	1·54630	1·53949	0·00681	1088	1233

* T_1, temperature at which edges are rounded; T_2, temperature at which the material is completely fused.

Numerous other values are given for the refractive indices, and the theoretical values for the pure end-members of the series are calculated. Determinations of the composition of the silicic acid by Tschermak's method gave metasilicic acid ($H_{12}Si_6O_{18}$) for the Vesuvian meionite, and for the others, mixtures in various proportions of $H_{12}Si_6O_{18}$ and $H_{10}Si_9O_{23}$. L. J. S.

Mesolite from Palagonia, Sicily. G. PONTE (*Zeitsch. Kryst. Min.*, 1911, **49**, 111; from *Atti Accad. Gioenia Sci. Nat. Catania*, 1908, [v], 1, No. XV).—White, radially fibrous masses from cavities in a palagonite tuff gave on analysis the following results, agreeing with the formula $Na_4CaAl_6Si_9O_{30},6H_2O+H_2O$:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.	H_2O.	Total.	Sp. gr.
46·61	26·36	4·82	11·28	0·24	10·87	100·18	2·188

Over sulphuric acid there is a loss of 2·89% of water, and with increasing temperature a gradual loss amounting to 7·49% at 360°.

L. J. S.

Chemistry of Cancrinite. STANISLAUS J. THUGUTT (*Jahrb. Min.*, 1911, i, 25—47).—Previous analyses of cancrinite show appreciable variations amongst themselves; for example, $Al_2O_3 : SiO_2$ ranges from 1 : 2 to 1 : 2·5. The best analyses give $Al_2O_3 : Na_2O = 1 : 1$. Analysis of rose-red cancrinite from Brevig, Norway, being a portion of the same material as that analysed by Lemberg in 1887, gave the results under I. This material is quite fresh and pure; the small amount of ferric oxide represents hæmatite, to which the red colour of the mineral is due, and the small insoluble residue is ægirite. The percentage of water shown in the analysis is that given by the coarse powder; the finely-powdered mineral gave 6·80% water (compare Thugutt, Abstr., 1909, ii, 1027). From this analysis the formula is deduced as:

$$H_{18}Ca_5Na_{24}Al_{22}Si_{24}C_6O_{119} = 8Na_2Al_2Si_3O_{10},3Na_2Al_2O_4,5CaCO_3,Na_2CO_3,9H_2O:$$

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	CO_2.	H_2O.	Insol.	Total	Sp. gr.
I.	35·58	28·24	0·12	6·91	0·16	18·46	6·35	4·36	0·16	100·34	2·46
II.	37·92	26·74	0·23	2·98	0·29	20·06	5·40	5·10	1·61	100·33	2·44
III.	34·92	24·58	0·17	1·77	0·26	19·70	4·38	7·96	6·22	100·36	2·43

Yellow cancrinite from Brevig gave anal. II.; this material is, however, impure, containing hæmatite, ægirite, and 13·07% of a decomposition product (natrolite). Four other analyses are given of fractionations obtained in heavy liquids from this material: the lightest portion containing 44·26% natrolite with a little hydrargillite.

The cause of the yellow colour of the mineral is discussed; it is attributed to the presence of mosandrite (two of the analyses show the presence of small amounts of cerium earths). Colourless, transparent crystals of cancrinite from Särna, Sweden, gave anal. III.; this material is, however, impure and not fresh, containing ægirite and 28·72% of secondary natrolite.

Cancrinite, when moistened with a 0·1% cobalt solution and strongly ignited, gives an intense blue coloration, thus differing from nephelite, sodalite, natrolite, etc., and from diaspore and hydrargillite, which give the blue colour at a much lower temperature. Although cancrinite is analogous in constitution to nephelite and sodalite, and has been derived from these, yet it differs from them in its mode of alteration: it passes through a soda-cancrinite to an end-product consisting mainly of natrolite. L. J. S.

Aluminium Silicate Minerals in Soils. RUDOLF VAN DER LEEDEN (*Centr. Min.*, 1911, 139—145).—A discussion of the opposed views as to whether the alkalis and alkaline earths present in soils in combination with aluminium silicate exist as zeolites or as "adsorption compounds." L. J. S.

Relations of Some Aluminous Silicate Weathering Products. RUDOLF VAN DER LEEDEN (*Centr. Min.*, 1911, 173—179. Compare preceding abstract).—Experiments were made on the decomposition of silicates by pure water. Stilbite from Iceland (anal. I.) was finely powdered, and one gram shaken for ninety-six hours with 100 c.c. of distilled water. The filtrate was turbid, and, on keeping, deposited a slight sediment; the clear liquid contained: SiO_2 2·6, Al_2O_3 4·0, CaO 5·0 mg.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	CuO.	Alkalis.	Loss on ignition.	Total.
I.	54·55	17·81	0·24	8·71	1·10	—	1·57	16·03	100·01
II.	21·37	32·89	0·81	1·91	0·91	0·69	1·77	39·67	100·02

When allophane from Visé, Belgium (anal. II.), was treated in the same way, there passed into solution SiO_2 2·4, Al_2O_3 2·8, CaO 1·5 mg. These results can be more directly compared by dividing the weights obtained by the percentages of each constituent in the mineral (for example, for SiO_2, $2·6/54·55 = 0·047$).

	Stilbite.	Allophane.
SiO_2	0·047	0·1
Al_2O_3	0·23	0·085
CaO	0·6	0·8

These factors would be unity if the material were completely soluble, whilst if it were partly soluble without decomposition they would be equal for each constituent. They therefore give a measure of the solubility of each oxide, and further indicate that there has been a decomposition of the mineral in each case. Analogous results were obtained when dilute acetic acid was used instead of water.

L. J. S.

[Titaniferous Melanite from Assynt, Sutherlandshire.] ALEXANDER GEMMELL (*Trans. Edinburgh. Geol. Soc.*, 1910, **9**, 417—419).—Several analyses are given of borolanite and related rocks from the neighbourhood of Loch Borolan. A garnet, D 3·663, isolated from ledmorite-pegmatite (a coarse-grained melanite-augite-syenite) from Bad na h'Achlaise gave the following results, agreeing with the garnet formula: $3(Ca,Fe,Mg)O,(Fe,Al,Ti)_2O_3,3(Si,Ti)O_2$.

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	H_2O (110°).	H_2O (+110°).	Total.
33·51	6·74	8·20	17·90	2·70	28·86	1·80	0·46	0·09	0·54	100·81

As described by S. J. SHAND (*tom. cit.*, p. 389), this melanite is dark brown, with a rhombic-dodecahedral form. L. J. S.

Constitution of Ilvaite. ENNIO BASCHIERI (*Zeitsch. Kryst. Min.*, 1911, **49**, 112; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1908, **17**, 31—34).—Employing Tschermak's method for the isolation of the silicic acid, the author concludes that ilvaite is a diorthosilicate, whilst, according to Himmelbauer it is a basic metasilicate. This discrepancy is to be ascribed to the imperfection of the method. Analysis of ilvaite from Elba used in the experiments gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	H_2O.	Total.
28·87	0·85	19·79	34·49	13·58	1·91	99·49

L. J. S.

A New Thermal Water. Prototype of a Modern Physico-chemical Study of a Mineral Water. Methods for the Estimation of Small Quantities of Lithium, Manganese, Antimony, Bromine, Fluorine, Rare Gases, etc. ARMAND GAUTIER and CHARLES MOUREU (*Compt. rend.*, 1911, **152**, 546—551).—An examination, stated to be more complete than any previously carried out, has been undertaken in connexion with a new spring at Nancy yielding 1870 litres per minute. The degree of ionisation of the dissolved salts as determined from the conductivity was about 90%. The radium emanation expressed in mg.-minutes per 10 litres was 0·46 for the evolved gas, and 0·082 for the water. Radium was determined after removal of emanation, and corresponded with $1·2 \times 10^{-11}$ grams of radium bromide per litre.

The following analytical results are in parts per 100,000: K 1·712, Na 37·888, Li 0·048, NH_4 0·054, Mg 1·560, Ca 9·114, Al 0·017, Fe 0·300, Mn 0·0008, Sb and Sn traces. Cl 57·838, Br 1·152, I 0·0004, F 0·114, SO_4 11·448, S 0·080, BO_3 trace, SiO_3 2·026, CO_3 9·272, $HAsO_4$ 0·00028, NO_3 0·036, PO_4 and NO_2 nil. Total 134·05; residue dried at 180°, 134·98. Oxygen consumed 0·105. Dissolved gases: argon (with traces of krypton and xenon), 45 c.c.; helium (with traces of neon), 19 c.c. The gas evolved at the spring contained CO_2 1·75, N_2 95·36, A 1·29, He 1·60%.

The following analytical methods are new. For lithium, 30 litres of water were concentrated, and the sulphates precipitated by lead acetate and barium chloride. Calcium, barium, magnesium, and ammonium were removed, and the dry residue taken up three times with concentrated hydrochloric acid, which extracts lithium chloride with small amounts of the other alkali chlorides. After evaporation to dryness, the lithium was removed by extraction with a mixture of absolute amyl alcohol and ether. The metal was finally precipitated as phosphate.

Bromine was estimated by distillation with chromic and sulphuric acid into potassium iodide solution and titration of the liberated iodine. Fluorine was determined after removal of silica, calcium, and magnesium, by precipitation in alcoholic solution as barium fluoride, followed by conversion into the sulphate.

Antimony was detected by conversion into the bromide and extraction with carbon disulphide. W. O. W.

Physiological Chemistry.

The Influence of Compressed Air on Blood-formation. ADELE BORNSTEIN (*Pflüger's Archiv*, 1911, **138**, 609—616).—Prolonged exposure of dogs and monkeys to compressed air (two atmospheres) produces a hydræmic condition with a diminution per c.c. of corpuscles and hæmoglobin. W. D. H.

Physiology of Blood-sugar. E. FRANK (*Zeitsch. physiol. Chem.*, 1911, **70**, 291—299).—In confirmation of Baudouin's statement, it is shown that the dextrose in the blood increases when large doses of dextrose (100—200 grams) are given by the mouth an hour or two previously; the urine is usually free from sugar, or only traces are present. Alimentary hyperglycæmia and glycosuria are probably due to insufficiency of liver action. There may, however, be certain slighter cases of a diabetic nature, in which, although the blood is rich in sugar, it may not pass into the urine, owing to functional disturbance of the kidneys. W. D. H.

The Distribution of Reducing Substances in Human Blood. H. LYTTKENS and J. SANDGREN (*Biochem. Zeitsch.*, 1911, **31**, 153—158. Compare Abstr., 1910, ii, 785).—The sugar was estimated in corpuscles and serum both before and after fermentation with yeast by means of Bang's method. The difference was taken to indicate the amount of dextrose. It was found that human blood-corpuscles contain practically no dextrose, the whole amount in the blood being in the serum. The normal sugar content of urine is not much less than that of blood. The normal dextrose content of rabbit's blood is much higher than that of human blood. The amount of dextrose in rabbit's blood-corpuscles is also extremely small. The authors explain the differences between their results and those obtained by other investigators (Michaelis, Rona, etc.). S. B. S.

The Dipeptide-Splitting Action of Blood-plasma, and Pathological Fluids. I. WALKER HALL and G. SCOTT WILLIAMSON (*J. Path. Bact.*, 1911, **15**, 351—352).—Specimens of blood-plasma and serum, pleuritic and other dropsical effusions, but not cerebro-spinal fluid, split up glycyl-tryptophan. The substance responsible for this action is precipitated with the globulin fraction, and obeys the laws of ferment action, but its properties do not agree with those of erepsin or trypsin. W. D. H.

Ester and Fat Hydrolysis in Blood and Serum. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1911, **31**, 345—354).—The hydrolysis of monobutyrin in aqueous solution can be measured by determining the changes in the surface-tension by Traube's drop method from a capillary tube, the number of drops falling in a given time from a given apparatus diminishing as hydrolysis proceeds. By this means the action of serum and blood from various sources on monobutyrin was determined. The sera of guinea-pigs and rabbits exert a strong action, whereas those of ox, pig, and sheep exert a weak action. In general, the sera act more weakly than the whole blood. S. B. S.

The Behaviour of Calcium in the Serum, and the Calcium Content of the Blood-corpuscles. PETER RONA and D. TAKAHASHI (*Biochem. Zeitsch.*, 1911, **31**, 336).—By means of the compensation dialysis method it was found that 25—35% of the calcium in serum is not diffusible. The calcium content of blood-corpuscles was also estimated by means of separate estimations in the whole blood and the serum, and the determination of the amount of corpuscles by the hæmatocrite method. By this means it was found that the corpuscles contain calcium (0·0025—0·0035%). The results confirm those of Hamburger obtained by physiological methods as to the calcium content of the corpuscles. S. B. S.

Blood-sugar. IX. The Permeability of Blood-corpuscles to Dextrose. PETER RONA and A. DÖBLIN (*Biochem. Zeitsch.*, 1911, **31**, 215—220).—Sugar was estimated in the whole blood and in the serum, and the percentage of corpuscles determined by the hæmatocrite method. In this way the percentage of sugar in the blood-corpuscles could be determined, both in the untreated blood and in the blood after addition of sugar. The sugar was estimated polarimetrically after separation of protein by dialysed iron hydroxide. The results lead the authors to the conclusion that the red blood-corpuscles are permeable to sugar. S. B. S.

The Amount of Oxyproteic Acids in Serous Fluids, and in the Blood in Normal and Pathological Cases. WINCENTY CZERNECKI (*Bull. Acad. Sci. Cracow*, 1910, *A*, 399—413).—The method employed was to separate the proteins by heating the liquid after acidifying by acetic acid, acidify the concentrated filtrate with sulphuric acid, precipitate the sulphates of the alkali metals by alcohol, and to precipitate the phosphates, urates, etc., by barium hydroxide. The

filtrate was then evaporated to dryness, and then extracted with alcohol-ether and, finally, alcohol. The nitrogen in the residue which contained the oxyproteic acids was estimated. The following estimations were also made: the total nitrogen, the total extractive nitrogen (that is, the total nitrogen after separation of proteins), the nitrogen in the copper acetate precipitate obtained from the protein-free liquid, and the specific gravity. The author tabulates the results obtained, which are chiefly of clinical interest, from serous fluids and bloods from a large number of normal and pathological cases.
S. B. S.

The Influence of Ether Narcosis on Body Temperature and Carbohydrate Metabolism. KARL GRUBE (*Pflüger's Archiv*, 1911, **138**, 601—608).—In confirmation of Selig's statement, it was found that ether narcosis is followed by temporary glycosuria, often accompanied by albuminuria in dogs. There is also a fall of body temperature, but if this is avoided by artificial warming, the effects on the urine do not occur.
W. D. H.

Nitrogenous Metabolism of the Coyote (Canis Latrans). ANDREW HUNTER and MAURICE H. GIVENS (*J. Biol. Chem.*, 1910, **8**, 449—464).—The coyote employed, whether in equilibrium or fasting, did not show, so far as nitrogen metabolism is concerned, any essential difference from a dog under similar conditions. The principal numerical details given relate to urea, ammonia, creatinine, creatine (exogenous in origin), allantoin, and purines. Urocanic acid was not found in the urine.
W. D. H.

The Effect of Chloroform on the Intermediate Protein Metabolism of the Dog. DOROTHY E. LINDSAY (*Bio.-Chem. J.*, 1911, **5**, 407—426).—In chloroform anæsthesia, the excretion of total nitrogen is distinctly increased; the urea nitrogen falls; the ammonia nitrogen, the allantoin nitrogen, and the amino-acid nitrogen rise; the creatinine nitrogen is unaffected, but creatine usually appears in the urine two or three days after the inhalation.
W. D. H.

Nuclein Metabolism in the Dog. PHŒBUS A. LEVENE and FLORENTIN MEDIGRECEANU (*Amer. J. Physiol.*, 1911, **27**, 438—447).—If allantoin is given, 31% is excreted unchanged, and the rest oxidised to urea; when sodium urate is given, 60% is excreted in the urine, 15% as allantoin, 2% as sodium urate, and the rest as urea; when hypoxanthine is given, 56% is excreted, of which 80% is in the form of allantoin, 2% as uric acid, and the remainder as urea. When inosin is given, 40% is excreted as allantoin, 4% as uric acid, 2% as purine, 4% as undetermined nitrogen, and the rest as urea. Feeding on hypoxanthine and inosin is often followed by prolonged disturbances of nitrogenous equilibrium, which can be avoided by giving sodium carbonate at the same time. When nucleic acid is given, 50% appears in the urine, of which 85% is in the form of allantoin and the rest urea. After feeding on thymus, 17% of the nitrogen is excreted as allantoin, 5% as uric acid, and the rest as urea. There was no increase of amino-acids in the urine in any experiment. The highest allantoin output follows feeding on nucleic acid and hypoxanthine. The first step in the disintegration of nucleic acid in the body is probably the liberation of purines and not of inosin. W. D. H.

Phosphorus Metabolism. J. P. GREGERSEN (*Zeitsch. physiol. Chem.*, 1911, **71**, 49—99).—On nitrogenous diet which contains phosphorus in an inorganic form only, the organism remains in phosphorus equilibrium, or may put on phosphorus. Organic phosphorus compounds can therefore be built up in the body from phosphates. On a nitrogen-free diet the loss of phosphorus is not affected if phosphates are given. On a nitrogenous diet free from phosphorus, but capable of maintaining nitrogenous equilibrium, the excretion of phosphorus falls markedly. On a phosphorus-free nitrogenous diet containing calcium and magnesium salts, the urine contains a minimal amount of phosphorus, but more leaves the body by the fæces. If calcium and magnesium salts are absent from the food, the urine usually contains more phosphorus than the fæces. The experiments were made on rats. W. D. H.

The Utilisation of Yeast in the Human Body. WILHELM VOLTZ and AUGUST BAUDREXEL (*Biochem. Zeitsch.*, 1911, **31**, 355—357).—In continuation of a former investigation (this vol., ii, 215), the food-value of constituents of yeast other than protein were determined. The amounts resorbed in the organism were found as follows: organic substances, 90%; protein, 86%; fat, 70%; fibre, 40%; nitrogen-free extractives, 100%. S. B. S.

Fasting Studies. I. Nitrogen Partition and Physiological Resistance as Influenced by Repeated Fasting. PAUL E. HOWE and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1911, **33**, 215—253).—An account in full detail of the effect on a dog of two successive fasts, a preliminary account of which has already appeared (compare Abstr., 1910, ii, 728). E. G.

Further Remarks on the Relationship between the Magnitude of Oxidation and Cytolysis of Sea-urchin's Eggs. JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, **31**, 168—169).—A reply to some recent criticisms of O. Warburg (Abstr., 1910, ii, 628; this vol., ii, 60). S. B. S.

Increase of Protein during the Fattening of Full-grown Animals. THEODOR PFEIFFER and K. FRISKE (*Landw. Versuchs-Stat.*, 1911, **74**, 409—465).—During the fattening of full-grown sheep the animal puts on nitrogen in the form of flesh. The worse the condition of the animal beforehand, the more marked is the putting on of flesh, and this occurs even although the diet is poor in protein, especially if given for long periods. W. D. H.

The Behaviour of Fats of Animal Organs in Antiseptic Preservation. NAGAMICHI SHIBATA (*Biochem. Zeitsch.*, 1911, **31**, 321—335).—The Kamagawa-Suto method of examination was employed. Concordant results were almost always obtained in the case of the fatty acids soluble in light petroleum, but in the cholesterol estimations the results were not always so satisfactory. After prolonged preservation (up to forty-seven days), even at summer temperature, no changes could be detected in higher fatty acids, and, as a rule, also in cholesterol. There is therefore no evidence of new fat formation during autolysis, and the results negative the suggestion that fat is formed from protein during fatty degeneration. The fact that there is an increase of stainable fat can be explained by assuming that during the changes, fat is set free from certain very complex combinations. S. B. S.

Cholesterol in Animal Tissues. ARTHUR LAPWORTH (*J. Path. Bact.*, 1911, **15**, 254—261).—Windaus' digitonin method for estimating cholesterol and its esters was found to be accurate. Extraction of the organs by methods which involve desiccation with plaster of Paris or anhydrous sodium sulphate does not lead to erroneous results. Free cholesterol and esters were found in kidneys, adrenals, a dermoid cyst, and brain. The proportion of free to combined cholesterol varies considerably with age in the same organ; more than 99% in the brain is free. W. D. H.

The Fate of Cholesterol in the Animal Organism. J. BROWINSKI (*Chem. Zentr.*, 1910, ii, 1072; from *Kosmos*, 1910, **35**, *Radziszewski Festband*, 557—561).—The substance extracted from the fæces of dogs kept on a flesh diet is shown to be cholesterol, on account of the chemical and optical properties and the elementary analyses both of the substance itself and of certain of its derivatives. Cholesterol is not therefore reduced to coprosterol in the intestine of the dog (compare Kusumoto, Abstr., 1909, ii, 79). W. J. Y.

Fish. CHRISTOPH ULRICH (*Arch. Pharm.*, 1911, **249**, 68—92).—The author has determined the "edible matter," moisture, fat, ash, pure ash (free from sodium chloride), phosphoric acid, "total nitrogen," protein, and "nitrogen-free extract" for twenty-five species of fish, figures being given in most cases for fresh, preserved, and cooked specimens of each species. The results are tabulated in detail in the original.

The fish are classified into "fat," containing 24·03% or more fat, and "lean," containing below 7·03% fat, both figures being calculated on the dry matter of the fresh fish. In general, the "edible matter" shows great variation, and over the whole series now examined ranges for fresh specimens from 54·1 to 76·5%, the former being yielded by herrings and the latter by haddock. Frying or baking, as opposed to boiling, generally increases the yield of "edible matter." Boiling usually reduces the amount of water, fat, and nitrogenous substance in the edible matter. Frying and baking increase the amount of fat in "lean" fish, due to absorption of added fat, but reduce the amount in "fat" fish. The various methods of preservation, such as "salting," "pickling," and "smoking," generally reduce all the constituents, but especially the nitrogenous matter. T. A. H.

Reactions in Gelatinous Media. RAPHAEL E. LIESEGANG (*Zeitsch. anal. Chem.*, 1911, **50**, 82—87).—The phenomena which result from the formation of precipitation membranes and dead space by diffusion in gelatinous media are shown to be of importance in connexion with chemico-physiological changes, and with certain operations involved in histological preparation work (compare Abstr., 1910, ii, 936, 1052). H. M. D.

The Effect of Ions Transported by the Current on the Primary Affinity for Colours, and the Conductivity of Polarised Nerves. Influence of the Cations Ca, Na, K on the Anodic Region. ALFRED SCHWARTZ (*Pflüger's Archiv*, 1911, **138**, 487—524). —A contribution to electro-physiology; the effect of the various constituents of Ringer's solution is studied. W. D. H.

Changes in the Excitability of the Vegetative Nervous System by Removal of Calcium. RICHARD CHIARI and ALFRED FRÖHLICH (*Arch. exp. Path. Pharm.*, 1911, **64**, 214—227).—Poisoning with hydrochloric acid, oxalic acid, and sodium oxalate increases the excitability of the nerve-endings of the vegetative (that is sympathetic and autonomic) nervous system towards adrenaline and pilocarpine. Adrenaline mydriasis can be produced in cats after chronic poisoning with arsenic, mercuric chloride, and sodium chlorate. The increase of excitability is attributed to precipitation of calcium or washing out of the calcium from the tissues. W. D. H.

The Influence of Phloridzin on Glycogen Formation in the Liver. BERNHARD SCHÖNDORFF and FRITZ SUCKROW (*Pflüger's Archiv*, 1911, **138**, 538—546).—This investigation was undertaken on account of the differences in the views held on the relative importance of the liver and the kidney in phloridzin diabetes. Phloridzin was found to have no effect at all on glycogen formation in the liver. W. D. H.

The Origin of Glycogen from Formaldehyde. BERNHARD SCHÖNDORFF and FRIEDRICH GREBE (*Pflüger's Archiv*, 1911, **138**, 525—537).—Grube (Abstr., 1908, ii, 307; 1909, ii, 328) stated that the liver of the tortoise is able to form glycogen from a dilute solution of formaldehyde perfused through it. A repetition of these experiments failed to confirm them. The usual result is that the perfused lobe is usually poorer in glycogen than the control lobe. W. H. D.

Cysteine in Animal Organs. VINCENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1911, **70**, 314—325).—After precipitation of extracts of liver, spleen, and thymus with ammonium or sodium sulphate, the filtrate gives an intense purple with sodium nitroprusside and ammonia. This is attributed to cysteine, and the substance in the organ extract agrees in all its reactions with those of cysteine prepared from cystine. Cysteine is regarded as an important primary constituent of animal cells. W. D. H.

Study of Autolysis by Physico-chemical Methods. RICHARD CHIARI (*J. Biol. Chem.*, 1911, **9**, 61—63).—Polemical and explanatory: a reply to Benson and Wells (Abstr., 1910, ii, 978). The author dealt with alterations in the state of the cells; Benson and Wells with direct effects on enzymes. The author's results agree with those of Claypon and Schryver in the existence of a latent period of five or six hours in the commencement of autolysis of the liver after death.

W. D. H.

Cutaneous Pigmentation in Normal and Pathological Conditions. WILLIAM DYSON (*J. Path. Bact.*, 1911, **15**, 298—322).—Melanotic pigment is a product of the nucleus of the epidermal cells; melanin is regarded as the protein portion after separation from complex lipoids in the nucleus. It is disposed of by the lymph stream. An increase of pigment can occur as a result of over-activity of the epidermis provoked by light, heat, etc., or of deficient drainage by the lymphatics.

W. D. H.

The Chemical and Biological Differentiation of the Three Proteins of Cow's and Human Milk. J. BAUER and ST. ENGEL (*Biochem. Zeitsch.*, 1911, **31**, 46—64).—The caseinogen was separated chemically, partly by thawing after long freezing, and the remainder by acetic acid; the globulin was separated from the caseinogen-free filtrate by magnesium (full saturation) or ammonium sulphate (half saturation); from the filtrate of the latter the albumin was precipitated by lactic acid. The biological differentiation was carried out by quantitative measurements of the antigen-complement binding capacity, when anti-sera for the various proteins were used as the source of complement, the hæmolytic action being employed as the test. A biological differentiation of caseinogen, albumin, and globulin could be detected. The globulin is more nearly allied to caseinogen than albumin. The colostrum proteins are similar to those of milk. The globulin and albumin from milk, serum, and colostrum appear to be identical. The proteins of human milk are similar to those of cow's milk.

S. B. S.

The Response of the Colostral Milk of Cows to the Schardinger Reaction. RICHARD REINHARDT and ERNST SEIBOLD (*Biochem. Zeitsch.*, 1911, **31**, 294—320).—The Schardinger reaction (decoloration of methylene blue-formaldehyde mixture) was investigated with the employment of Schern's thermodiascope. The reaction varies under different conditions and with different fractions of a single milking. The results obtained by the authors are chiefly of veterinary interest.

S. B. S.

The Cutaneous Elimination of Nitrogen, Sulphur, and Phosphorus. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1911, **9**, 21—24).—Two men did daily uniform work, wore clothes of the same weight, and did not suffer from obvious perspiration; their bodies and underclothing were daily washed with alcohol and 0·5% solution of sodium carbonate. The washings were collected, concentrated, and analysed. The average elimination in the two individuals was, in case A (average of twenty-eight days): sulphur 0·028, phosphorus 0·003, and nitrogen 0·190 gram per diem. In case B (average forty-five days) the respective figures were 0·015, 0·002, and 0·160. The figures are too low, as the hair was omitted to be washed. W. D. H.

Analyses of the Urine of the Fox, Dog, and Coyote. PHILIP B. HAWK (*J. Biol. Chem.*, 1910, 8, 465—478).—The three animals named were placed on uniform diets, and estimations of total nitrogen, ammonia, creatine, and creatinine made in their urine. The figures obtained are given in full, and slight differences are noted. Urocanic acid was not sought for. W. D. H.

The Presence of Allantoin in Certain Foods. H. ACKROYD (*Bio.-Chem. J.*, 1911, 5, 400—406).—The whole quantity of allantoin excreted by man on a milk and vegetable diet may be derived directly from the food. Milk, white bread, French beans, and green peas all contain small quantities of allantoin, but none could be isolated from eggs, bananas, or rhubarb. W. D. H.

The Oxyproteic Acids and their Part in Animal Metabolism. STANISLAUS BONDZYNSKI (*Chem. Zentr.*, 1910, ii, 1069, from *Kosmos*, 1911, 35, *Radziszewski Festband*, 680—694).—A general account of the work of the author and his pupils on the derivatives of oxyproteic acids in the urine and other fluids of the body. Four of these compounds have been isolated from human urine: autoxyproteic acid (C 43·21%; H 4·91%; N 24·40%; S 0·61%; O 26·33%); oxyproteic acid (C 39·62; H 5·64; N 18·08; S 1·12; O 35·54%); *allo*-oxyproteic acid (C 41·33, H 5·70; N 13·55; S 2·19; O 37·23%; and urochrome (C 43·09; H 5·14; N 11·15; S 5·09; O 35·53%), the two last of which are probably direct oxidation products of protein. From the barium contents of their salts (24·6—37% Ba), the molecules must contain a large number of carboxyl groups, and these compounds cannot therefore be classed as polypeptides, as was done by Abderhalden.

Urochrome forms the chief pigment of the urine, and the daily excretion of this substance in normal human urine is 0·54—0·69 gram, which may rise to 1·19 gram under pathological conditions. From 1·5—6·8% of the total nitrogen, and about 98% of the sulphur of normal urine, are derived from these acids.

Urine also contains other organic acids which may be extracted with ether, and of these the daily excretion is equivalent to about 11 grams of sodium. Oxyproteic acids also occur in human blood-serum in sufficient quantity to account for 25·9—40% of the total nitrogen. Under certain pathological conditions as much as 81·7% of the oxyproteic acids present in serum consists of urochrome.

The author draws the conclusion that most of the nitrogen of blood-serum is present in the form of oxyproteic acids and other organic acids, and not as urea. These acids must play a part in the neutralisation of the bases of the body, and in the reaction of its tissues.

W. J. Y.

Estimation of Urobilin in the Excreta and its Value as a Measure of Hæmoglobin Metabolism. G. C. E. SIMPSON (*Bio.-Chem. J.*, 1911, **5**, 378—389).—Most of the urobilin formed is excreted usually with the fæces. In constipation, the urobilin of the urine rises. The total output of urobilin represents the total breakdown of hæmoglobin; that in the urine indicates the absorption capacity of the intestinal wall. The liver can deal with a very large amount of hæmoglobin before unaltered hæmoglobin overflows into the urine. W. D. H.

Urorosein Pigments of the Urine. VINCENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1911, **71**, 1—6).—The urorosein group contains three members: *α*- or normal urorosein, *β*-urorosein, and nephrorosein. The colour and spectroscopic appearances, and the changes these undergo when exposed in amylic alcohol solution to sunlight, are described. They are absent from normal urine, but are found in various pathological cases: nephrorosein in convalescence from scarlet fever, in chronic tuberculosis, etc. Accepting the view of Salkowski and Herter that urorosein has a chromogen which is *β*-indoleacetic acid, a product of intestinal putrefaction, the view is advanced that the occurrence of the pigments is related to intestinal conditions, and is principally seen when there is constipation, or when proteins are not readily absorbed, as on a milk diet. W. D. H.

Origin of Immune Substance. J. P. MCGOWAN (*J. Path. Bact.*, 1911, **15**, 262—281).—After spleen, thyroid, kidney, the leucocyte and lymphatic organs are excluded by extirpation and otherwise, the injection of ox corpuscles into the rabbit still produces the production of the immune substance on the third day. As the same result follows feeding on ox-blood, the conclusion is drawn that the production of such substances is an exaggeration of a normal process which deals with food protein; and the liver, situated as it is on the direct path of foreign material entering the circulation, is regarded as the possible seat of the formation of anti-substances. W. D. H.

The Limit of Glycuronic Acid Combination in Rabbits Immunised Against Enzymes. JUHO HÄMÄLÄINEN and LENNART SJÖSTRÖM (*Skand. Arch. Physiol.*, 1910, **24**, 113—126).—In rabbits immunised against emulsin, and then fed on borneol and its compounds, the amount of borneol excreted in the urine in combination with glycuronic acid is increased, and may be doubled. The effect is more marked with *l*- than with *d*-borneol. A similar effect is noted if thymol is given instead of borneol, and this is regarded as evidence that thymolglycuronic acid has a *β*-glucoside structure. W. D. H.

The Nature of Turbid Swelling. [Parenchymatous, Albuminous, or Granular Degeneration.] MARTIN H. FISHER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 159—167).—Experiments have been made to determine the nature of the turbid swelling exhibited by the cells of the liver, kidney, etc., under certain pathological conditions, When pieces of fresh liver or kidney are placed in distilled water, the organs develop a grey colour and exhibit the phenomenon of turbid swelling. In dilute ($0{\cdot}005N$) solutions of acids (lactic, formic, acetic, tartaric, hydrochloric, sulphuric, or nitric), the swelling takes place much more quickly. The addition of salts to the acid solutions sometimes increases the rapidity of the change, in other cases it causes a diminution. In the absence of acids, the specific effects of the various salts are exhibited in the same manner. In alkaline solutions the turbid swelling is not observed.

The turbid swelling is supposed to be connected with the production of acid in the affected cells, and this increases the affinity of the colloids for water. The development of the turbidity resembles closely the precipitation of casein in its general characters. The swelling and the turbidity are therefore both primarily due to the formation of acids in the cells. This results in an increased absorption of water, whereby swelling is caused, and also in the precipitation of proteins within the cells. Experimental observations are cited in support of this view. H. M. D.

Chemical Changes in the Liver in Certain Pathological Processes. B. J. SLOWTZOFF and L. W. SOBOLEFF (*Biochem. Zeitsch.*, 1911, **31**, 234—242).—Concurrently with pathological-morphological changes in the liver, the chemical changes were investigated in certain cases of disease (syphilis, cirrhosis, etc.). Preliminary investigations showed that the amount of blood still contained in the washed-out liver made but little difference in the results. In cases of cirrhosis due to congestion, it was found that side by side with degeneration as studied histologically, there is an increase in the water-content, and the quantity of fat becomes sub-normal. The liver becomes richer in extractives, and poorer in nucleins and peroxydases. In syphilis the composition of the liver remains normal, but there is a marked decrease in ferment-content. S. B. S.

The Peptide-splitting Ferments of Gastric Contents in Cancer. I. WALKER HALL and G. SCOTT WILLIAMSON (*J. Path. Bact.*, 1911, **15**, 352—353).—The gastric contents in cases of cancer decompose glycyltryptophan. This confirms a statement previously made by Neubauer and Fischer (*Arch. klin. Med.*, **97**, Hefte 5—6); certain precautions, however, are necessary in carrying out the test.
W. D. H.

Creatine and Creatinine Excretion in Diabetes Mellitus. M. ROSS TAYLOR (*Bio-Chem. J.*, 1911, **5**, 362—377).—Creatine is constantly present in diabetic urine, even if the diet is free from creatine. This is regarded as due to increased endogenous protein katabolism. Total creatinine excretion is not increased in diabetes even on a diet rich in meat; but the amount even on a creatine-creatinine-free diet varies to a certain extent with the intake of nitrogen. W. D. H.

The Theories of Experimental Diabetes. E. FRANK and S. ISAAC (*Arch. exp. Path. Pharm.*, 1911, **64**, 293—328).—A discussion of the causes of diabetes when experimentally produced by adrenaline, by extirpation of the pancreas, and by phloridzin; the importance of the liver functions in producing the condition is insisted on. The internal secretion of the pancreas is believed to act as an amboceptor to enable the liver to fix glycogen; pancreatic diabetes is, therefore, due to interference with glycogen fixation, whereas phloridzin diabetes is a condition in which the kidneys themselves participate, and is due to interference with dextrose fixation. W. D. H.

Studies on Glycosuria. EDWARD S. EDIE, BENJAMIN MOORE, and HERBERT E. ROAF (*Bio-Chem. J.*, 1911, **5**, 325—361).—A general consideration of the varied causes of glycosuria. Some experimental facts on the production of this condition by inhalation of carbon dioxide and by anæsthetics are given. In one dog deprived of its pancreas, a combination of extracts of pancreas, duodenum, and liver caused a temporary disappearance of the sugar from the urine; but later, in the same dog and in other dogs, the administration of the extracts produced no effect whatever. W. D. H.

Does Dextrose Arise from the Digestion of Cellulose? GRAHAM LUSK (*Amer. J. Physiol.*, 1911, **27**, 467—468).—From experiments on phloridzinised dogs this question is answered in the negative. W. D. H.

So-called Oxaluria. S. SERKOWSKI and MOZDZENSKI (*Zeitsch. physiol. Chem.*, 1911, **70**, 264—278).—The examination of a large number of urines is given in detail, and the possible meanings of excretion of oxalates discussed, but no general conclusions are drawn. The most important point, however, appears to be that increase in acid phosphates favours the precipitation of oxalates, and therefore the occurrence of such a precipitate does not necessarily mean an increase of oxalate excretion. W. D. H.

Lævulosuria. OSCAR ADLER (*Pflüger's Archiv*, 1911, **139**, 93—130).—A historical review of lævulosuria is given, together with an account of the methods of detecting lævulose and separating it from dextrose in the urine. Alimentary lævulosuria is fairly readily produced, but in diabetes the condition is a rare one. In 1490 cases of diabetes it occurred in 0·13%. Some clinical details of a few cases are given; in a few cases there is evidence of heredity. Lævulose is not found in acidosis. W. D. H.

The Clinical Importance of E. Goldschmiedt's Glycuronic Acid Reaction in Infants' Urine. ERNST MAYERHOFER (*Zeitsch. physiol. Chem.*, 1911, **70**, 391—397. Compare Abstr., 1910, ii, 555, 759).—The importance of this reaction in the urine of suckling children is that it is an indication of intestinal putrefaction; urines often give it which do not give the indican reaction. W. D. H.

Employment of Chromium Salts for Combating Plague. PAUL KOENIG (*Chem. Zeit.*, 1911, **35**, 205—206).—The process consists in applying 5—10% solution of sodium dichromate to bodies of animals, excrementitious matters, and places infected with plague. Other dichromates and chromates may be employed, but are less convenient, and permanganates are less effective.

The results of numerous experiments with plants showed that chromates act with extraordinary power and rapidity as poisons on protoplasm. N. H. J. M.

The Action of Lecithin from Different Sources in the Wassermann Reaction. Carl H. Browing, J. Cruickshank, and W. Gilmour (*J. Path. Bact.*, 1911, 15, 361—362).—The general result obtained shows that the amount of complement absorbed in the presence of syphilitic serum is greatest with heart lecithin and least with brain and egg-yolk lecithin. Such biological differences confirm observations as to differences in the chemical constitution of phosphatides from various sources. It has not been yet determined which of them is of chief importance in bringing about the syphilis reaction. W. D. H.

The Influence of Adrenaline on Muscular Activity. Mme. Wanda Radwańska (*Bull. Acad. Sci. Cracow*, 1910, *B*, 8, 728—736).—From experiments on frogs, the following conclusions are drawn: injection of adrenaline into the substance of voluntary muscles increases their contractile force, and relieves fatigue; the total amount of work done is diminished by removal of the suprarenal capsules, but can be raised to the normal by treating such frogs with adrenaline. Normal frogs, and frogs without suprarenals but treated daily with adrenaline, possess in their nerves a higher excitability (ten-fold) than those without suprarenals simply. W. D. H.

The Effect of Oxygen and the Salts of the Blood on the Action of Adrenaline. Erich Siegel (*Pflüger's Archiv*, 1911, 138, 617—637).—In previous researches it has been stated that the activity of adrenaline is destroyed by oxidation. It was, however, found that the power adrenaline possesses of dilating the frog's pupil was not affected by oxidising agents. In the presence of blood-serum this is also true. Distilled water after some hours dilates the pupil; physiological salt solution usually contracts the pupil, but does not affect the subsequent action of adrenaline. The chlorides of calcium and potassium in the concentrations in which they occur in serum have no effect either on the pupil or on the action of adrenaline. A mixture of the three salts in the proportion in which they occur in serum has the same effect as physiological sodium chloride solution.

W. D. H.

Influence of Urethane in the Production of Glycosuria in Rabbits after the Intravenous Injection of Adrenaline. Frank P. Underhill (*J. Biol. Chem.*, 1911, 9, 13—18).—The subcutaneous administration of adrenaline in the dilution 1 : 1000 produces glycosuria in rabbits more readily than the same amount introduced intravenously in greater dilution. If the dilution is 1 : 500,000 or 1 : 125,000, no glycosuria ensues unless the animal is under urethane narcosis.

W. D. H.

The Relation between Chemical Constitution and Physiological Action; Substances with Unstable Carbon–Nitrogen Linking. HERMANN EMDE (*Chem. Zentr.*, 1910, ii, 1477; from *Festschrift Deut. Apoth. Ver.*, 1910, 85—105).—A number of instances are discussed in which unsaturated compounds are more poisonous than the corresponding saturated compounds, with a view to determining whether the double linking in those compounds which owe their toxcity to its presence causes, at the same time, a marked instability in the molecular linking. A number of experiments were carried out on quaternary ammonium compounds containing a double linking to ascertain the effect of the position of this double bond on the stability of the carbon–nitrogen linking, and the ease with which cleavage took place at this point under the action of nascent hydrogen was taken as the measure of the stability of this linking. It was found that this carbon–nitrogen linking is unstable in those substances containing an aliphatic double bond in the $\alpha\beta$-position (C⁚C·N), but not in the $\beta\gamma$-position (C⁚C·C·N), whilst the opposite held in the case of a double bond in the benzene ring. The presence of a benzene radicle in the molecule, however, modifies this rule in those substances containing a double bond in the open-chain, since cinnamyltrimethylammonium chloride shows little stability, although the double bond is in the $\beta\gamma$-position.

When compounds containing more than one cinnamyl or benzyl group in the molecule are acted on by sodium amalgam, only one of these groups is split off as phenylpropylene or toluene, and the others remain attached to the nitrogen in the tertiary amine. If both cinnamyl and benzyl groups are present, only the cinnamyl group is split off. Similar experiments have been carried out by Runne with compounds obtained from benzylamine by substitution in the side-chain. The quaternary ammonium compounds corresponding with aminophenylpropanol and with aminophenylbutanol are acted on by sodium amalgam according to the equations:

$$NMe_3Cl{\cdot}CHPh{\cdot}CHMe{\cdot}OH + H_2 = CH_2Ph{\cdot}CHMe{\cdot}OH + NMe_3 + HCl.$$

$$NMe_3Cl{\cdot}CHPh{\cdot}CH_2{\cdot}CHMe{\cdot}OH + H_2 = CH_2Ph{\cdot}CH_2{\cdot}CHMe{\cdot}OH + NMe_3 + HCl.$$

The carbon–nitrogen linking in phenylethyltrimethylammonium chloride is rendered unstable by the double bond in the benzene ring in the $\gamma\delta$-position (C⁚C·C·C·N), since this compound is decomposed by sodium amalgam, and to this instability is attributed, in part, the physiological action of derivatives of phenylethylamine, such as *p*-hydroxyphenylethylamine, hordenine, adrenaline, ephedrine and ψ-ephedrine.

From the observation of Runne and of Schmidt and Bümming, that the hydrochlorides of the amino-alcohol, NHMe·CHPh·CHMe·OH, and of ephedrine are converted by heating into methylamine hydrochloride, together with benzyl methyl ketone and phenyl ethyl ketone, the conclusion is drawn that ephedrine and ψ-ephedrine are β-methylamino-α-phenylpropanol, NHMe·CHMe·CHPh·OH.

Phenylethyltrimethylammonium chloride, $CH_2Ph\cdot CH_2\cdot NMe_3Cl$, was prepared in the following manner. ω-Nitrostyrene was reduced at 0° with zinc dust and acetic acid to the *phenylacetaldehydeoxime*, $CH_2Ph\cdot CH:NOH$, m. p. 105°, and this further reduced by sodium amalgam to *phenylethylamine*, $CH_2Ph\cdot CH_2\cdot NH_2$. The *aurichloride* forms yellow needles, melting at 98—100°, and the *platinichloride*, orange scales, decomposing at 246—248°. This was then converted into *phenylethyltrimethylammonium iodide*, colourless plates and needles, m p. 230·5°, and then to the chloride by means of silver chloride. The *aurichloride* forms yellow plates and needles, melting at 156°, and the *platinichloride*, orange-red needles. Sodium amalgam decomposes it into trimethylamine and a non-nitrogenous substance, probably ethylbenzene.

W. J. Y.

Physiological Action of Some Sodium Camphenephosphinates. JOHN A. GARDNER and W. LEGGE SYMES (*Bio-Chem. J.* 1911, **5**, 390—399).—Sodium α- and β-camphenephosphinates differ but little in their physiological effects; both are far less active than sodium pyrophosphate, but more so than the orthophosphate. The effects are chiefly on the cerebral nervous systems, and their comparative inertness is due to rapid excretion.

W. D. H.

Pharmacology of Diglycollosalicylic Acid. ALFRED CHISTONI (*Chem. Zentr.*, 1910, ii, 989, from *Arch. Farmacol. sperim.*, 1910, **9**, 416—429).—Experiments carried out *in vitro* on this compound, $O(CH_2\cdot CO\cdot O\cdot C_6H_4\cdot CO_2H)_2$, show that it is converted into its constituents to some extent in distilled water at 20°, completely and rapidly in weak alkaline solution, in weak acid solution after one and a-half hours at 20°, or forty minutes at 39°, and in the gastric juice from dogs after twenty-five minutes at 39°. The maximum dose which may be given to animals without causing vomiting is 0·20 gram per kilo.; the minimum lethal dose is 0·55 gram per kilo. for dogs, and 1·80 gram per kilo. for rabbits. The salicylic acid appears always in the urine and not in the fæces of the animals, and the normal reaction of the urine is not altered by it.

Diglycollic acid, $O(CH_2\cdot CO_2H)_2$, is less poisonous than the above compound.

W. J. Y.

The Behaviour of *p*-Hydroxyphenylaminoacetic Acid in the Animal Body. KONRAD FROMHERZ (*Zeitsch. physiol. Chem*, 1911, **70**, 351—359).—Schotten first showed that phenylaminoacetic acid was, in part, excreted as mandelic acid. It was found in the present research that the hydroxy-acid is reduced *in vitro* to *p*-hydroxyphenylglyoxylic acid and *p*-hydroxymandelic acid; the latter is racemic, and so differs from that found in the urine of cases of atrophy of the liver by Schultzen and Ries. If *p*-hydroxyphenylglyoxylic acid is given to animals, there is no *p*-hydroxymandelic acid in their urine. Further, on feeding with *p*-hydroxyphenylaminoacetic acid, the corresponding ketonic acid is formed, of which the lævorotating constituent is largely excreted unchanged, but there is no reduction to *p*-hydroxymandelic acid.

W. D. H.

The Effects of Certain Animal Extracts on the Blood-Vessels. J. A. CAMPBELL (*Quart. J. exp. Physiol*, 1911, 4, 1—18).—Experiments with suprarenal and pituitary extracts were made in the vessels of the limbs, lung, heart, kidney, spleen, portal vein, carotid artery, superior vena cava, and superior mesenteric artery. Suprarenal extract causes marked constriction in all cases, except on the vessels of heart and lungs. In the heart, it has usually no effect, but sometimes slight constriction is seen; slight constriction in the lung vessels is rather more frequent than in the heart vessels. The pituitary extract contains at least two substances, one causing contraction and the other relaxation; each produces its characteristic effect on all the arteries except the renal, where contraction is hardly ever obtained, the result being nearly always relaxation. W. D. H.

The Laboratory Air and its Deleterious Constituents. JOSEF HABERMANN, WILHELM KULKA, and E. HOMMA (*Zeitsch. anal. Chem.*, 1911, 50, 1—11).—The present article relates to hydrogen sulphide. The authors examined fifty samples of air from laboratories, the volume of hydrogen sulphide varying from 0·00015 to 0·2 volume per 1000. In no case did any of the workers complain of unpleasant symptoms. L. DE K.

The Disordered Metabolism in Phosphorus Poisoning. E. FRANK and S. ISAAC (*Arch. exp. Path. Pharm.*, 1911, 64, 274—292).—In the early stages of phosphorus poisoning the liver cells are stimulated, so that their glycogen disappears and sugar passes into the circulation; in later stages the liver loses its power to store glycogen, and its assimilating functions are destroyed. W. D. H.

Chemical Changes in the Liver after Phosphorus Poisoning. B. J. SLOWTZOFF (*Biochem. Zeitsch.*, 1911, 31, 227—233).—After acute phosphorus poisoning the weight of the liver decreases. The quantity of fat thereby increases, whereas that of the protein decreases. This is due chiefly to the breakdown of the phosphorus-free protein constituents. Of the nucleoproteins, the water-soluble undergoes the greatest amount of decomposition. The liver after phosphorus poisoning contains less peroxydase and protease, but more amylase.
S. B. S.

The Removal of the Poisonous Properties of Strychnine and Cocaine by Peripheral Nerves. TOYOTANE WADA (*Pflüger's Archiv*, 1911, 139, 141—163).—An emulsion of strychnine or cocaine with the sciatic nerves from several kinds of animals was filtered after three hours, and injected into frogs. The toxic characters of the alkaloids were found to be removed. Previous heating of the nerves at 100° does not affect the result. Blood and striped muscle do not produce the effect. In the central nervous system the white matter is more effective than the grey in this connexion.
W. D. H.

Persistence of Strychnine in a Corpse. MARSHALL P. CRAM and PHILIP W. MESERVE (*J. Biol. Chem*, 1910, 8, 495—496).—Strychnine was still found in a corpse which had been buried twelve months previously in a damp grave. The spinal cord was the only organ where it was discoverable, as this was better protected than the other organs from the action of the water in the grave, which was acid from the embalming fluid which had been used. W. D. H.

Veronal. A. GRÖBER (*Biochem. Zeitsch.*, 1911, **31**, 1—31).—Veronal is far more toxic than has hitherto been supposed, being 3—4 times more toxic for cats and rabbits and 2—2½ more toxic for dogs. It has a marked action on the abdominal vessels, which causes a periodic rise and fall in the blood-pressure. It is therefore contraindicated in cases where there is an injury in the functions of the vessels (as in typhus abdominalis, etc.). In treatment of cases of poisoning, the abdominal vessels should be compressed, and the patient kept warm and given oxygen inhalations. S. B. S.

The Action of Cobra Poison. IVAR BANG and ERNST OVERTON (*Biochem. Zeitsch.*, 1911, **31**, 243—293. Compare Abstr., 1910, ii, 229).—With tadpoles in cobra poison solution (1 in 1,000,000) the whole nervous system is completely paralysed within twenty-four hours. If the strength of the solution does not exceed 1 in 400,000, or 1 in 500,000, the circulation remains, even after several days, intact, and the animals recover, although very slowly, if transferred back again to pure water. If the concentrations exceed this amount, the toxic effects are no longer reversible, and the skin epithelium is gradually attacked. After several immersions and recoveries, the animals are still paralysed by the same concentration as was active at the first immersion. The poison penetrates about as quickly as chloral hydrate, but somewhat more slowly than most narcotics. Calcium salts depress the toxicity, and in solutions of ½% calcium chloride (solutions above this concentration are themselves deleterious to tadpoles) about one hundred times more poison is necessary to produce the effect which can be produced in the absence of the salt. Solutions of calcium hydroxide are still more efficient in this respect than are those of the chloride. Magnesium and sodium salts have a similar action, but it is very much weaker than that produced by the calcium salts. Antivenin in the solution also diminishes the toxic effects. The so-called neurotoxin, which is apparently identical with hæmolysin, is absorbed by blood-corpuscles much more rapidly from isotonic sugar solutions than from isotonic salt solutions. The corpuscles charged with neurotoxin can give it up again to solutions which are weaker in the poison. Neurotoxin is also taken up by lecithin, cholesterol, and olive oil. The process is reversible. The toxicity of bee-poison to tadpoles is also diminished by the presence of calcium chloride, although not to the same extent as is cobra poison. S. B. S.

Crotalotoxin from the Venom of the North American Clapper Snake (Crotalus adamanteus). EDWIN S. FAUST (*Arch. exp. Path. Pharm.*, 1911, **64**, 244—273).—Crotalotoxin was prepared from the dried venom by Schmiedeberg's "copper alkali" method, and is the substance to which is due the effect on the central nervous system, especially on the respiratory centre. It is free from nitrogen, and has the formula $C_{34}H_{54}O_{21}$, or $C_{17}H_{26}O_{10},\frac{1}{2}H_2O$. Ophiotoxin from the cobra has the formula $C_{17}H_{26}O_{10}$. These two substances have much the same action, but the local action of the crotalotoxin is more manifest. It is a member of the sapotoxin group. Given by the mouth it is practically harmless. It has no effect on blood-coagulation; it is a neurotoxin, a cytotoxin, a cytolysin, a hæmorrhagin, and a hæmolysin. Crotalotoxin, ophiotoxin, and bufotalin (from the toad, $C_{34}H_{46}O_{10}$) are all in the same pharmacological group, and are regarded as derivatives of cholesterol. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Formation of *d*-Gluconic Acid by Bacterium Savastanoi. CARL L. ALSBERG (*J. Biol. Chem.*, 1911, **9**, 1—7).—The olive tubercle organism above named when grown aërobically in certain sugars forms acid. In the case of dextrose the acid formed is *d*-gluconic acid. The amount of material metabolised is large when compared with that in germinating seeds or man. This bacterium converts daily an amount of energy equal to 448 calories per kilo. of organisms. The corresponding figure in man is 35. W. D. H.

Antigen Formation in Protein-free Culture Media. I. Tuberculin. ERNST LÖWENSTEIN and ERNST P. PICK (*Biochem. Zeitsch.*, 1911, **31**, 142—152).—The medium employed for the tubercle bacillus contained in 1 litre of water 6 grams of asparagine, 6 grams of ammonium lactate, 3 grams of neutral sodium phosphate, 6 grams of sodium chloride, and 40 grams of glycerol. The tuberculin was obtained after several months' culture. The active product was a heat-stable, dialysable, uncoagulable substance, yielding no biuret reaction, but capable of precipitation by tannic acid, potassio-mercuric iodide, and mercuric sulphate. It is destroyed by pepsin in acid solution and trypsin in alkaline solution, but not by either acid or alkali in the concentrations employed in these experiments. Its possible polypeptide character is suggested. S B. S.

Methods of Detecting Indole in Bacteria Cultures. Formation of Indole by Typhaceæ. H. TELLE and E. HUBER (*Centr. Bakt. Par.*, 1911, i, **58**, 70—79).—Indole can be detected in dilutions of 1 : 200,000 by means of the Salkowski-Kitasato test, and in dilutions of 1 : 2,000,000 and 1 : 5,000,000 by Ehrlich's reaction and by Crossonini's modification respectively (*Arch. Hyg.*, 1910, **72**, 161). In both cases the results are better in distilled water and in peptone water than in broth. Salts, especially nitrites in the Ehrlich test, interfere with the reaction. The red coloration, frequently observed when nitrites and sulphuric acid are added to cultures, hardly ever occurs with Ehrlich's test in absence of indole.

The sensitiveness of the nitrosoindole reaction is increased by extracting the red colouring matter with amyl alcohol or ethyl acetate; with Ehrlich's reagent chloroform may be employed.

In cultures of Typhus, Paratyphus, *Bacillus Suipestifer*, and in Gärtner cultures the production of indole could not be detected either directly or by distillation, even after prolonged growth, in cultures containing 5—10% of peptone. N. H. J. M.

Two New Isomerides of Thymol. C. GUILLAUMIN (*Chem. Zentr.*, 1910, ii, 1049; from *Bull. Sci. Pharmacol.*, 1910, **17**, 373—380).—The two new isomerides of thymol (Abstr., 1910, i, 375) are rather less poisonous than naturally-occurring thymol. *Bacillus typhosus* is killed with the same quantity of *p*- or *m*-thymol, whilst the *o*-thymol is only half as active. Naturally-occurring thymol is also superior to the others as an anthelmintic. W. J. Y.

Action of Bacillus lactis aërogenes on Dextrose and Mannitol. II. Investigation of the βγ-Butanediol and the Acetylmethylcarbinol Formed; Effect of Free Oxygen on their Production; Action of B. lactis aërogenes on Fructose. GEORGE S. WALPOLE (*Proc. Roy. Soc.*, 1911, *B*, **83**, 272—286).—The crude glycol produced by the action of *B. lactis aërogenes* on dextrose contains two optically inactive βγ-butanediols, which yield diphenylurethanes melting respectively at 199·5° and 157°. The former greatly predominates (over 90%). Small quantities of the phenylurethanes of other unknown glycols were obtained.

Acetylmethylcarbinol is formed from βγ-butanediol by *B. lactis aërogenes* in presence of oxygen, and the yield from dextrose is increased by oxygen. Lævulose is decomposed in similar manner. N. H. J. M.

The Fermentation of Citric Acid in Milk. ALFRED W. BOSWORTH and M. J. PRUCHA (*J. Biol. Chem.*, 1911, **8**, 479—482).—During the souring of milk, the citric acid contained in it is changed into acetic acid and carbon dioxide. Of the common dairy bacteria tested, the one only one found to have the power to decompose citric acid was *Bacillus lactis aërogenes*, two molecules of acetic acid originating from every one of citric acid. In the process of cheese-making, the citric acid of milk is entirely fermented before the curd is pressed. W. D. H.

Decomposition of Different Sugars by Bacteria. JOH. MENDEL (*Centr. Bakt. Par.*, 1911, ii, **29**, 290—330).—The optimum concentration of sugars for fermentation varies from 6 to 10%, according to the bacteria employed. Decomposition will, however, continue with much greater concentrations, and only ceases with 30—50%. Dextrose is attacked by all bacteria in concentrations up to 25—30%. Maltose is attacked by *Bacillus lactis aërogenes* in solutions containing 50%. Lactose is readily attacked, except by *B. vulgare.*

The amount and composition of the acids produced depend on the bacteria, on the kind of sugar employed, and on the concentration.

The total acid is generally high with *B. coli*, *B. Fitzianus*, and *B. lactis aërogenes*. The relations of volatile to non-volatile acids do not show any regularity, except in the case of lactose, which, with all the bacteria employed, yielded greater proportions of volatile acids with increased concentration.

Bacteria, such as *B. cloacae* and *B. lactis aërogenes*, which ferment vigorously, oxidise the cleavage products more completely, with production of gas, than other microbes under similar conditions. The relation of carbon dioxide to hydrogen varies with different bacteria, different sugars, and different concentrations. Methane was never produced.

Indole is produced in 1% peptone solutions containing 5% of sodium chloride more frequently in presence of maltose than with other sugars. The production of indole does not seem to be influenced by acidity (compare Smith, *J. exper. Med.*, 2). N. H. J. M.

Fat-splitting by Bacteria. N. L. Söhngen (*Proc. Akad. Wetensch. Amsterdam*, 1911, **19**, 667—680).—Numerous bacteria exist which separate fats anaerobically, oxidise them aerobically, and dinitrify nitrates and nitrites when present, all these processes being due to the secretion of lipase by microbes. Several fat-splitting organisms produce two lipases: α-lipase, which acts both in acid and in alkaline solutions, and β-lipase, which is formed in acid media, but only becomes active after neutralisation. The bacteria thrive well when supplied with fat as exclusive form of carbon, and ammonium chloride as source of nitrogen.

The injurious effect of fat-splitting organisms on the quality of dairy products is chiefly due, in addition to their lipolytic properties, to the production of bitter and odoriferous substances from proteins and casein N. H. J. M.

The Bulgarian Ferment. Jean Effront (*Compt. rend.*, 1911, **152**, 463—465. Compare this vol., ii, 61).—The discrepancies between the author's earlier results and those of Bertrand (this vol., ii, 140) as to the action of the Bulgarian ferment on milk are explained by the fact that the ferments employed by the two observers were not identical, this having been established by an examination of Bertrand's ferment by the author. The difference in the action of the two ferments is due, however, to differences in their mode of cultivation rather than to any specific difference in the bacteria themselves. The commercial Bulgarian ferment, employed therapeutically, contains bacteria characterised by an intense proteolytic activity. The total acidity produced in milk by Bertrand's preparation is high and the volatile acidity low, whilst the converse tends to be the case with the therapeutic products. The results confirm the author's view that the clinical effects following the sour milk treatment depend, not on the production of lactic acid, but on the proteolytic activity of the enzymes administered. W. O. W.

The Temperature Optimum of Physiological Processes. Miss J. van Amstel and G. van Iterson, jun. (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 598—607).—From the investigation of the action of yeast, the conclusion of Rutgers is confirmed that the theory of Duclaux-Blackman will not explain the occurrence of an optimum temperature. W. D. H.

Sugar-free Yeast Fermentation. I. CARL NEUBERG and ARNOLD HILDESHEIMER (*Biochem. Zeitsch.*, 1911, **31**, 170—176).—It was found that by the action of hydrogen peroxide and iron salts on acetone, in addition to methylglyoxal (pyruvaldehyde), a non-volatile substance fermentable by yeast was formed. It is suggested that this is possibly either the corresponding alcohol or acid, formed from the aldehyde by Cannizaro's reaction. Experiments indicate that the salts of pyruvic acid can, on treatment with yeast, undergo fermentation with evolution of carbon dioxide. S. B. S.

Chemical Composition and Formation of Enzymes. III. HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, **71**, 14—30. Compare Abstr., 1910, i, 345, 796).—A. *Influence of Phosphates on the Invertase and Zymase System of the Living Yeast-cell.*—Yeast was treated during several hours, on the one hand, with water, and, on the other, with dilute solutions (less than 1%) of pure or neutralised monosodium or monopotassium phosphate. It was then quickly dried in a vacuum, and the amount of invertase determined. The phosphate treatment was without effect; treatment with stronger solutions (10%) of phosphate weakened the invertase.

Similar experiments made on the fermentative power of yeast, using pure monophosphate, showed that the treatment diminished the activity of the dried yeast, but increased that of the fresh yeast. Treatment with neutralised phosphate was favourable to the activity of both yeast preparations.

B. *Dynamics of Enzyme Reactions of Yeast-cells.*—The invertase of living yeast-cells within the limits of experimental error shows the characteristics of a unimolecular change. The relation between the inversion constants at 20° and 30° is 2·04. Chloroform has no influence in retarding the invertase, which is considered to be independent of the protoplasm. The inversion and fermentation constants of a number of samples of yeast are compared. For any one yeast with the same sugar concentration the ratio appears to be constant, but varies with the nature of the yeast. Top yeast appears to contain a very small proportion of invertase.

The inversion of sucrose takes place inside the cells, and the invertase does not pass out into the aqueous solution. Dried yeast preparations only give qualitative and not quantitative information as to the enzyme content of the living cell. E. F. A.

Soil-bacteriological Investigations. B. HEINZE (*Chem. Zentr.*, 1910, ii, 404; from *Landw. Jahrb.*, **39**, *Erg.-Band* III, 314—343).—The number of organisms in the soil is increased by repeated mechanical operations and by addition of straw, sugar, starch, and organic nitrogen, but not to any extent by sodium nitrate or ammonium sulphate. Fallow is favourable to pectin, cellulose and humus ferments, to the organisms which produce ammonia and nitrates, and to *Azotobacter*.

Fixation of nitrogen by *Azotobacter* and other organisms requires an abundance of organic matter and a neutral or slightly alkaline reaction. The power of fixing nitrogen, when diminished or lost, can be restored by suitable cultivation. Humus and phosphoric acid are very favourable to *Azotobacter*. N. H. J. M.

The Bactericidal Action of the Emanation from Radium. Hans Jansen [with Prytz] (*Chem. Zentr.*, 1910, ii, 1076—1077; from *Övs. K. Danske Vidensk. Selskabs. Forh.*, 1910, 295—331).—Surface cultures of *Bacillus prodigiosus* were exposed to air charged with different quantities of radium emanation. The air was charged by circulating it over radium bromide in a closed apparatus by means of a Prytz pump, the circulation being continued until the desired concentration of emanation was obtained, which was determined by Sieveking's method, and was expressed in Mache units. The cultures were contained in glass vessels connected with the apparatus.

It was shown that the bactericidal action was not great, 345 to 400 units per c.c. of air being necessary to kill the cultures. The action also required time; thus 1150 units per c.c. had only a slight action in one hour, and 766 units per c.c. required forty-eight hours to render the cultures sterile. Air containing less than 127·5 units per c.c. had no noticeable action. W. J. Y.

The Fat destroying Action of Moulds and the Behaviour of the Fat of Organs in Putrefaction. Kohshi Ohta (*Biochem. Zeitsch.*, 1911, **31**, 177—194).—The Kamagawa-Suto method of fat and cholesterol estimation was employed. The investigations with pure cultures on air-dried beef confirm the observation of Kumagawa that a loss of fat takes place. Five different kinds of moulds were investigated, the actions of which differed quantitatively from one another. *Actinomucor repens* has the strongest action, destroying 60% of liver fat within six weeks. *Penicillium glaucum* under the same conditions destroys only 6—8%. The attempts to cultivate *Actinomucor* on simple fat media did not succeed. The author shows that sources of error may take place in fat estimations during hydrolysis, owing to the fact that the moulds are not destroyed by alkali and enclose certain quantities of fat. They must therefore be specially extracted. During ordinary putrefaction, certain coloured substances in addition to the fat pass into the light petroleum extract, and increase of this extract gives no evidence as to the formation of new fat during putrefaction. S. B. S.

Production of Lactic Acid by Moulds. K. Saito (*Centr. Bakt. Par.*, 1911, ii, **29**, 289—290).—Cultivations of *Rhizopus chinensis* in Koji worts, beer worts, and in a mineral nutritive solution with peptone and dextrose produced *l*-lactic acid when kept for a week at 35°.

Previous experiments with cultures of *Rhizopus* in mineral solutions containing sugar and ammonium nitrate (*ibid.*, 1904, **13**, 154) failed to show production of alcohol. Recent results, however, obtained with Lindner's method showed that *Rhizopus* ferments dextrose, lævulose, maltose, galactose, melibiose, and dextrin, but not sucrose, lactose, inulin, and raffinose. N. H. J. M.

The Action of Strontium Salts on Algæ. OSCAR LOEW (*Flora*, 1911, **102**, 96—112).—Since algæ will live for some time in solutions of strontium salts, it may be supposed that strontium does not displace any of the essential metallic elements, calcium, magnesium, etc., from their position in the protoplasm complex. Such injurious effect as is produced is mainly on the chlorophyll bodies, which lose their power of making starch and their normal green colour, and finally die. Calcium chloride has no such action, even in 1% solution. Needle-shaped crystals appear in the cells of *Spirogyra* growing in solutions of strontium chloride, but not of calcium chloride; they are probably an organic salt, and their presence shows that something is being precipitated which normally remains in solution or is oxidised.

The author considers that the nuclei and the chloroplasts of the higher algæ are calcium compounds of nucleo-proteins, because any thing that precipitates calcium, *e g.*, potassium oxalate or sodium fluoride, has a strongly toxic effect. Hence calcium chloride is inert towards the chloroplasts, while strontium chloride is not.

On the other hand, the lower algæ do not require calcium, and therefore are not affected by potassium oxalate, or, to any great extent, by sodium fluoride, neither are magnesium salts toxic.

E. J. R.

Influence of Acidity on Germination. Mlle. G. PROMSY (*Compt. rend.*, 1911, **152**, 450—452).—The author does not agree with the usual view that the presence of acids is unfavourable to germination. Experiments carried out with citric, tartaric, malic, oxalic, and acetic acids show that these acids have a distinctly beneficial action on germinating grains, the respiratory quotient being raised and the rate of growth accelerated. The optimum concentration of citric acid in the case of tomato seeds was 0·3%, a solution of this strength raising the respiratory quotient from 0·72 to 1·08. The effects observed, however, do not appear to be general; thus *Ricinus* seeds were unaffected by organic acids. The respiratory quotient of seeds is not affected by mineral acids. W. O. W.

Protein Formation in Ripening Seeds. II. ERNST SCHULZE (*Zeitsch. physiol. Chem.*, 1911, **71**, 31—48. Compare Abstr., 1910, ii, 644)—Unripe fruit of the vetch (*Vicia sativa*) were gathered late in August, divided into hulls and unripe seeds, and these analysed separately. The hulls contained very much more asparagine than the unripe seeds, but less arginine, although the difference in this respect was not so great as with peas and with *Phaseolus vulgaris*, owing probably to the *Vicia* seeds being nearly ripe.

Asparagine in quantities varying from 1 to 2% of the dried plant was found in young plants, harvested during May and June, of *Vicia sativa*, *Trifoleum pratense*, and *Medicago sativa.* The two former also contained guanosine, whilst leucine was obtained from the *Vicia*, and perhaps also from the *Medicago.* The amount of asparagine in young leguminous plants increases when they are stored for a few days in the dark.

A detailed investigation has shown that young leguminous plants only contain mere traces of arginine; in peas, a little was obtained from the roots, but none from the above-ground portions. It is considered that the influx of arginine to the seeds must at the best be very small, and that therefore arginine is formed in the seeds.

In the ripening seed, as in young leaves, asparagine is used for the synthesis of protein, and, in general, the synthesis of protein takes the same course in both parts of the plant.

A comparison of the non-protein nitrogen compounds in the unripe seeds and in the rest of the plants shows that tryptophan is rapidly used by the seeds, glutamine only slowly. Further investigation in this direction is expected to indicate more completely those of the non-protein nitrogenous constituents which pass into the seed and are used for protein synthesis. E. F. A.

The Respiration Enzymes of Plants. W. Zaleski (*Biochem. Zeitsch.*, 1911, **31**, 195—214).—The author has investigated the effect of extraction with various solvents on the respiration enzymes in different plants. Extraction with ethyl alcohol generally diminishes the respiratory process as compared with similar treatment with acetone and ether. Methyl alcohol, as in the case of yeasts, destroys the respiratory processes entirely. The nature of the substances exerting influence on these processes is still unknown. When the process has been partly destroyed by extraction with alcohol, it can be restored by the addition of dibasic phosphates. Methyl alcohol, on the other hand, appears either to destroy the ferments entirely, or to remove the co-ferments. S. B. S.

The Physiological Rôle of Calcium Salts. Oscar Loew (*Münch. med. Woch.*, 1910, No. 49).—A summary of the author's work on this subject, intended for pharmacologists. E. J. R.

Production of Amino-acids in Plants, and the Action of Formaldehyde on Potassium Cyanide. Hartwig Franzen (*Chem. Zentr.*, 1911, i, 983—985; from *Sitzungsber. Heidelberger Akad. Wiss.*, 1910)—It is suggested that amino-acids are produced from formaldehyde, the first assimilation product of carbon dioxide, and hydrogen cyanide, the first assimilation product of nitrates. Treub assumes that nitrates are first converted into hydrogen cyanide, and that this unites with formaldehydes and ammonia, forming amino-nitriles, which are then hydrolysed to amino-acids. This hypothesis is extended, and a number of examples are given showing how the production of various amino-acids can be explained. Glycine, for instance, would be formed by the union of formaldehyde with hydrogen cyanide, the subsequent addition of ammonia with elimination of water, followed by the hydrolysis of the nitrile. Alanine could be produced in a similar manner from acetaldehyde formed by the plant from malic acid; phenylalanine from phenylacetaldehyde, or from cinnamic acid with addition of ammonia.

Aspartic acid is produced by the condensation of the nitrile of glycollic acid (2 mols.) to malic acid nitrile, which, with ammonia, yields aspartic acid nitrile. It is suggested that polypeptides may be formed by the interaction of acid amides and α-hydroxynitriles.

N. H. J. M.

Active Albumen and Tannin in Plant Cells. OSCAR LOEW and THOMAS BOKORNY (*Flora*, 1911, **102**, 113—118).—Polemical against C. van Wisselingh and against Czapek.

E. J. R.

Excretion of Mineral and Organic Substances by Roots and Stomata. PIERRE MAZÉ (*Compt. rend.*, 1911, **152**, 452—456).—The results of experiments on maize are quoted, from which it is seen that the composition of the plant ash is altered from time to time by excretion of organic and inorganic salts through the roots and stomata. Dextrose and malic acid have been shown to pass out from the roots.

W. O. W.

Soluble Carbohydrates in Asparagus Roots. FRED W. MORSE (*J. Amer. Chem. Soc.*, 1911, **33**, 211—215).—The work described in this paper is part of an investigation of the composition of the asparagus plant, with special reference to its manurial requirements.

Analyses were made of roots collected in November of the second year after setting, and dried at 50°. The average composition of the dry material of sixteen roots was as follows: proteins (N × 6·25), 11·03%; fat, 1·00%; fibre, 15·39%; nitrogen-free extract, 66·34%; ash, 6·24%. The roots contained little or no reducing sugars, but the total sugars amounted to 41·43% (calculated as invert-sugar), the pentosans to 8·78%, and galactans to 1·04%. The chief carbohydrate present was not sucrose, but, on hydrolysis, yielded dextrose and lævulose in proportions varying with different root extracts. These results agree with those of Wichers and Tollens (Abstr., 1910, ii, 885, 886), but the latter authors found that solutions of the sugar-like carbohydrate reduced Fehling's solution before hydrolysis. This difference is probably due to the fact that Wichers and Tollens examined roots collected in April and July instead of November.

Tanret (Abstr., 1909, i, 634) isolated two distinct carbohydrates from asparagus roots, but the author has not had an opportunity of confirming these observations.

E. G.

Basic Constituents of Helianthus annuus. E. BUSCHMANN (*Arch. Pharm.*, 1911, **249**, 1—6).—Sunflower florets, which are largely employed as a domestic remedy in Russia, are shown to contain betaine and choline.

A concentrated alcoholic extract of the florets was dissolved as far as possible in water, the bases precipitated with bismuth-potassium iodide solution, and recovered from the precipitate by decomposing this with white lead and extracting with water. On adding dilute hydrochloric acid and concentrating, betaine hydrochloride crystallised out. The mixture of betaine and choline hydrochlorides remaining in the mother liquors was separated into its constituents by precipitation with mercuric chloride, the mercuri-chloride of choline being insoluble in water. T. A. H.

Chemical Examination of the Root of Lasiosiphon Meissnerianus. HAROLD ROGERSON (*Amer. J. Pharm.*, 1911, **83**, 49—56).—It is shown that the acrid properties of this root are due to the presence of an amorphous resin.

That portion of an alcoholic extract of the root which was soluble in water contained tannin and a reducing sugar, which furnished *d*-phenylglucosazone. The portion insoluble in water consisted of a dark brown resin, which when inhaled was irritating to the nostrils, and when applied to the tongue produced a burning sensation. On extraction with light petroleum, it yielded some dark green resin, which, on hydrolysis with alcoholic potassium hydroxide, gave (1) a mixture of palmitic and oleic acids with a small amount of a third acid more unsaturated than oleic acid, and (2) a *phytosterol*, $C_{27}H_{46}O,H_2O$, m. p. 132—133°, $[\alpha]_D - 30\cdot6°$, crystallising from a mixture of ethyl acetate and alcohol in flat needles, and yielding an *acetyl* derivative, m. p. 110°.

On fusion with melted potassium hydroxide the resin gave a mixture of volatile fatty acids composed chiefly of formic and butyric acids. A small amount of a substance giving a green coloration with ferric chloride was also obtained.

No evidence of the presence of an alkaloid or glucoside in the root was obtained. T. A. H.

The Composition of Malt-embryos. KIYOHISA YOSHIMURA (*Biochem. Zeitsch.*, 1911, **31**, 221—226).—Histidine, choline, and betaine were isolated, but not arginine, vernine, or asparagine. The division of the nitrogen between protein, ammonia, and non-protein nitrogen was also determined. The ordinary methods of isolation, which are described in detail, were employed. Sucrose was not present, but maltose and dextrose were. The conclusions as to the sugars were drawn by the application of Jolles' method of determining the changes in polarisation due to treatment with sodium hydroxide. S. B. S.

The Tannin Substances of the Roots in the Genus Vitis in Relation to the Disease Caused by Phylloxera. L. PETRI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 57—65).—The roots of many kinds of vine contain a substance which gives a blue coloration with ferric chloride. The sap shows with varying intensity the characteristic tannin reactions, and the substances responsible for them can be extracted with alcohol at 70—80°. The quantity of the tannin substances present appears to bear some relation to the susceptibility of the species to *Phylloxera*, the amount being greatest where the susceptibility is least. R. V. S.

Analysis of Zygadenus intermedius. I. FRED. W. HEYL and L. CHARLES RAIFORD (*J. Amer. Chem. Soc.*, 1911, **33**, 206—211).—An account is given of a preliminary investigation of *Zygadenus intermedius*, a plant which sometimes causes the poisoning of sheep and cattle. Estimations have been made of the pentosans, fibre, proteins, and ash in the leaf, flower, bulb, and root, and the results are recorded. Starch was present in the bulb to the extent of 23 53%, but was absent from other parts of the plant. Examination of alcoholic extracts showed that the leaf, bulb, and root contained resin, sucrose, reducing sugars, and dextrin, which were estimated in each case. An alkaloid was found in all parts of the plant, the leaves containing about 0·3—0·5%, and the bulbs 0·24—0·39%. E. G.

Injury to Pines by Furnace Gases. KARL FEIST (*Arch. Pharm.*, 1911, **249**, 7—9).—Gases evolved during the roasting of clay ironstone near Giessen contained about 0·3% of sulphur dioxide, and caused damage to pine woods in the neighbourhood. Comparison of the ash from (*a*) pine needles from healthy trees, and (*b*) pine needles from trees injured by the furnace gases, showed that the latter was greater in amount, contained more sulphates, and was less alkaline than the former, in spite of the fact that the soils in which the two trees were growing contained about the same quantities of sulphates. Investigations by Fricke and others have shown, on the contrary, that plants damaged by furnace gases do not accumulate sulphates in the leaves, but, as a rule, these investigations have been made on plants the leaves of which have a shorter life-period than pine leaves. T. A. H.

Comparative Toxicity of Essential Oils Towards Higher Vegetation. HENRI COUPIN (*Compt. rend.*, 1911, **152**, 529—531).—Fifty-one essential oils have been examined as to their effect on plants when these are exposed for several days to the action of the vapours. Three were without toxic effect, the others were detrimental in different degrees, and in some cases (aniseed and neroli oil) brought about death of the plants. W. O. W.

Lead Arsenate in Viticulture, and the Consumption of Fresh and Dried Grapes. L. MOREAU and E. VINET (*Ann. Chim. anal.*, 1911, **16**, 94—96).—When vines are sprayed before flowering, only a minute quantity of poison can be detected on the grapes even at a period long anterior to picking, and at picking time none could be detected. On the other hand, when the spraying took place after flowering there was a little arsenate found on the grapes, and in these circumstances danger might arise to the consumer. E. J. R.

Transformation of Proteins into Fats during the Ripening of Cheese. MAXIMILIAN NIERENSTEIN (*Proc. Roy. Soc.*, 1911, *B*, **83**, 301—304).—Old Cheddar cheese was found to contain free cholesterol, cadaverine, putrescine, and aminovaleric acid, the amounts of these substances being sufficient to account for the increased weight of the ether extract frequently observed. The assumption that fat is produced from proteins during ripening does not seem to be justified. N. H. J. M.

Biological Investigation of Honey. EDMOND MOREAU (*Ann. Falsif.*, 1911, **4**, 65—66).—The author has detected the presence of catalase, amylase, and invertin in honey, but anaeroxydases and aeroxydases could not be discovered. The volume of oxygen liberated from hydrogen peroxide by the catalase present in various samples of French honey (5 grams) varied 4 to 6 c.c. when the honey contained much protein, and from 0·3 to 0·7 c.c. in the case of samples containing but a small amount of protein. The samples showing the higher catalase content also contained the greater quantities of amylase. W. P. S.

Methoxyl in Soil Organic Matter. EDMUND C. SHOREY and ELBERT C. LATHROP (*J. Amer. Chem. Soc.*, 1911, **33**, 75—78).—Robertson, Irvine, and Dobson (Abstr., 1907, i, 894) found that two specimens of humic acid obtained from peat, when treated by Zeisel's method, yielded results showing the presence of 1·71 and 2·47% of methoxyl, whilst an artificial specimen prepared from sucrose gave 6·47%.

Methoxyl estimations have been made with the ten soils which were used for the pentosan estimations (this vol., ii, 146). Two of these soils did not contain any methoxyl; five of them gave results showing a ratio of methoxyl carbon to total carbon varying from 0·051 to 0·087; and the remaining three gave ratios 0·317, 0·717, and 1·590. These results show that the quantity of methoxyl in a soil does not bear any relation to the total organic matter present.

The origin of the methoxyl group in the soil is discussed, and it is pointed out that the most important source is the lignocellulose of vegetable tissues. E G.

Cholesterols in Soils: Phytosterol. OSWALD SCHREINER and EDMUND C. SHOREY (*J. Biol. Chem.*, 1911, **9**, 9—11).—In previous work the authors have described a cholesterol in soils in the free condition. It was named agrosterol, and differs from any cholesterol previously described in its melting point. In plants, cholesterols are usually combined as esters. The most common of these, phytosterol, was identified in soils in the present research. It is in combination probably as an unchanged plant residue. W. D. H.

Function of Manganese in Manuring. LUIGI BERNARDINI (*Chem. Zentr.*, 1910, ii, 406; from *Staz. sper. agrar. ital.*, 1910, **43**, 217—240).—The chief effect of manganese is the production of soluble calcium and magnesium compounds from insoluble forms, so that manganese manure may be considered as an indirect calcium-magnesium manure. N. H. J. M.

Dissolved Matter Contained in Rain-Water Collected at Lincoln, New Zealand. GEORGE GRAY (*Canterbury Agric. Coll. Mag.*, 1910, **24**; Reprint, 12 pp.).—Analyses of monthly samples of rain-water from July, 1907, to June 1909. The average yearly amounts were as follows:

	Rainfall, inches.	N. per million		N. per acre (lb.)			% of Total N.	
		as ammonia.	as nitrates.	as ammonia.	as nitrates.	Total.	as ammonia.	as nitrates.
1907–8...	21·48	0·170	0·238	0·795	0·766	1·561	50·9	49·1
1908–9...	32·11	0·094	0·117	0·686	0·851	1·537	44·6	55·4

	Per million			Per acre (lb.)		
	dissolved solids.	chlorine.	sulphuric anhydride.	dissolved solids.	chlorine.	sulphuric anhydride.
1907–8......	24·7	6·1	3·28	120·18	29·75	15·79
1908–9......	22·6	5·5	2·86	164·34	40·02	20·78

An analysis of the dissolved solids in a sample representing the year 1908–9 gave the following results: volatile solids, 2·37; K_2O, 0·77; Na_2O, 8·14; CaO, 1·35; MgO, 0·63; SiO_2, 1·60; SO_3, 2·86; Cl, 5·53, and CO_2, 1·74 per million of rain.

Compared with the earlier analyses made in 1884–8 (*Proc. Austral. Assoc.*, 1888, **1**, 138), the results show a slight increase in the amount of ammonia, and an increase in sulphates, due to the increase in population and manufactories. The chlorine is a good deal lower than in the earlier period, owing to diminished winds.

A sample of rain (three days) from Campbell Island contained: total solids, 172·5; N as ammonia, 0·084; N as nitrates, 0·084; and Cl, 77·5 per million. Sea-water collected off the New Zealand coast was found to contain 0·025 and 0·090 per million of nitrogen as ammonia and as nitrates respectively. N. H. J. M.

Analytical Chemistry.

Air-Trap for Burettes, Reagent Reservoirs, etc. HEINRICH GÖCKEL (*Chem. Zeit.*, 1911, **35**, 279).—A small absorption apparatus for attaching to the tops of burettes, etc., is described. It consists of two glass bulbs connected at their tops by means of a glass tube. This tube extends into both bulbs, and reaches nearly to the bottom of each. A side-tube at the top of one bulb enables the apparatus to be attached to the top of a burette or a reservoir, whilst a tube on the other serves as the inlet for the air. The bulbs are about one-third filled with a liquid, such as sulphuric acid, alkaline pyrogallol solution, etc., so that moisture, oxygen, or other gas may be absorbed from the air before the latter enters the burette or reagent reservoir. The passage of the air causes the liquid to flow backwards and forwards from one bulb to the other as the air enters or is expelled from the burette, etc., the current of air at the same time bubbling through the liquid. W. P. S.

Capillary Analysis. ISIDOR TRAUBE (*Ber.*, 1911, **44**, 556—560).—The capillarity constant, a physical property of liquids which is very easily measured by the author's dropping method, has been neglected almost entirely for analytical purposes. The author indicates how the property may be utilised for the detection of very minute traces of colloid poisons (anions, cations, alkaloids, acids) in colloidal media, and for the examination of milk. C. S.

A Modified Drying Tube. W. H. McIntire (*J. Amer. Chem. Soc.*, 1911, **33**, 450—451).—In order to add to the rigidity of the ordinary U-tube, a strut of glass with practically the same coefficient of expansion connects the upper ends of the limbs. Sealed to the middle of the strut is a perpendicular glass rod with a loop at the upper end, so that the tube may be suspended for weighing, thus obviating the use of platinum or copper wire. T. S. P.

The Scientific Foundations of the Systematic Separation of Combustible Gases. Georges de Voldere (*Zeitsch. anal. Chem.*, 1911, **50**, 137—153).—The author discusses the principles of quantitative gas analysis in reference to gaseous mixtures containing hydrogen, oxygen, nitrogen, carbon monoxide, carbon dioxide, and hydrocarbons of the series C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, and C_nH_{2n-6}. The relationship between the usual gasometric method and the theoretical scheme is indicated. H. M. D.

Estimation of Bromine in Presence of Chlorides and Iodides. Paul Clausmann (*Bull. Soc. chim.*, 1911, [iv], **9**, 188—192).—The process described is a modification of that used by Déchan (Trans., 1886, **49**, 682) and in a modified form by Carnot (*Traité d'anal. min. Tome* **2**, p. 366), and consists in heating the material, usually the residue of a mineral water, with a solution of chromic acid in dilute sulphuric acid in a flask having a long neck drawn out into a sealed capillary. When the reaction is complete, the flask is cooled, attached to a condenser, the capillary broken, the bromine formed distilled into a slightly acid solution of potassium iodide, and the liberated iodine titrated with *N*/100-sodium thiosulphate. If very little bromine is present, the iodine set free is estimated colorimetrically by extraction with carbon disulphide and comparison with solutions of iodine of known strength in the same solvent. If both iodides and bromides are present in the residue, a preliminary estimation of the iodine should be made by means of nitrous sulphuric acid and carbon disulphide. Traces of bromine in such residues may be detected by Baubigny's fluorescein test (Abstr., 1897, ii, 385).

The water of the Lanternier spring, Nancy, contains 0·01152 gram bromine (=0·01713 KBr) and 0·000004 gram iodine per litre. The "alum" spring at Aix-les-Bains, Savoy, contains 0·000168 gram bromine and 0·000032 gram iodine per litre, and the "sulphur" spring 0·000288 gram bromine and 0·000042 gram iodine per litre, as determined by this method. T. A. H.

Estimation of Bromine, Fluorine, Lithium, and Antimony in Mineral Waters. Armand Gautier and Charles Moureu (*Compt. rend.*, 1911, **152**, 546—551).—See this vol., ii, 300.

Estimation of Dissolved Oxygen. Ludwig W. Winkler (*Zeitsch. angew. Chem.*, 1911, **24**, 341—343).—The method proposed depends on the formation of a brownish-yellow coloration when water containing dissolved oxygen is treated with ammonia and a chloro-derivative of quinol, which is sold as a photographic developer under the name of "adurol." The water to be examined is filled into a flask, 0·5 c.c. of an ammoniacal ammonium bromide solution are added (this solution is prepared by dissolving 50 grams of ammonium bromide in 10% ammonia, so that the whole has a volume of 100 c.c.), and then a small quantity of the reagent. After completely filling the flask with the water, the contents are mixed, and the coloration compared with that given by water completely saturated with oxygen. The ammonium bromide is added for the purpose of preventing the precipitation of calcium carbonate and magnesium hydroxide. In the case of waters containing but little dissolved oxygen, sodium chloride solutions of various concentrations may be used as comparison liquids. Under 760 mm. pressure, 1 litre of saturated sodium chloride solution at 20° contains 1·07 c.c. of dissolved oxygen after it has been thoroughly aerated; at the same pressure and temperature 1 litre of $3N$-sodium chloride solution contains 2·25 c.c. of oxygen, and 1 litre of $N/1$-sodium chloride 4·39 c.c. of oxygen. W. P. S.

Estimation of Total Sulphur in Urine. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1910, **8**, 499—502).—The author defends his method against the criticisms of Denis (this vol., ii, 66). W. D. H.

Estimation of Sulphur Dioxide in White Wines. R. RICHTER (*Pharm. Zeit.*, 1911, **56**, 148—149).—*Total sulphur dioxide.*—Fifty c.c. of the sample are delivered from a pipette into a flask containing 25 c.c. of N-potassium hydroxide; the end of the pipette should dip into the liquid. After gently shaking a few times, the solution, after an interval of fifteen minutes, is mixed with 10 c.c. of dilute sulphuric acid (1 : 3), and then titrated with $N/50$-iodine with starch as indicator.

Free sulphur dioxide.—Fifty c.c. of the sample are delivered from a pipette into a flask filled with carbon dioxide, 5 c.c. of dilute sulphuric acid are added, and the solution is titrated with iodine.

The organically-combined sulphur dioxide is found by difference.
L. DE K.

New Method for Estimating Sulphuric Acid and Sulphates. VICTOR AUGER and M. GABILLON (*Compt. rend.*, 1911, **152**, 441—443).—The method which consists in reducing the sulphate by means of hydrogen iodide and titrating the hydrogen sulphide formed with standard iodine solution, is said to be accurate to the extent of 1 in 300. It is not applicable to the estimation of barium sulphate.

The sulphate is heated at 80—110° for twenty to twenty-five minutes with potassium iodide and a mixture of phosphorous, phosphoric, and pyrophosphoric acids in a long necked flask having a side-tube. The gases liberated are carried away in a current of dry carbon dioxide, the iodine vapour removed by passing through a tube containing calcium iodide, and the hydrogen iodide absorbed by a solution of the gas containing phosphorous acid. The hydrogen sulphide is absorbed in zinc acetate solution, and titrated in the usual way. It is important to avoid the presence of metaphosphoric acid (which causes too vigorous reduction) and of moisture in the reduction flask. W. O. W.

Volumetric Estimation of Sulphuric Acid or Sulphates. Fernand Repiton (*Mon. Sci.*, 1910, [iv], **24**, 382—384).—Briefly, the process is as follows: the solution is acidified with hydrochloric acid, heated to boiling, and mixed with a known volume of *N*/4-barium chloride. The liquid is transferred to a 150 c.c. measuring flask, and, after adding ammonia in excess, a volume of *N*/4-potassium dichromate equal to that of the barium chloride used is added. It is recommended to add to the ammonia a little calcium chloride to decompose any carbonate present. When cold, the solution is diluted to the mark, and 50 c.c. of the clear filtrate are taken for the purpose of estimating the excess of chromic acid present.

A new process for this is described. The solution is mixed with an excess of hydrochloric acid, and 0·1 gram of mercuric chloride dissolved in water is added. After introducing a few lumps of marble to create an atmosphere of carbon dioxide, *N*/4-stannous chloride recently titrated with *N*/4-potassium dichromate is added until a slight turbidity of mercurous chloride is formed. The difference between the two chromate titrations represents the sulphuric anhydride. L. de K.

Qualitative Analysis of Complex Mixtures of Salts. B. Moreau (*Bull. Sci. Pharmacol.*, 1910, **17**; Reprint, 6 pp.).—A number of tests and processes are given for detecting the presence of two or more substances in mixtures of the same when the substances interact with one another or yield similar reactions. The following substances are dealt with, an outline of the tests recommended being given in parentheses: Sulphate in the presence of sulphide (boil with hydrochloric acid to expel hydrogen sulphide and test for sulphate in residual solution); sulphate and sulphite (liberation of sulphur dioxide); sulphite and thiosulphate (precipitation of sulphur from the thiosulphate by acids; sulphites yield a red coloration when treated successively with sodium nitroprusside, zinc sulphate, and potassium ferrocyanide); nitrate, sulphite, and sulphide (nitrate detected by formation of ammonium picrate); phosphate and arsenate (molybdic acid does not yield a precipitate with arsenates in the cold); chloride, bromide, or iodide, and sulphide (precipitate sulphide with a zinc salt); nitrate and chlorate (the nitrate yields ammonia when treated with zinc and sodium hydroxide), etc. W. P. S.

[Analysis of Hyposulphites.] Karl Jellinek (*Zeitsch. anorg. Chem.*, 1911, **73**, 93—134).—See this vol., ii, 278.

Estimation of Ammonia in Urine. Otto Folin (*J. Biol. Chem.*, 1910, **8**, 497—498).—The use of sodium carbonate is still maintained to be better in most cases in spite of Steel's criticisms (this vol., ii, 68), for even if a sediment of magnesium-ammonium phosphate is present in certain urines, that deposit can be dissolved by acid and kept in solution by potassium oxalate. W. D. H.

The Phenolsulphonic Acid Method for the Estimation of Nitrates in Water. III. and IV. The Chief Sources of Error in the Method. Emil M. Chamot, D. S. Pratt, and H. W. Redfield (*J. Amer. Chem. Soc.*, 1911, **33**, 366—381, 381—384. Compare Abstr., 1910, ii, 545).—III. Phenolsulphonic acid reagents containing monosulphonic acids are subject to change with age and yield results which are greatly affected by temperature, concentration, variations in the character of the alkali used, and in time of contact between the reagent and the water residue, etc. They cannot be satisfactorily employed with permanent standards.

In order that accurate results may be obtained, chlorides, carbonates, and organic matter must be removed before applying the test. Chlorides are best eliminated with silver sulphate, and organic matter by the use of "aluminium cream."

Nitrites present in small amount do not appreciably affect the final results, but when present in large amount they must be destroyed or corrected for.

Waters containing much magnesium or iron compounds yield residues the particles of which are penetrated only with great difficulty by the sulphonic acid reagent.

IV. The phenolsulphonic reagent, which must contain no monosulphonic acid (compare preceding section), is best prepared as follows: 25 grams of pure phenol are dissolved in 150 c.c. of concentrated sulphuric acid, 75 c.c. of fuming sulphuric acid, containing 13% SO_3, are added, and the mixture heated for two hours at 100°. The results are not always trustworthy with this reagent when the water contains over 50 parts per million of nitrogen as nitrates, whilst serious discrepancies arise should the nitrate content be over 80 parts per million.

In determining the nitrates in water, chlorides and organic matter must first be removed, as mentioned in the preceding section. If the nitrites present are in excess of one part per million of nitrogen, they must first be destroyed by heating the sample with a few drops of hydrogen peroxide.

The phenolsulphonic reagent prepared as above may be used as a permanent standard. A series of standards prepared from tripotassium nitrophenoldisulphonate (Abstr., 1910, ii, 545) are also recommended. This latter compound is best prepared by adding finely powdered potassium nitrate, in very small portions at a time, to the cold disulphonic acid reagent, prepared as above. The resulting solution is diluted, dry barium carbonate added until a deep yellow colour is obtained, the precipitate collected, and well washed with boiling water. The barium in the filtrate and washings is precipitated with potassium carbonate, and the required potassium salt obtained in the usual manner. The standards are not prepared by direct weighing, but by comparison with a known weight of potassium nitrate treated with the sulphonic acid reagent in the usual manner.

All attempts to sulphonate *o*-nitrophenol with fuming sulphuric acid at 100° resulted in violent explosions. T. S. P.

Estimation of Inorganic and Organic Phosphorus in Meats. HARRY S. GRINDLEY and E. L. ROSS (*J. Biol. Chem.*, 1910, 8, 483—493).—The neutral ammonium molybdate method as modified by Emmett and Grindley, the magnesia mixture method of Forbes and his colleagues, and the barium chloride method of Siegfried and Singewald give practically the same results for inorganic phosphorus in cold aqueous extracts of beef. The coagulation of the protein in such extracts does not change organic into inorganic phosphorus to any appreciable extent. W. D. H.

Estimation of Phosphoric Acid by Neumann's Method. J. M. KRASSER (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 198—200).—The author finds that this method (precipitation of the phosphoric acid with molybdic acid, boiling the washed precipitate of ammonium phosphomolybdate with a known quantity of *N*/2-sodium hydroxide solution, and titration of the excess of the latter, the loss of alkalinity due to the removal of the ammonia being a measure of the phosphoric acid) yields trustworthy results. W. P. S.

Partial Analysis of Natural Phosphates as a Guide to Their Conversion into Superphosphates. P. HARDY and JOS. VANDORMAËL (*Bull. Soc. chim. Belg.*, 1911, **25**, 43—57).—In converting natural phosphates into superphosphates, sulphuric acid is used up, not only in converting tricalcium phosphate into calcium hydrogen phosphate, but also in decomposing the subsidiary constituents, such as iron phosphate, aluminium silicate, calcium fluoride, and calcium and magnesium carbonates. Complete analyses are given of three natural phosphates. From comparison of these results with (1) results of analyses of superphosphates made from the phosphates, (2) factory data regarding the manufacture of these superphosphates, and (3) calculated quantities of sulphuric acid necessary for the conversion of all the ingredients known to be present in the crude phosphates used, it is shown that all the data necessary for determining the quantity of sulphuric acid needed to effect the conversion of a given sample of natural phosphates can be obtained with sufficient accuracy by determining the total lime, phosphoric acid, sulphuric acid, alumina, and ferric oxide. T. A. H.

Estimation of Potassium as Potassium Platinichloride. HEINRICH FRESENIUS and PAUL H. M. P. BRINTON (*Zeitsch. anal. Chem.*, 1911, **50**, 21—35). Experiments with pure potassium chloride and mixtures of it with sodium chloride, calcium chloride, magnesium chloride, and barium chloride; also on the use of alcohol of different strength when separating potassium and sodium chlorides by the platinum chloride process.

Small proportions of calcium, magnesium, or barium chlorides do not interfere, but when present in excess, it is advisable to remove these before the treatment with platinum chloride. Alcohol of 80 vol. % is recommended for removing the excess of platinum chloride and the double sodium compound.

The weighed potassium platinichloride if at all lumpy should be redissolved in boiling water and evaporated in the platinum dish on a not quite boiling water-bath, and then again dried at 130° for at least two hours. L. DE K.

Volumetric Estimation of Potassium by the Cobaltinitrite Method. OLIVER M. SHEDD (*J. Ind. and Engin. Chem.*, 1910, **2**, 379). —A detailed account of numerous experiments based on the work of

Drushel (Abstr., 1908, ii, 66, 735) on the estimation of potassium (especially in soils) by the cobaltinitrite method; the following procedure was found to give the most uniform results. The solution containing the potassium salt (after the preliminary work to bring it to this stage is completed) is evaporated down to a volume of about 5 c.c., slightly acidified with acetic acid, and 15 c.c. of fresh nitrite reagent added. The larger amount of nitrite reagent facilitates filtration, and ensures an excess of reagent after evaporation; the solution is then evaporated on the water-bath until the contents become a thick syrup, but long heating must be avoided; the remainder of the analysis is carried out as previously described. F. M. G. M.

Estimation of Lithium. Ernst Murmann (*Zeitsch. anal. Chem.*, 1911, **50**, 171—174).—Lithium chloride may be extracted from its mixtures with alkali chlorides by means of pyridine. The solution is evaporated, and the residual mass converted into lithium sulphate and weighed as such.

It is as well to dissolve the undissolved chlorides in water, to evaporate to dryness, and to once more extract with pyridine, which is then added to the main solution, although it is almost superfluous to do so.

The old phosphate process for the estimation of lithium gives very untrustworthy results, and should not be employed. L. de K.

Colour Reactions of Calcite and Aragonite. Stanislaus J. Thugutt (*Chem. Zentr.*, 1910, ii, 1084; from *Kosmos*, 1910, **35**, *Radziszewski Festband*, 506—512).—The sensitive reaction proposed by Meigen for the identification of aragonite is not suitable for use in the case of dark-coloured specimens of the mineral. For such specimens, Congo-red or an alkaline solution of alizarin may be employed; with these reagents aragonite is coloured pink, whilst calcite remains uncoloured. Silver chromate is a still better reagent, as, under definite conditions as to temperature and concentration, it colours aragonite a deep red, whilst calcite remains unaffected. The coarsely-powdered mineral should be treated with *N*/10-silver nitrate solution for one second, then washed, and moistened for a moment with 20% potassium dichromate solution. Aragonite is 1800 times more sensitive towards silver chromate than is calcite.

W. P. S.

Separation and Estimation of Barium in the Presence of Calcium and Magnesium by the Action of Acetyl Chloride in Acetone on the Mixed Chlorides. Frank A. Gooch and C. N. Boynton (*Amer. J. Sci.*, 1911, [iv], **31**, 212—220).—The method depends on the precipitation of hydrated barium chloride from its aqueous solution by means of a mixture consisting of four parts of acetone and one part of acetyl chloride; calcium and magnesium chlorides, if present, are not precipitated by this reagent. A concentrated solution of the mixed chlorides is placed in a beaker, which is immersed in a water-bath at a temperature of 15°, and about 30 c.c. of the reagent are added at the rate of 2 drops a second; this rate may be increased to about 5 drops a second when most of the barium chloride has been precipitated. The precipitate is then collected on an asbestos filter, washed with acetone, dried at 135°, or ignited at a dull-red heat, and weighed as anhydrous barium chloride. The quantity of reagent mentioned is sufficient for the precipitation of 0·1 gram of barium chloride in the presence of 0·5 gram of calcium and magnesium chlorides; the salts should be dissolved in the smallest possible volume of water. The method cannot be recommended for the separation of barium from strontium. W. P. S.

The Electrolytic Estimation of Zinc in Ores. GEO. KEMMERER (*J. Ind. Engin. Chem.*, 1910, **2**, 375).—The account of an investigation undertaken to ascertain whether the zinc content of an ore can be rapidly and accurately determined electrolytically, previous workers having stated that too high results are usually obtained; the conclusions drawn are that if the electrolyte contains 20—25 grams of sodium hydroxide, and a current of $ND_{100} = 3{\cdot}1\ A$ is employed, that rapid and accurate determinations can be carried out.

The electrolytic cell consisted of a cylindrical nickel gauze cathode which fitted loosely into a 150 c.c. Jena beaker, and a revolving propeller-shaped anode. The cathode surface was about 160 sq. cm., whilst the anode was rotated about 600 times per minute.

Weighed pieces of zinc were dissolved in nitric acid, 2 c.c. of sulphuric acid added, and the solution evaporated until dense fumes of sulphur trioxide were evolved; after cooling, it was transferred to the beaker, diluted to 100 c.c., solid sodium (or potassium) hydroxide added, and the hot solution rapidly electrolysed. When deposition was complete, the cathode was removed without opening the switch, plunged into a large beaker of water, dried with absolute alcohol and ether which had been distilled over sodium, heated at 70—100°, cooled, and weighed atonce.

The application of this method to a carbonate ore which was previously treated by the modified Waring method (compare Low's "Technical Methods of Ore Analysis") is also described in the original. F. M. G. M.

Estimation of Copper in Pyrites. I. MAJEWSKI (*Chem. Zentr.*, 1910, ii, 1092; from *Kosmos*, 1910, **35**, *Radziszewski Festband*, 597—601).—The author prefers to fuse the pyrites with six times its weight of potassium persulphate, instead of the treatment with hydrochloric and nitric acids recommended by Fresenius, in order to obtain the copper in solution. W. P. S.

Volumetric Estimation of Free Acid and Basic Alumina in Aluminium Salts. THOMAS J. I. CRAIG (*J. Soc. Chem. Ind.*, 1911, **30**, 184—185).—To estimate the free sulphuric acid, an excess of normal potassium fluoride is added to the solution of the aluminium sulphate; this yields potassium sulphate and insoluble potassium aluminium fluoride ($AlF_3,3KF$); as both these salts are neutral, the free sulphuric acid can be titrated by means of standard alkali, using phenolphthalein as indicator. The potassium fluoride solution is prepared by dissolving the pure salt in distilled water, bringing to D 1·45, and neutralising, if necessary, with potassium hydroxide or sulphuric (hydrofluoric) acid until about 1 c.c. in 10 c.c. of distilled water shows a faint pink colour with phenolphthalein. Insoluble matter is removed, the clear solution diluted until it has D 1·35 (0·5 gram of potassium fluoride per c.c.), and preserved in a glass bottle internally coated with wax.

In the actual estimation a solution containing about 1—3 grams of alumina per 200 c.c. is used; 20 c.c. of the clear solution are added gradually and with constant stirring to 10 c.c. of the potassium fluoride solution previously diluted with 50 to 60 c.c. of distilled water, and 0·5 c.c. of 0·2% phenolphthalein solution. Standard alkali is then added until a faint but permanent pink colour is obtained.

If the original sulphate is basic, that is, contains the salt $Al_2O(SO_4)_2$, a deep red colour is developed on the addition of the fluoride and phenolphthalein. A rough titration is then made by adding standard acid until the colour is destroyed. To another portion of the clear basic solution, an excess of standard sulphuric acid is added, heat is applied to ensure combination between the basic salt and acid, and the excess of acid left is titrated as in the case of a specimen containing free acid.

If sodium salts are present, it is advisable to add 20 to 30 c.c. of a neutral saturated solution of potassium sulphate to the solution of the aluminium salt before it is mixed with the potassium fluoride. By this means the formation of insoluble basic double fluorides is avoided. If ammonia is present, it must be removed by heating with a known excess of standard alkali, and it is essential that in every case insoluble matter should be removed before adding the potassium fluoride.

Free acid can be estimated in the case of iron and zinc salts by a similar method, but a larger excess of potassium fluoride is necessary. J. J. S.

Application of "Cupferron" in Quantitative Analysis.

REMIGIUS FRESENIUS (*Zeitsch. anal. Chem.*, 1911, **50**, 35—43).—A series of experiments to try the accuracy of Baudisch's "cupferron" process (Abstr., 1910, ii, 76). The results show that the method is trustworthy for the estimation of ferric iron in the presence of aluminium, chromium, nickel, cobalt, zinc, alkali earths, and also manganese (ferromanganese, ores of manganese). Copper is precipitated with the iron, but may be removed from the precipitate by treatment with ammonia. In the estimation of copper, the "cupferron" process gives good results in the absence of lead and bismuth. L. DE K.

Efficiency of Borax Bead Tests for Nickel and Cobalt.

LOUIS J. CURTMAN and P. ROTHBERG (*J. Amer. Chem. Soc.*, 1911, **33**, 188—189).—Experiments have been made to ascertain the extent to which nickel and cobalt can be detected in presence of each other by means of borax bead tests. It has been found that a blue bead, indicating the presence of cobalt, is obtained up to a point at which the ratio Ni : Co is 30 : 1. If the proportion of nickel is still further increased, beads of an uncertain brownish colour are produced, until the ratio Ni : Co = 50 : 1, when a decidedly brown bead is formed, demonstrating the presence of nickel. It follows therefore that borax beads can only serve as confirmatory tests, and are not trustworthy unless the results are positive. E. G.

An Organic Reagent for Chromium. PAUL KOENIG (*Chem. Zeit.*, 1911, **35**, 277—278).—An aqueous solution of sodium 1 : 8-dihydroxynaphthalene-3:6-disulphonate is a very sensitive reagent for chromium; it yields a red or violet coloration with chromic acid, chromates, or dichromates, the reaction being obtained with as small a quantity as 0·0008 mg. of chromium. The reaction also allows chromium to be detected in the presence of iron, as solutions of iron salts yield a green coloration which is destroyed immediately by the addition of phosphoric acid, whilst the violet coloration due to chromium is not affected. The test may be rendered quantitative by comparing the coloration obtained with that produced by a known quantity of chromium, and is particularly useful for detecting the presence of small quantities of chromium in the ashes of plants. W. P. S

Volumetric Estimation of Molybdenum. EDMUND KNECHT and F. W. ATACK (*Analyst*, 1911, **36**, 98—100).—The apparatus consists of an eight-ounce conical flask carrying a trebly perforated rubber cork. One perforation is fitted with a Bunsen valve, not closed as customary with a solid glass bead, but fitted at the top with a glass tube into which fits a small india-rubber stopper. Through this passes a platinium wire to which is attached a rod of pure zinc. Another hole carries a tube connected with an apparatus for generating carbon dioxide, and the third one carries the adapter for the burette.

The molybdenum solution (= about 0·05 gram of the metal) is placed in the flask, and, after adding a few pieces of granulated zinc (the zinc rod being lifted out of the solution), the stream of carbon dioxide is kept up until the zinc has completely dissolved. The rod is then lowered for a short time to ensure complete reduction, and then removed and washed with recently boiled water introduced down the valve from a wash-bottle. The warm solution is then titrated with a 4% standardised solution of methylene-blue (Knecht, *J. Soc. Dyers*, 1905, **21**, 9) until the characteristic blue shade is obtained.

The presence of iron does not interfere with the process, but titanium, tungsten, chromium, and vanadium should be absent. L. DE K.

Determination of Minerals by Colour Reactions. PAUL GAUBERT (*Bull. Soc. franç. Min.*, 1910, **33**, 324—326).—L. Lévy (Abstr., 1887, 304, 305) employed the colour reactions given by certain organic substances (morphine, codeine, α- and β-naphthol, resorcinol, phenol, etc.) dissolved in strong sulphuric acid for the detection of titanic, columbic, tantalic, stannic, molybdic, vanadic, antimonic, arsenic acids, etc. When this method has been applied to minerals, it has been usual first to decompose the mineral. This is, however, unnecessary; the finely powdered mineral need only be treated for some hours with the acid solution in a watch-glass or test-tube. In certain cases the addition of a suitable amount of water accelerates the production of the colour. In addition to the organic substances indicated by Lévy, papaverine may also be used. This gives with sulphuric acid a red tint, which turns to blue with vanadic, tungstic, chromic, and titanic acids, and to brown with stannic acid. This affords a ready means of distinguishing between cassiterite, rutile, and zircon; and, by the rapidity of the coloration, between wulfenite (very quickly) and vanadinite and crocoite (slowly). The titanium minerals, rutile, brookite, anatase, ilmenite, sphene, and keilhauite, give a crimson colour with morphine, and they can be distinguished the one from the other by the velocity of the reaction. L. J. S.

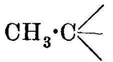
Detection and Estimation of Small Quantities of Antimony. PHILIP SCHIDROWITZ and HAROLD A. GOLDSBROUGH (*Analyst*, 1911, **36**, 101—103).—A colorimetric method intended for fractions of a milligram of antimony in a volume of 10 c.c. After adding 0·5 c.c. of hydrochloric acid and 0·1 c.c. of a 10% solution of gum acacia, so as to ensure a colloidal sulphide, hydrogen sulphide is passed and the coloration compared with a standard solution in a colorimeter, as usual.

In some cases a provisional separation of the antimony by Reinsch's test is unavoidable. The copper with the deposit is heated at 70° for a few minutes with 5 c.c. of 5% potassium hydroxide, 10 c.c. of water, and an excess of permanganate. The solution is poured off, boiled, filtered, and any permanganate still present destroyed by boiling with 1 c.c. of solution of tartaric acid. The colourless solution is then suitably diluted, and an aliquot part made up to 10 c.c., when it is tested as directed. The results are decidedly too low, but admissible in the circumstances. L. DE K.

Estimation of Gold and Silver in Rich Copper Ores. JULIUS LOEVY (*Chem. Zeit.*, 1911, **35**, 278).—It is recommended that ores containing large quantities of copper be mixed with sand in such quantity that the quantity of copper is reduced to 6%; the mixture is then fused in a crucible in the ordinary way. The resulting button of lead may be cupelled directly in order to obtain the gold and silver present. W. P. S.

Separation of Platinum and Tin. LOTHAR WÖHLER and A. SPENGEL (*Zeitsch. anal. Chem.*, 1911, **50**, 165—171).—The authors arrive at the following conclusions: The separation of platinum and tin cannot be effected by means of reducing agents; from alloys, the tin cannot be properly extracted with acids, and the sulphides cannot be separated by means of strong hydrochloric acid or sodium hydroxide. The separation may be carried out by volatilising the tin sulphide in a current of hydrogen sulphide or in a current of bromine, but this is a tedious process. Hydrolytic decomposition by means of sulphuric acid requires heating at 150—200° in a sealed tube. The best and safest plan is to heat the solution of the mixed chlorides with dilute sulphuric acid, which precipitates the tin oxide. Without removing the deposit, the platinum is then recovered electrolytically, using a current of at first 1·1, later 1·5—1·7 volt; $ND_{100} = 0·2$ ampere, temperature 50—60°. L. DE K.

The Action of Potassium Permanganate on Organic Compounds. JOSEPH HETPER (*Bull. Acad. Sci. Cracow*, 1910, *A*, 601—605).—The author finds that, under certain definite conditions, a large number of organic compounds can be oxidised completely by potassium permanganate, which can therefore be used for their estimation. In general, all compounds soluble in water, alkalis, or phosphoric acid, and containing ·OH groups, can be oxidised, such as polyhydric alcohols, sugars, phenols, and hydroxy acids. The solution of the substance is heated on the water-bath for one and a-half hours with *N*/5-potassium permanganate solution containing 20 grams of crystallised phosphoric acid per litre. The excess of permanganate is then determined.

On the other hand, compounds containing the radicle  are not fully oxidised, neither are those containing CH_3, especially if it is near to a CO_2H group. The author has worked out a schematic representation for the analysis of known organic substances.

Incidentally he points out that solutions of potassium permanganate containing phosphoric acid undergo practically no change on keeping.

E. J. R.

Estimation of Quinol. JOHANNES PINNOW (*Zeitsch. anal. Chem.*, 1911, **50**, 154—164).—Quinol may be completely extracted from its aqueous solutions by extraction with ether in a Partheil apparatus. The ether is then evaporated, and the residue dried in a water-oven to constant weight.

Quinol may also be estimated by boiling for six minutes with Fehling's solution; the precipitate is ignited, and then converted into metallic copper by heating in a current of hydrogen. As, however, the reduction depends on the concentration of the solution, reference should be had to tables. Potassium quinolsulphonate also similarly reduces the Fehling's solution; 1 mol. of quinol = about 6 atoms of copper.

Although Fehling's solution is not reduced by sulphites, these strongly affect the reducing power of quinol, which may be increased one and a-quarter or even one and a-half times. L. DE K.

Nylander's Test for Dextrose. A. GOLDSOBEL and E. SONNENBERG (*Chem. Zentr.*, 1910, ii, 1095; from *Kosmos*, 1910, **35**, *Radziszewski Festband*, 571—584).—The authors have investigated this test, and recommend the following method of applying it: Twenty c.c. of the solution under examination and 20 c.c. of the same solution diluted with 10 parts of water are treated in separate flasks with 2 c.c. of Nylander's reagent (basic bismuth salt with 12·5% of sodium hydroxide); the mixtures are boiled for ten minutes under a reflux apparatus. While the mixtures are still hot, the precipitates are collected on filters, washed thoroughly with water, and examined for any traces of blackening, this coloration being obtained when dextrose is present. The control experiment with the diluted solution is necessary, for the reason that the reaction does not take place if the solution contains more than 5% of the sugar. W. P. S.

Estimation of Reducing Sugars. Stanley R. Benedict (*J. Biol. Chem.*, 1911, **9**, 57—59).—In place of Fehling's solution, the following mixture is recommended as it is more sensitive, and keeps well indefinitely: copper sulphate 18, sodium carbonate 200, sodium citrate 200, and potassium thiocyanate 125 grams, 5% potassium ferrocyanide solution 5 c.c., and water up to a litre. The copper sulphate is the only constituent which needs careful weighing. Twenty-five c.c. of the mixture are reduced by 0·05 gram of dextrose and by 0·053 of lævulose. The ferrocyanide prevents precipitation of the cuprous oxide, and the end-point is the disappearance of the blue colour. W. D. H.

[A Simple Method for the Estimation of Sugar in Blood.] E. Frank (*Zeitsch. physiol. Chem.*, 1911, **70**, 408. Compare Michaelis and Rona, this vol., ii, 73; Moeckel and Frank, Abstr., 1910, ii, 116). —A question of priority in relation to the methods of removing protein from blood. It is admitted that Michaelis and Rona were first. W. D. H.

Estimation of Amylaceous Substances in Dressed Provisions. P. Carles (*Ann. Chim. anal.*, 1911, **16**, 89—90).—Food chemists are often called on to ascertain whether starch has been fraudulently added to dressed provisions such as patés, galantines, etc., and the general method of procedure is to convert the starch into sugar. The author has examined the fresh and genuine livers of various animals, and finds that all of them contain reducible substances which must be allowed for in the estimation. The quantities found were equivalent to the following percentage amounts of starch: duck 1·39, goose 1·93, bullock 2·23, pig 2·77, calf 8·01. E. J. R.

Some New Tests. Fred Klein (*J. Ind. Engin. Chem.*, 1910, **2**, 389).—The following distinctive reactions are described:

(1) To distinguish between anhydrous and glacial acetic acid: the former yields a red precipitate of amorphous selenium when boiled with a crystal of selenious acid (or, preferably, sodium selenite), whilst with glacial acetic acid the solution remains clear.

(2) To differentiate between methyl and ethyl alcohols: if dilute, the alcohol must be concentrated by distillation; a small quantity is then treated with a few drops of selenic acid (H_2SeO_4) and a trace of silver halide (preferably bromide), when ethyl alcohol yields a colourless, amorphous precipitate, soluble on the addition of water, whilst a solution of methyl alcohol (common wood spirit) remains clear, or, in exceptional circumstances, a crystalline precipitate is deposited. This test can also be employed for esters.

(3) To distinguish between the alkaloids: the extracted alkaloid is

(*a*) dissolved in sulphuric acid (94—95%), and (*b*) a trace of sodium selenite (Na_2SeO_3) then added, the solution warmed, and the following colour reactions are observed.

Strychnine, (*a*) slight coloration, (*b*) brown. Digitaline, (*a*) slight coloration, (*b*) brown. Aconitine, (*a*) slight coloration, (*b*) brown. Atropine, (*a*) slight coloration, (*b*) brown. Brucine, (*a*) rose-pink, (*b*) brown. Morphine and cocaine, (*a*) green in cold, (*b*) black precipitate. Codeine, (*a*) light brown, (*b*) black precipitate. Caffeine and sparteine, (*a*) no coloration, (*b*) no coloration. Veratrine, (*a*) cherry-red, (*b*) purple. Quinine, (*a*) slight coloration on heating, (*b*) purple. Cantharidine, (*a*) no coloration, (*b*) with addition of alcohol a slight purple coloration in the cold, which darkens on heating.

(4) To detect small quantities of petroleum in turpentine when the official test has proved unsatisfactory: a copper sulphate solution (5—10%) is treated with about half its volume of petroleum, and a crystal of potassium iodide added to the clear solution; this dissolves with a purple coloration, and, after shaking, slowly turns a yellowish-brown; in the case of turpentine the mixture with copper sulphate is not clear; potassium iodide gives a purple-red colour, which, with pure turpentine, turns green after shaking. The presence of "rosin" can be detected by its odour and the brown coloration of the solution.

(5) A test for nitric acid: the acid must have a minimum concentration of 40%, and, if more dilute, should be evaporated to dryness in the form of a salt; the reagent employed consists of a trace of powdered tellurium in fuming sulphuric acid (2—3 c.c.), which forms an eosin-coloured solution, and is then treated with 95% sulphuric acid (1—2 c.c.). Two equal portions of this solution are heated until decolorised, to one is added the nitrate, to the other a drop or more of the reagent, both tubes are slightly warmed, and the one containing the nitrate treated with a further quantity of the reagent, when immediate decolorisation occurs, whereas the other one remains an eosin-red colour. This method is stated to be applicable to the quantitative estimation of nitric acid. F. M. G. M.

Estimation of Tartaric Acid. ARNOLD HECZKO (*Zeitsch. anal. Chem.*, 1911, **50**, 12—20).—A criticism of the Goldenberg method for the analysis of crude tartars, etc. (*ibid.*, 1907, **47**, 57). This process, although technically accurate, suffers from three defects: (1) The end-point in the titration must be ascertained by means of an external indicator (litmus paper). (2) The solubility of potassium hydrogen tartrate is sensibly affected by the temperature and presence of other salts. (3) Calcium tartrate is not always entirely decomposed by boiling with potassium carbonate.

In the author's opinion the direct standardisation of the volumetric alkali with 1 gram of pure potassium hydrogen tartrate cannot be recommended. 1·5 Gram of the acid tartrate should be submitted in every respect to the same process as the actual sample, using, in fact, the same amount of potassium carbonate, acetic acid, and alcohol as directed by Goldenberg. The source of error (2) will thus be eliminated. L. DE K.

Estimation of Total Tartaric Acid [in Crude Materials].

ARNOLD HECZKO (*Zeitsch. anal. Chem.*, 1911, **50**, 73—81).—From 3 to 6 grams of the sample (according to grade) are treated with 20 c.c. of 2*N*-sulphuric acid, and the whole is then boiled for two minutes. When cold, the mass is transferred to a 200 c.c. flask and diluted with 92—94% alcohol up to the mark. One hundred c.c. of the filtrate are then treated in a 300 c.c. Erlenmeyer flask with 3 c.c. of glacial acetic acid and 10 drops of a cold saturated solution of potassium chloride. Sixteen c.c. of a solution of 20 grams of potassium acetate in 100 c.c. of alcohol are then added drop by drop from a burette with constant stirring. After half an hour, the liquid is poured off from the precipitate, which is then washed twice, by decantation, with 40 c.c. of 97% alcohol and, finally, on the Gooch filter with another 80 c.c of alcohol.

After removing the adhering alcohol by suction at the pump, the potassium hydrogen tartrate is dissolved in 200 c.c. of boiling water, and at once titrated with *N*/5-potassium hydroxide, using litmus paper as external indicator. The volumetric alkali is checked by operating on 1·5 gram of pure potassium hydrogen tartrate in the way described, but using only half the quantities of the various reagents.

L. DE K.

Assay of Vintage Marcs for Tartaric Acid. Separate Estimation of Potassium Hydrogen Tartrate and Calcium Tartrate.

P. CARLES (*Bull. Soc. chim.*, 1911, [iv], **9**, 199—202; *Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 561—564).—The process consists in extracting the marc (residues from the wine-presses), first with water containing sodium carbonate to remove potassium hydrogen tartrate (solution *A*), and then with dilute hydrochloric acid to remove the tartaric acid present as calcium tartrate (solution *B*). Both solutions are concentrated, and the tartaric acid they contain separately precipitated, dried, and weighed as calcium tartrate. Full details of the method of carrying out the estimation are given in the original.

T. A. H.

Rapid Estimation of the Volatile Acidity of Wines and Fermented Beverages.

PHILIPPE MALVEZIN (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 560—561).—The method depends on the solubility of the volatile acids in ether. Ten c.c. of the wine or other liquid are shaken with 10 c.c. of ether, and, after separation has taken place, 5 c.c. of the ethereal solution are pipetted into a flask containing 5 c.c. of neutral alcohol. The contents of the flask are then titrated with *N*/10-sodium hydroxide solution, using phenolphthalein as the indicator. The acidity is calculated from the formula:

$$\frac{(2A-0\cdot2)\times25\times1\cdot63}{6}.$$

W. P. S.

Estimation of the Acidity of Fats and Oils, Especially Lubricating Oils.

HEINRICH LOEBELL (*Chem. Zeit.*, 1911, **35** 276—277).—Results of experiments carried out by the author show that a mixture of alcohol and ether is an unsuitable solvent to employ for dissolving a fat or oil previous to the titration of its acidity; when phenolphthalein is used as the indicator, the end-point of the titration is not distinct, and the results obtained are always too high. Still less satisfactory results are obtained if alkali-blue is employed as the indicator. The employment of a mixture of alcohol and benzene, however, allows concordant and trustworthy figures to be obtained. Aqueous *N*/10-barium hydroxide may be used for titrating the acidity of oils when the latter have been dissolved in a mixture of alcohol and benzene. W. P. S.

Estimation of Lecithin in Oil. WILHELM FRESENIUS and LEO GRUNHUT (*Zeitsch. anal. Chem.*, 1911, **50**, 90—106).—The method is based on the estimation of the phosphoric acid yielded by oxidation of lecithin; the phosphoric acid is weighed as yellow phosphomolybdate precipitate.

Fifty grams of the oily liquid are introduced into a 200 c.c. cylinder divided to 1 c.c., and 100 c.c. of absolute alcohol are added. After shaking gently for twenty minutes, the layers are allowed to separate, and the volumes of the lower oily layer and the upper alcoholic layer (o_1 and a_1) are read off. Of the latter, 75 c.c. (v) are taken for the first phosphoric estimation (p_1), and, the pipette being rinsed with absolute alcohol, the original volume is restored by adding alcohol up to the mark. The mixture is again shaken, and allowed to settle, when the volumes (o_2 and a_2) are read off and 75 c.c. of the alcoholic layer are taken for the second phosphoric acid estimation (p_2). The calculation is effected by means of the following formula:

$$x = \frac{p_1^2 a_1 o_1 + p_1 p_2 (o_1 a_2 - o_2 a_1)}{v(p_1 o_1 - p_2 o_2)}.$$

The alcoholic solution is evaporated to dryness, and the residue fused with a mixture of sodium carbonate (3 parts) and sodium nitrate (1 part). The mass is then dissolved in the smallest possible quantity of hot water, cooled, neutralised with nitric acid, made up to 50 c.c., and then 2·5 c.c. of nitric acid (D 1·4) and 75 c.c. of Jörgensen's molybdate solution added. L. DE K.

The Occurrence and Quantitative Estimation of Trimethylamine in Human Urine. TOSAKU KINOSHITA (*Zentr. Physiol.*, **24**, No. 17. Reprint 4 pp.).—The ammonia, etc., was distilled off from urine under diminished pressure in the presence of magnesium oxide, and collected in hydrochloric acid. The acid solution was then evaporated to dryness, and the methyl groups in the residue thus obtained determined by the Herzig-Meyer process. As the result, extremely small traces of trimethylamine could be detected in human urine, and these, the author suggests, are possibly due to decomposition of other products. S. B. S.

Estimation of Hexamethylenetetramine (Urotropine) in Urine. FRITZ SCHROTER (*Arch. exp. Path. Pharm.*, 1911, **64**, 161—166).—The urine is acidified with acetic acid, and a saturated solution of mercuric chloride added. The precipitate so obtained, after washing, is transferred to a flask containing a concentrated solution of sodium chloride, and heated on the water-bath. After cooling, this is filtered, and the mercury precipitated from the filtrate by potassium hydroxide and filtered off. The nitrogen is then estimated by Kjeldahl's method, and from this the urotropine present is calculated.

W. D. H.

Estimation of Urea. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1911, **9**, 25—28).—Benedict's method is preferred to Folin's, because it is easier; "there is no use in calculating results to the third place of decimals when the interpretation cannot go beyond the first place."

W. D. H.

Analysis of Coca Leaves. E. BIERLING, K. PAPE, and A. VIEHOVER (*Arch. Pharm.*, 1910, **248**, 303—336).—The authors have investigated upwards of twenty methods which have been proposed for the analysis of coca leaves, and find that the methods described by Keller, Panchaud, de Jong, Fromme, and the Swiss Pharmacopœia are the simplest, but have the drawback that the filtration of the ethereal extract of the leaves causes some of the solvent to evaporate, and, consequently, the percentage of alkaloid found is too high. These methods are similar in principle, the alkaloid being liberated from the leaves by means of ammonia and extracted with ether; the ethereal solution is then extracted with hydrochloric acid, the alkaloids are again liberated by means of ammonia, and separated with ether. Cocaine, cinnamylcocaine, benzoyl-ψ-tropine, and *iso*atropylcocaine are estimated together, but not hygrine or benzoylecgonine; the latter is insoluble in ether, whilst the former, although slightly soluble, is removed when the residue of alkaloids is warmed. For pharmaceutical purposes, a modification of de Jong's process (Abstr., 1909, ii, 276) is recommended. The authors consider that the broad-leaved Bolivian and Peruvian coca leaves should be made official, as these leaves are free, or practically free, from cinnamylcocaine, benzoyl-ψ tropine, and *iso*atropylcocaine, and the cocaine is accompanied by only hygrine and benzoylecgonine.

W. P. S.

Sources of Error in the Folin Method of Estimating Creatinine. ALONZO E. TAYLOR (*J. Biol. Chem.*, 1911, **9**, 19—20).—The personal equation and the absence of a standard light are sources of error in this colorimetric method. The influence of the urinary pigment and the presence of bile are very disturbing factors.

W. D. H.

Estimation of Nicotine in Concentrated Tobacco Juice. RICHARD KISSLING (*Chem. Zeit.*, 1911, **35**, 98).—A reply to Schröder (this vol., ii, 163). The author, who is now engaged on a colorimetric process, thinks that by his method a complete separation of nicotine from ammonia and allied bases is guaranteed.

L. DE K.

Estimation of Nicotine in Concentrated Tobacco Juice. H. ULEX (*Chem. Zeit.*, 1911, **35**, 121).—Ten grams of the sample are diluted with 1—3 c.c. of water, and then mixed with a sufficiency of a mixture of 1 part of soda-lime and 5 parts of gypsum. The mass obtained is powdered, sifted, and placed for an hour in a desiccator over sulphuric acid to get rid of ammonia fumes. The nicotine is now isolated by distillation. For this purpose the powder is placed in a flask containing 1½ litres of boiling water, and an extra 3 or 4 grams of alkali are added, also 4 grams of paraffin to prevent frothing. After collecting 1 litre of distillate, another litre of water is introduced into the distilling flask, and a second litre of distillate is collected. The nicotine is finally titrated with *N*/2-hydrochloric acid; 1 c.c. = 0·081 gram of the alkaloid. L. DE K.

Estimation of Nicotine in Concentrated Tobacco Juice. JULIUS TÓTH (*Chem. Zeit.*, 1911, **35**, 146).—A reply to his critics (this vol., ii, 163; preceding abstracts). The author upholds the technical accuracy of his process. L. DE K.

Estimation of Nicotine in Concentrated Tobacco Juices. RICHARD KISSLING (*Chem. Zeit.*, 1911, **35**, 200. Compare preceding abstracts).—The author points out that the high results obtained by Ulex's method for the estimation of nicotine in tobacco juices is probably due to the liberation of large quantities of ammonia by the action of the soda-lime on the nitrogenous substances present. The method also possesses certain other defects. W. P. S.

Estimation of Nicotine in Tobacco Extracts. J. LEISTER (*Chem. Zeit.*, 1911, **35**, 239—240).—A reply to Schröder (this vol., ii, 163). The author states that the method proposed by Ulex (preceding abstracts) gives trustworthy and concordant results, if care is taken to thoroughly powder the soda-lime mixture so as to facilitate the evaporation of any ammonia present. L. DE K.

Estimation of Morphine in Opium and in Opium Preparations. LÉON DEBOURDEAUX (*Chem. Zentr.*, 1910, ii, 1097; from *Bull. Sci. Pharmacol.*, 1910, **17**, 382—385).—It is pointed out that about 10% of the morphine contained in opium is insoluble in water and alcohol, and is only obtained in solution by the addition of calcium hydroxide. In the analysis of preparations containing opium these should always be treated with calcium hydroxide before the morphine is extracted. W. P. S.

Glucoside Reactions: Convallamarin and Convallarin. C. REICHARD (*Pharm. Zentr.-h.*, 1911, **52**, 183—188).—The author describes the reactions of convallamarin and convallarin, two glucosides occurring in the roots and leaves of *Convallaria majalis*; the former is soluble in water and in alcohol, and it is similar to digitalin in its physiological action, whilst the latter is insoluble in water and acts solely as a purgative. When treated with nitric acid, convallamarin yields a colourless solution which changes in a few hours to yellow, whilst convallarin gives a yellow solution which gradually becomes red. If the nitric acid solutions are evaporated and the residues treated with a drop of ammonia, convallamarin yields a yellow coloration, changing in a few hours to dark green, and convallarin gives a pure white precipitate. The most characteristic reaction of the two glucosides is that obtained with sodium iodate. Convallarin, when treated with equal quantities of sodium iodate and water, gives a white residue on drying the mixture, whilst convallamarin yields a moist, amorphous mass, which is coloured bright yellow on the addition of hydrochloric acid ; this acid does not change the colour of the convallarin-sodium iodate residue. Stannous chloride gives a yellow coloration with convallamarin after several hours' contact, and a red coloration with convallarin. Reactions with many other reagents are also described. W. P. S.

Estimation of Glycyrrhizin and Sugars in Liquorice Root and Extract. Ella Eriksson (*Arch. Pharm.*, 1911, **249**, 144—160). —A process is described for the estimation of dextrose, sucrose, and glycyrrhizin in liquorice root and extract, and the results of the application of this process to various commercial samples of these products are tabulated (compare Hafner, Abstr., 1900, ii, 318, 775 ; Zetzsche, *Pharm. Centr.-h.*, 1901, 277 ; Tschirch and Cederberg, Abstr., 1907, i, 545 ; Tschirch and Gauchmann, *ibid.*, 1908, i, 898 ; 1909, i, 328 ; ii, 85 ; Parry, *Chem. and Drug.*, 1910, Jan.). Parry's process gives results in good agreement with those obtained by the method now described.

Ten grams of the powdered root or extract are extracted in the cold with slightly alkaline water, and the solution made up to 200 c.c. if necessary. Of this, 40 c.c. are taken and 40 c.c. of alcohol added, and the mixture filtered quickly. To the filtrate 30 c.c. of Fehling's solution, prepared by Allihn's method, are added ; the mixture is set aside for thirteen to fourteen hours, and the precipitated cuprous oxide collected in an Allihn tube, washed, reduced (or oxidised), and weighed, and the amount of dextrose calculated from the result. The filtrate is poured into 30 c.c. of boiling Fehling's solution, the mixture boiled during three minutes, diluted with half its volume of water, and the cuprous oxide formed, collected, treated as before and weighed, and the amount of sucrose calculated from the result. In the filtrate glycyrrhizin may be estimated directly by long boiling with Fehling's solution, or it may be precipitated with dilute sulphuric acid, redissolved in alkali, Fehling's solution added, and the mixture boiled during fifteen hours. In either case the amount of glycyrrhizin may be calculated from the weight of cuprous oxide produced, with the knowledge that a reduction corresponding with 360 parts of dextrose is equivalent to 896 parts of glycyrrhizin.

In the roots examined, the dextrose varied from *nil* to 3·8%, sucrose from 2·4 to 6·5%, glycyrrhizin from 6·49 to 8·15%. In the extracts the corresponding ranges were 2·7 to 7·8%, 4·5 to 13·6%, 9·8 to 23·9%. It is probable that dextrose does not occur in the fresh root, but is produced by fermentation during drying. In preparing the extract a considerable loss of glycyrrhizin appears often to occur. T. A. H.

Estimation of Indigotin in the Presence of Starch. William Thomson (*J. Soc. Dyers*, 1911, **27**, 49—51).—Synthetic indigo is sometimes adulterated by the addition of starch, and the presence of this substance interferes with the estimation of the indigotin in such samples. The author has employed several different methods for estimating indigotin in mixtures containing known quantities of synthetic indigo and starch, and finds that Rawson's permanganate process (with salt precipitation of the sodium indigotindisulphonate) yields low results, the loss increasing with the quantity of starch present; after the samples had been treated with 4% hydrochloric acid in order to invert the starch, and the resulting sugar washed away, Rawson's process yielded better results. Bloxam's tetrasulphonate process gave more uniform results; synthetic indigo, however, showed only 82% of indigotin by this process. W. P. S.

Identification and Estimation of Proteins in Honey. EDMOND MOREAU (*Ann. Falsif.*, 1911, 4, 36—41).—The proteins of honey which are coagulable by heat may be separated into two substances, albumin and globulin, by treatment with magnesium sulphate. A 20% solution of the honey is neutralised, and the solution is saturated with magnesium sulphate; after the lapse of twenty-four hours, the precipitated globulin is separated by filtration, washed with a saturated solution of magnesium sulphate, and then heated to a temperature of 100°. The globulin is thus coagulated, and may be washed with water and weighed. The filtrate from the globulin is now acidified with acetic acid and boiled, when the albumin is precipitated. The filtrate from the albumin gives a precipitate with potassium mercuric iodide in the presence of acetic acid, denoting that honey contains proteoses or peptones, or both. Albumoses may be detected by means of a reagent (Esbach's) consisting of an aqueous solution of picric and citric acids, whilst the biuret reaction, when applied to a solution of honey from which albumoses have been precipitated with ammonium sulphate, will show the presence of peptones. In 10 samples of honey examined, the author found from 0·394 to 1·50% of total proteins, 0·09 to 0·40% of albumin, and 0·05 to 0·92% of globulin. In certain samples the albumin was present in greater quantity than the globulin, whilst in others the contrary was found to be the case. W. P. S.

An Improved Form of Heller's Test for the Detection of Albumin, Especially in Urine. FRANZ MICHEL (*Chem. Zeit.*, 1911, 35, 183).—In carrying out this test in the usual way, care has to be taken that the concentrated nitric acid and the solution to be tested do not mix, as otherwise, the nitric acid tends to dissolve the albumin and a turbid zone between the liquids is not obtained. The author, in order to prevent the liability of mixing, saturates the nitric acid with ammonium nitrate. In testing urine for the presence of albumin, 2 c.c. of the reagent are placed in a test-tube, and 1 c.c. of the urine is introduced by means of a pipette; if albumin is present, a turbid zone appears at the junction of the two liquids, and if the test-tube be shaken gently the whole of the urine layer becomes turbid. This is not the case if ordinary concentrated nitric acid is used, as the turbidity dissolves at once. W. P. S.

Assay of [Commercial] Gelatin. JULIUS HEROLD, jun. (*Chem. Zeit.*, 1911, **35**, 93—94).—A 20% jelly is prepared, and, after congealing for half an hour at 19°, its melting point is ascertained. Simultaneously, a 20% jelly is prepared from a mixture of equal parts of pure gelatin and glutose (prepared by heating gelatin with ammonia in a sealed tube at 100°), and its melting point is taken, or a 10% jelly of pure gelatin may be used. From the difference in the melting point (a), the proportion of glutin may be deduced from the formula: $a/1{\cdot}2 = x/82$; $x = \%$ of glutin.

A special form of apparatus for determining the melting points is described. By melting point is understood the temperature at which a column of the jelly no longer adheres to a glass vessel, which consequently commences to sink. L. DE K.

Benzidine as a Reagent for the Recognition of Blood Stains. TORQUATO GIGLI (*Boll. chim. farm.*, 1910, **49**, 955—956).—The stained fabric or an aqueous extract of it is treated with 2 to 4 drops of a solution of 5 grams of pure benzidine in 10 c.c. of glacial acetic acid, and 1 or 2 drops of hydrogen peroxide (3%) are added. The presence of blood is indicated by the immediate appearance of a blue coloration. The sensibility of the reaction carried out in this way is very great, much more in fact than was supposed by Adler, who first suggested the test. In the absence of blood, a blue coloration may appear, but only after a time. The author considers that the reaction does not suffice to affirm the presence of blood with finality, but the absence of the coloration does prove that blood is absent from a suspected stain. R. V. S.

Characteristic Reactions of Toad Poison. GIOVANNI BUFALINI (*Chem. Zentr.*, 1910, ii, 1670—1671; from *Arch. Farmacol. sperim.*, 1910, **9**, 559—568).—An aqueous solution of toad poison (secretion of skin glands) yields a red coloration when submitted to Ehrlich's diazo-reaction; this red colour is insoluble in ether, and is similar to that given by cholesterol. The addition of mineral acids changes the coloration to yellowish-red or yellow. The coloration is not produced when the poison has been treated previously with hydrogen peroxide. *p*-Aminoacetophenone gives a violet coloration, which changes to orange-red on the addition of ammonia; in hydrochloric acid solution, *p*-dimethylaminobenzaldehyde yields a blue coloration, which is insoluble in ether, chloroform, benzene, carbon disulphide, light petroleum, etc.; this reaction does not take place in acetic acid solution, and only feebly in alcoholic solution. When the poison is treated with sulphuric acid, an emerald-green coloration is produced, which is destroyed by the addition of oxidising or reducing substances. Michler's ketone does not give a coloration (compare Abstr., 1910, ii, 1096). W. P. S.

General and Physical Chemistry.

Refraction and Dispersion of Light in Certain Gases GEORG GRUSCHKE (*Ann. Physik*, 1911, [iv], 34, 801—816).—The refractive indices of carbon monoxide and dioxide have been determined for six different wave-lengths between the limits λ = 6678 and λ = 4471. Observations were also made on carbon suboxide, C_3O_2, but this gas was admixed with a large proportion of carbon dioxide. H. M. D.

Dispersion and Absorption of Chromium and Manganese in the Visible and Ultra-violet Spectrum. VSÉVOLOD FRÉEDERICKSZ (*Ann. Physik*, 1911, [iv], 34, 780—796).—In continuation of an investigation of the optical constants of the metals, the author has determined the refractive and absorption indices of chromium and manganese by Voigt's method. Curves are drawn which show the variation of the optical constants with the wave-length of the incident light. H. M. D.

Dispersion in Vapours of the Alkali Metals. PENRY V. BEVAN (*Proc. Roy. Soc.*, 1911, 85, *A*, 58—76. Compare Abstr., 1910, ii, 914).—Dispersion measurements have been made with sodium and rubidium vapours, and the dispersion curves have been drawn for several absorption lines. If attention be confined to the effects of dispersion near any single pair of lines, the constant of the dispersion formula appropriate to this line increases with the temperature of the vapour used. A relation cannot be found between the constants of different metals, as there is no evidence as to what temperatures should be chosen as corresponding temperatures.
C. H. D.

The Glow Discharge and the Emission of the Alkali-Metal Vapours. GEORG GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1911, 13, 183—192. Compare Gehlhoff and Rottgardt, Abstr., 1910, ii, 679).—Observations have been made relating to the nature of the glow discharge and of the emission spectra exhibited by tubes containing cæsium vapour admixed with helium. The helium lines disappear from the spectrum of the positive glow at very small pressures of the cæsium vapour. On the other hand, these lines are still evident in the spectrum of the negative glow when the pressure of the cæsium vapour has attained relatively high values.

Experiments at different temperatures in which the partial pressure of the helium are kept constant have shown that the cæsium lines of the principal and sub-series are exhibited by the positive glow. The negative glow spectrum shows the sub-series lines, and the lines of the spark spectrum brightly and the principal series lines feebly. When a spark gap is introduced into the circuit, the principal and sub-series lines disappear from the spectrum of the positive glow.

These and other observations support the author's view that the principal series lines are excited by slowly moving, the sub-series lines by more rapidly moving, electrons, and the lines of the spark spectrum by electrons of still greater velocity. H. M. D.

The Absorption Spectra of Lithium and Cæsium. PENRY V. BEVAN (*Proc. Roy. Soc.*, 1911, **85**, *A*, 54—58. Compare Abstr., 1910, ii, 370).—The absorption spectrum of lithium vapour has been examined at a red heat in a steel tube. The lines of the principal series are tabulated and there is, in addition, a fluted region between λ 4500 and λ 5500, corresponding fairly closely in position with the sodium fluted region. The wave-lengths of the lines are in good agreement with the values calculated by Hicks' formula (*Phil. Trans.*, 1910, **210**, 58). Some cæsium lines have also been re-determined, the vapour being obtained by the action of sodium and potassium on cæsium chloride, so that the absorption is somewhat masked. The differences from the values calculated from Hicks' formula all have the same sign. C. H. D.

The Effect of Pressure on Arc Spectra. III. Silver: λ 4000 to λ 4600. IV. Gold. W. GEOFFREY DUFFIELD (*Phil. Trans.*, 1911, *A*, **211**, 33—73).—Photographs of the arc spectra of silver and gold have been taken in air at pressures varying from 1 to 200 atmospheres. For silver, data are recorded for the region $\lambda = 4000$ to $\lambda = 4600$, and in the case of gold from $\lambda = 3550$ to $\lambda = 5100$. The observations indicate that with increase of pressure, the lines broaden, and are displaced towards the red end of the spectrum. At higher pressures the line spectrum disappears, and is replaced by a banded spectrum, which then passes into a continuous spectrum. Details are recorded which show the broadening, displacement, and reversal effects, and the relative intensities of the line and banded spectra at different pressures. In the case of gold, none of the lines were found to undergo reversal. In the experiments with the arc spectrum of gold, it has been found that the electrodes undergo a physical change which causes the melting point to rise. This may be due to a direct influence of pressure on the metal, or to the passage of the arc current through the electrodes, or it may be an annealing effect. H. M. D.

An Extremely Long-Waved Radiation of Mercury Vapour. HEINRICH RUBENS and O. VON BAEYER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 339—345).—It has been found that a mercury arc lamp emits a small proportion of very long-waved rays, the mean length of which is about 300μ (0·3 mm.). These can be isolated by making use of the arrangement of quartz lenses which has been described in a previous paper. To obtain the rays in appreciable quantity, the energy consumption in the arc should be fairly high, and the authors employed a current of 4 amperes at 100 volts, the length of the arc being 8 cm. The long-waved radiation consists of two parts, that of greater mean wave-length being due to the mercury arc, the portion of shorter wave-length to the heated quartz walls. The former can be separated by allowing the rays to pass through a 2 mm. plate of fused quartz, or, better, through a disk of black cardboard.

The absorption of the filtered and unfiltered rays, as well as the long-waved rays emitted by a Welsbach burner, has been measured for a large number of different substances.

The isolation of these long-waved mercury rays corresponds with an extension of the previously known ultra-red spectrum by one and a-half octaves. H. M. D.

The Long-waved Portion of the Spark and Arc Spectra of Copper. MATTHIAS ARETZ (*Zeitsch. wiss. Photochem.*, 1911, 9, 256—269). —Measurements have been made of the wave-lengths and intensities of the lines in the spark spectrum of copper between $\lambda = 470$ and $\lambda = 578$ $\mu\mu$, and in the arc spectrum between λ 500 and λ 700 $\mu\mu$. The photographic records show seventy-one lines, which have not been indicated by previous observers.

There is a marked difference in the structure of two spectra. In passing from the arc to the spark spectrum, the maximum of the curve showing the distribution of the spectral energy is shifted towards the region of smaller wave-lengths. Both spectra exhibit a considerable number of blurred and ill-defined lines. H. M. D.

The Ultra-violet Absorption Spectrum of Aqueous Solutions of Neodymium Chloride. GREGORY P. BAXTER and TRUMAN S. WOODWARD (*J. Amer. Chem. Soc.*, 1911, 33, 270—272).—The ultraviolet absorption bands furnished by an aqueous solution of neodymium chloride have been examined. The neodymium chloride was a highly-purified sample, the only impurity being a trace of the corresponding praseodymium salt.

The wave-lengths of the middle of the various bands are recorded, and the data compared with those of previous observers.

H. M. D.

Ultra-violet and Ultra-red Phosphorescence. W. E. PAULI (*Ann. Physik*, 1911, [iv], 34, 739—779. Compare Abstr., 1909, ii, 777). —The phosphorescent bands emitted by calcium, strontium, barium, and zinc sulphides when admixed with small quantities of various metallic "impurities" have been examined. The methods of preparation of the phosphors, which have been found to give the best phosphorescent effects, are described in detail. In many cases, the temperature and time of heating are of great importance. Strontium phosphors give, in general, the best results when heated for considerable periods at a very high temperature. On the other hand, barium phosphors become less active if subjected to high temperatures in the course of preparation.

When the phosphorescent alkaline earth sulphides are excited by means of Röntgen or cathode rays, the same bands are exhibited as when excited by sparks between zinc electrodes. In some cases, the excitation by means of cathode rays is accompanied by a special momentary phosphorescence effect, which extends a long way into the ultra-violet region.

A calcium silver potassium phosphor has been found which emits only ultra-violet light, the phosphorescent band having a maximum at about 350 $\mu\mu$. On the other hand, a calcium nickel phosphor containing small quantities of calcium fluoride and potassium fluoride has been prepared which emits ultra-red rays, the band having a maximum at about 790 $\mu\mu$.

The influence of temperature between $-180°$ and $200°$ has been examined, and the experimental data are discussed from the point of view of the theory put forward by Lenard. H. M. D.

Piezo-optical Behaviour of Ammonium Chloride. ST. KREUTZ (*Bull. Acad. Soc. Cracow*, 1911, 118—122).—The author has investigated the changes in the optical properties of crystals of ammonium chloride which are brought about by the application of pressure at right angles to the different faces. These show that ammonium chloride behaves similarly to fluor-spar but that ammonium, sodium, and potassium chlorides belong to three of the four possible different types. From a comparison of the effects produced by pressure on the one hand, and by the inclusion of foreign substances on the other, the conclusion is drawn that the double refraction effects which are observed when small quantities of foreign substances are present in cubic crystals, are due to stresses set up by disturbance of the crystalline structure. H. M. D.

Natural and Magnetic Rotatory Polarisation. EUGÈNE DARMOIS (*Ann. Chim. Phys.*, 1911, [viii], **22**, 247—281, 495—589. Compare Abstr., 1908, ii, 747; 1910, i, 52; i, 398).—The object of the investigation was to ascertain whether Wiedemann's law (*Ann. Phys. Chem.*, 1851, **82**, 215) is of general application. The law states that the natural rotatory dispersion for an optically active substance is proportional to its magnetic rotatory dispersion, but according to the present author the fact that this is approximately true for quartz, as Wiedemann found, is merely fortuitous, other substances examined showing marked departures from the law. The experiments were carried out on α- and β-pinene, pinene hydrochloride and hydrobromide, camphene, limonene, *d*- and *l*-camphor, borneol, and *iso*borneol, none of which were found to obey the law. All the compounds showed considerable absorption in the ultra-violet, and in the case of β-pinene and camphor, abnormal natural dispersion, whilst the magnetic dispersion remained normal; in this region of the spectrum, also, Wiedemann's law appears to have no significance whatever.

The purity of the substances under observation was established by taking advantage of the principle that for a mixture of two optical antipodes the rotation is different from that of either constituent, whilst the dispersion remains the same. The application of this to the case of turpentine oils has already been described in part. The French, German, and American oils each contain only two hydrocarbons, β-pinene, identical with Wallach's nopinene, and an α-pinene having a different rotatory power in each oil. *d*-α-Pinene was obtained by the fractionation of Aleppo oil (Vèzes, Abstr., 1909, i, 818); it has $[\alpha]_D^{15}$ $+48{\cdot}4°$, D^{15} 0·8625, n_D^{15} 1·468. Pure β-pinene prepared by repeated fractionation of the French oil has b. p. 164°, $[\alpha]_D$ $-22{\cdot}1°$, D^{15} 0·875, n_D^{15} 1·478.

Application of the method to synthetic borneol (from pinene hydrobromide) shows that the low rotatory power is due to admixture with *l-iso*borneol. W. O. W.

Differentiation by Chemical Development of Latent Images Obtained by means of Silver Chloride and Bromide Emulsions. AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWETZ (*Compt. rend.*, 1911, **152**, 766—768. Compare Abstr., 1910, ii, 916).—A solution containing 1% of sodium quinonesulphonate and 5% of anhydrous sodium sulphite has the property of rapidly developing the latent image in silver bromide emulsions, but is without action on the silver chloride images. This differential action does not occur unless the sulphite is present. Solutions of pyrogallol, quinol, or catechol containing sodium sulphite or sodium hydrogen sulphite act somewhat in the same way, but the difference in their reducing power towards the two halides is less distinct.

W. O. W.

Condensation Nuclei Produced by the Action of Light on Iodine Vapour. GWILYM OWEN and HAROLD PEALING (*Phil. Mag.*, 1911, [vi], **21**, 465—479).—It has been shown previously (Abstr., 1907, ii, 843; 1908, ii, 565) that the gas obtained by the volatilisation of solid carbon dioxide contains large numbers of nuclei which act as centres for the condensation of super-saturated water vapour. Similar experiments with camphor, naphthalene, benzoic acid, and iodine show that such nuclei are not formed in the case of these substances. If, however, moist air (or oxygen) containing iodine vapour is acted on by light, condensation nuclei are produced in large numbers. These nuclei are very unstable, and disappear in a few seconds in the dark. The nuclei are not electrically charged, and are not produced when the expansion apparatus contains hydrogen, carbon dioxide, or coal gas in place of air (or oxygen). Further, they are not formed if the water in the apparatus is replaced by ethyl alcohol.

Experiments, in which the moist mixture of air and iodine vapour was illuminated for different short intervals of time, indicate that the nuclei increase in size under the influence of the light, and attain a maximum size in less than one second. With different sources of light (arc lamp, fish-tail burner, Nernst light screened by red glass, and diffused daylight) the same results were obtained.

After the iodine has been allowed to remain in the apparatus for some days, the production of nuclei no longer takes place; the phenomenon is again observed, however, if the glass walls of the apparatus are washed with water.

If air containing iodine vapour is introduced into the expansion apparatus through a plug of glass wool, the number of nuclei produced is much greater than when iodine is in direct contact with the cloud-chamber. This action becomes less marked as the amount of air-iodine vapour mixture thus introduced increases. These observations indicate that the surface of the glass modifies the process of formation of the condensation nuclei, but a satisfactory explanation has not yet been obtained. H. M. D.

Measurement of the Range of the α-Particles of Uranium by the Scintillation Method. A. Foch (*Le Radium*, 1911, 8, 101—104).—A spherical glass flask of 97 mm. diameter, was covered internally with a thin layer of uranium acetate by evaporating in it an ethereal solution of the salt. At the centre a screen of zinc sulphide was placed, which was viewed by a lens outside the flask, and the pressure of the air was varied. From the curve connecting the number of scintillations observed per minute and the pressure of air, it was deduced that the range of the α-particles of uranium is 2·68 cm. of air at 760 mm. pressure. The curve was not a linear function of pressure, but showed at the middle of the range a sharp change of direction, as if the radiation consisted of two groups of α-particles, the second group having less than half the range given. Photographs taken by inclining a photographic plate backing a zinc sulphide screen to a surface of uranium oxide also show a decided variation of density at about half the range of the α-particles.
F. S.

The Ionisation of Different Gases by the α-Particles from Polonium and the Relative Amounts of Energy Required to Produce an Ion. T. Smith Taylor (*Phil. Mag.*, 1911, [vi], 21, 571—579; *Amer. J. Sci.*, 1911, [iv], 31, 249—256).—The Bragg ionisation curves for the α-rays of polonium have been taken in various gases and compared with the formula given by Geiger: $I = c/(r - x)^{1/3}$, where x is the distance of the source of rays, r a constant representing the average range of the α-rays, and c a constant. On the assumption that the ionisation produced at any point is proportional to the consumption of kinetic energy of the α-particle, c depends on the relative energy required to produce an ion in the different gases. The theoretical and experimental curves are in good agreement. The relative energy required to produce an ion varies from 1·01 for hydrogen to 0·73 for carbon disulphide (air = 1·00), the heavier and more complex gases and vapours being more readily ionised than the lighter ones. The assumption that the ionisation produced by an α-particle is proportional to the energy consumed is fully confirmed.
F. S.

The Radiations of the Alkali Metals. Émile Henriot (*Compt. rend.*, 1911, 152, 851—853).—To test the view that cæsium may be emitting β-radiations of too low velocity to ionise gases, the charge transported by the salts of potassium, rubidium, and cæsium in a vacuum was investigated. For rubidium and potassium salts the existence of a negative current in a vacuum, due to the expulsion of β-radiations, was readily established, the current being for rubidium about five times as great as for potassium. But with cæsium salts no certain current could be observed. This phenomenon is to be distinguished from the photo-electric effects observed with the alkali metals themselves, even in the dark (J. J. Thomson). Some experiments on this effect showed that the current became the more and more feeble as greater precautions are taken, and is not then within the range of detection by the electrometer. The only way to follow it beyond this range is by an electroscope, but this involves some illumination of the leaf during readings. The experiments support the views of Dunoyer that the effects are to be ascribed to disturbing influences. F. S.

Secondary γ-Rays Produced by β-Rays. J. A. GRAY (*Proc. Roy. Soc.*, 1911, *A*, **85**, 131—139).—Previous attempts to detect the generation of γ-rays at the point of impact of the β-rays on metals, using the rays of radium, have been unsuccessful, but with the β-rays of radium-*E* a clear effect of this kind has been put into evidence, the γ-radiation normally accompanying the β-radiation of radium-*E* being very feeble. The radium-*E* preparation consisted of lead sulphate which had been separated from an old radium solution to which lead had been added in order to remove the radium-*D*. It was free from radium. The β-rays were arranged to fall on a radiator, so arranged that any γ-rays generated in the radiator would affect a γ-ray electroscope. A clear effect due to the radiator was observed, which could be prevented by cutting off the β-rays by a few sheets of paper. The production of γ-rays increased with the atomic weight of the radiator from graphite to lead, and was roughly proportional to it. In other experiments the β-rays were deflected by a magnet on to the radiator, and the production of both incident and emergent γ-rays from the radiator subjected to β-rays was observed. In the experiments with a layer of active material between 0·3 and 0·4 mm. thick, consisting chiefly of lead sulphate, the secondary γ-rays were equal to about one-fourth of the γ-rays from the active material itself. Absorption measurement showed a much higher absorption of the secondary γ-rays in materials of high atomic weight than in those of low atomic weight, the new radiation resembling *X*-rays in this respect. The γ-radiation of radium-*E* may be entirely of secondary origin. F. S.

Effect of Temperature on the Ionisation of a Gas. J. H. CLO (*Le Radium*, 1911, **8**, 108—112).—An iron vessel heated by an electric current and containing air or hydrogen, the pressure of which was measured and used to determine the temperature, was subjected to the γ-rays of radium. The ionisation was measured by an electrometer by the constant deflection method. The ionisation was found to be independent of the temperature within 0·2% up to 600° in air and up to 430° in hydrogen. A variation in the mean kinetic energy of the molecule from 1 to 2 does not affect the stability of the atom sufficiently to alter its ionisation by one-tenth per cent. F. S.

The Charges on Ions in Gases and Some Effects that Influence the Motion of Negative Ions. JOHN S. TOWNSEND (*Proc. Roy. Soc.*, 1911, *A*, **85**, 25—29).—The principle of the experiments was to allow a stream of ions, produced by secondary Rontgen rays in gases, to pass through a circular aperture in a thin plate.

After traversing an electric field of known strength for a certain distance, the ions are received: (1) on a flat disk the size of the aperture, and (2) on a flat ring surrounding the disk, the ratio of the quantities of ions in (1) and (2) being found. If the ions follow the ordinary laws of diffusion, this ratio depends only on the product of the number of ions (N), the charge on the ion (e), and the electric force (X), and is independent of the pressure of the gas. Investigations with hydrogen, oxygen, and carbon dioxide confirmed the results formerly obtained with air. The value of the product Ne for negative ions under a variety of circumstances is always the same as in electrolysis of liquids, namely, $1{\cdot}22 \times 10^{10}$. This is also true for the positive ions when the secondary X-rays originate at a bright metallic surface, but high values are obtained when the surface is coated with vaselin, showing that some of the ions produced by the more penetrating rays carry double charges.

In perfectly dry gases at low pressure the ratio, before referred to, is no longer independent of pressure, but the determinations of Ne may be made with higher pressures and low electric force. The negative ions assume the corpuscular state in dry gases at low pressure. The mass of the ion can be calculated from its diffusion coefficient. In ordinary circumstances the mass of the negative ion in air is eleven times the mass of the molecule of carbon dioxide. When X is 0·9 volt per cm., and the pressure is 10 mm., the mass of the negative ion in perfectly dried air is only one forty-third of the mass of the molecule of carbon dioxide. F. S.

The Mobility of Ions Produced in Air by Sulphate of Quinine in Process of Hydration. Maurice de Broglie and L. Brizard (*Compt. rend.*, 1911, **152**, 855—856).—Owing to the rapid recombination of the ions produced by quinine sulphate in process of hydration, the ions are localised in a very thin layer at the surface of the salt. On applying an electric field, the ions of the corresponding sign are readily extracted, but a current of air is then not able to carry them away. The separation has been effected by placing the active salt at the surface of the small central electrode of a very large cylindrical condenser, where the electric field is intense and extracts the ions from the layer in which they are produced. At the sides of the condenser the field is feeble, and a transverse current of air partly removes the ions. Concordant results with many specimens of quinine sulphate have shown that the mean velocity for the two ions is 1 cm. per second in a field of 1 volt per cm.

F. S.

Mobility of the Positive Ions Produced in the Oxidation of Copper. Adolfo Campetti (*Atti R. Accad. Sci. Torino*, 1911, **46**, 242—254).—The mobility of the positive ions produced during the oxidation of copper in dry air at 500° is found to be about 0·0016 cm. per second, and this indicates that they are large ions, comparable with those produced in the slow oxidation of phosphorus. It is thus established that ions of considerable mass may be produced and continue to exist even at comparatively high temperatures.

R. V. S.

Chemical Actions and Ionisation by Splashing. LÉON BLOCH (*Ann. Chim. Phys.*, 1911, [viii], **22**, 370—417, 441—495. Compare Abstr., 1903, ii, 206; 1904, ii, 117; 1905, ii, 72; 1908, ii, 1032; 1909, ii, 395, 781; 1910, ii, 32, 381, 480; this vol., ii, 176).—A résumé of work previously published, with further experimental details and diagrams of the apparatus employed. The phosphorescence of Delépine's sulphur compounds (Abstr., 1910, i, 295, 545) is due to oxidation unaccompanied by ionisation.

W. O. W.

Homogeneous Röntgen Radiation from Vapours. J. CROSBY CHAPMAN (*Phil. Mag.*, 1911, [vi], **21**, 446—454).—The value of λ/ρ, the absorption coefficient divided by the density, in aluminium of the homogeneous secondary X-radiation from bromine, has been determined for vapour of ethyl bromide, solid sodium bromide, and bromine hydrate, and found to be 16·3, independent of the nature of the compound. The radiation is absorbed exponentially, and the value lies on the smooth curve connecting atomic weights with the values of λ/ρ. The same experiments, with vapour of ethyl iodide and solid iodine, gave the value 2·3 for λ/ρ. The amount of secondary radiation from ethyl bromide when hydrogen and carbon dioxide respectively were used to convey the vapour was nearly the same. This disproves the theory that the secondary X-radiations result from the bombardment of the atoms by ejected corpuscles; for carbon dioxide would absorb the corpuscles far more than hydrogen, so that in the latter gas more secondary X-radiation should be generated.

F. S.

Cathode Luminescence in Minerals. ALFREDO POCHINETTO (*Nuovo Cim.*, 1911, [vi], i, 21—64. Compare Abstr., 1910, ii, 89).—The behaviour of artificial minerals under the cathode rays is very closely analogous to that of the natural minerals; the differences are not greater than those observed between natural minerals from different sources. The most notable difference observed is that only the synthetic specimens of sapphire show dichroism.

Well-crystallised specimens of calcite from different sources give the same cathode luminescence with the same characteristics, whilst aragonite gives a different luminescence. The luminescence of calcite has been ascribed to the presence of traces of manganese, and the question is discussed why aragonite, which also contains manganese, gives a different result.

It has been stated by previous observers that the nature of the spectrum of the cathode luminescence is independent of the velocity of the exciting rays, but this is not generally true. It applies to natural and synthetic willemite, but not to spodumene or distene.

Twin crystals show in general a luminescence much less polarised than do simple crystals of the same substance.

The phenomena of dichroism in cathode luminescence are due to the different degree of polarisation of the radiations constituting the spectrum of the light emitted, and are undoubtedly due to the presence of impurities in the minerals. The phenomena of double luminescence, previously met with only in diopside, have now been observed under suitable conditions in spodumene, kunzite, and distene.

The duration of the residual luminescence is the smaller the shorter the excitation, and, in general, the extinction of the luminous vibrations is most rapid for radiations corresponding with short waves. G. S.

The Heat Generated by Radioactive Substances. WILLIAM DUANE (*Amer. J. Sci.*, 1911, **31**, 257—268. Compare Abstr., 1909, ii, 534, 637; 1910, ii, 816).—This paper consists for the most part of a connected account of researches already published, but contains details of the present method of employing the differential vapour calorimeter designed by the author. The radioactive substance is placed inside of a tube, half of which is iron and the other half nickel, the surfaces between the metals being parallel to the axis of the tube. A current is passed through this tube to cool the junction and compensate for the heat developed by the radioactive substance inside the tube, so that the calorimeter is used as a null instrument, and effects varying from 0·001 to 2 gram-calories per hour can be measured without any alteration of the arrangement. The heat generated by a polonium preparation was found to decrease with time at a rate nearly the same as its known rate of change, and was equal to a quantity of radium producing the same ionisation as the polonium. F. S.

The Heat Liberated During the Absorption of Electrons by Different Metals. OWEN W. RICHARDSON and H. L. COOKE (*Phil. Mag.*, 1911, [vi], **21**, 404—410).—The conclusion, before arrived at for platinum, that when slow moving electrons are received by the metal, part of the heat developed was independent of the kinetic energy of the electrons, has been confirmed by experiments with gold, nickel, copper, silver, palladium, aluminium, phosphor-bronze, and iron. This heat, which is considered to be the thermal equivalent of the difference of potential energy of the electrons inside and outside the metal, corresponds with from 4·5 to 7·5 volts. Four of the mean values found agree with a mean value 7·11 volts, and the other five with a mean value 5·35, the value being influenced by the nature and state of the thermionic emitter, rather than by the nature of the receiving metal. The gas pressure exerts no influence provided it is low. The thermionic emission from an osmium filament becomes unstable at a certain temperature. Two ranges of stability, in which the normal laws are followed, exist, the one at low and the other at high temperature. F. S.

Phenomena which Accompany the Transport of the Active Deposit. E. M. WELLISCH (*Ber. Deut. physikal. Ges.*, 1911, **13**, 159—171).—An attempt is made to explain the results of different observers who have investigated the behaviour of the particles of the active deposits of radium and thorium in an electrical field and in different gaseous media. It is assumed that atomic residues are uncharged, except when associated with a gaseous ion. During the period of this association, the atomic residues will move under the influence of an electric field, and the fact that the active deposit collects almost entirely on the cathode, indicates that the atomic residues have a very great affinity for a positive charge. In its motion through the electric field, a particular ion will be successively associated with different atomic residues, but under given conditions its association period will be represented by a definite fraction of its total period of existence.

This theory accords with the fact that the variation of the quantity of the active deposit, which collects on the cathode, with the strength of the electric field is very closely similar to the variation of the current with the field strength. An explanation of the observations of Rutherford and others relative to the dependence of the quantity of the active deposit collected at the cathode on the pressure of the surrounding gaseous medium, is also afforded in terms of the author's theory. H. M. D.

Separation of Ionium and Actinium from Certain Residues, and on the Production of Helium by Ionium. BERTRAM B. BOLTWOOD (*Proc. Roy. Soc.*. 1911, *A*, **85**, 77—81; *Le Radium*, 1911, **8**, 104—106).—A description is given of the technical treatment of certain "actinium residues" derived from the radiferous residues of Joachimsthal pitchblende. The solution in hydrochloric acid, after treatment with hydrogen sulphide, was precipitated with ammonia. The hydroxides obtained were dissolved and precipitated with oxalic acid in neutral solution. The precipitate, after ignition and solution in hydrochloric acid, was precipitated with hydrogen peroxide.

The product weighed 160 grams, the initial weight of material being 21·2 kilos. It contained 20% of the total initial activity, and consisted of rare earths and calcium. The thorium contained in it, separated by the usual processes, weighed as oxide 1·8 grams. It contained the ionium, and had an activity 3000 times that of uranium oxide. From a measurement of the number of α-particles emitted per second, the amount of ionium was deduced to be that in equilibrium with 5·3 mg. of radium.

Very little actinium was separated with the hydrogen peroxide precipitate. Some was found in the mother liquor from the first ammonia precipitation. The ammonium salts were separated by crystallisation and boiling with hydrochloric and nitric acids. From the resulting solution ammonia precipitated about 10 grams of material, containing an amount of actinium estimated to be in equilibrium with 30 mg. of radium. Its activity increased rapidly for four months, when it was 20,000 times that of uranium oxide, and actinium emanation was freely generated.

The thorium oxide preparation, containing ionium, sealed up for 125 days in a Jena glass tube generated 0·031 cu. mm. of helium. The theoretical amount, calculated from the rate of emission of α-particles, is 0·0595, and the difference may be due to the retention of the helium by the solid, even after ignition in a Jena glass tube.

F. S.

Present-day Problems Concerning Radium. WLADIMIR I. VERNADSKY (*Bull. Acad. Sci. St. Pétersbourg*, 1911, 61—72).—In this lecture, the author traces the discovery of the radioactive elements and the formulation of the theory of radioactivity, and discusses the relation of radiation to the energetic theory of matter. T. H. P.

The Radium Content of Some Uranium Earths. WILHELM MARCKWALD and ALEXANDER S. RUSSELL (*Ber.*, 1911, **44**, 771—775).—The method of estimating the radium was to dissolve the minerals in concentrated sulphuric acid, with addition of a crystal of potassium nitrate as oxidising agent, if necessary, to liberate the emanation, which was measured; barium sulphate and radium sulphate being easily soluble in sulphuric acid, the emanation is completely expelled. The ratio of radium to uranium, taken for Joachimsthal pitchblende as 100, was 98·1 for thorianite (Java) and 101·5 for African pitchblende, the difference being within the experimental error. For autunites (Autun, France, and Guarda, Portugal), the ratio varied from 20·7 to 68·0. In lieu of the view advanced by Soddy, that these minerals are of very recent formation, an alternative explanation is favoured. The mineral being of loose formation, as compared with the dense oxides of uranium, the helium may escape, and the lead and radium may be removed by the action of percolating water. Ionium was separated from the minerals by addition of cerium and precipitation with hydrofluoric acid, and estimated by means of its α-radiation. For pitchblendes the ratio between ionium and radium was constant, but for autunites it was less, and varied from 76 to 93% of the former ratio. This is in favour of the percolation hypothesis, as if the minerals were of recent formation they should be nearly free from ionium. For two specimens of carnotite the ionium ratio was 92 and 72% of that in pitchblende. For rutherfordin (UO_3,CO_2), the alteration product of African pitchblende, the radium ratio was 85% of the equilibrium ratio for the surface layers, the full amount being present in the interior of the crystal. F. S.

The Radioactivity of the Thermal Waters of the Yellowstone National Park. RICHARD B. MOORE and HERMAN SCHLUNDT (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. X., 189—190).—The activity of the thermal waters of Yellowstone Park is of the same order as that of European springs, and shows considerable variations. The radioactivity is almost entirely due to dissolved gases. Most of the waters examined contain only radium emanation, but sixteen out of eighty-two sources yield also thorium emanation. The deposits of travertine at Mammoth Hot Springs contain about 8×10^{-12} gram of radium per gram, or two and a-half times that of the rock from which they are derived, and five times that of the general igneous rock of the Park. Less uranium is contained in these deposits than the radium content requires. C. H. D.

The Radioactivity of the Spring Sediments of Teplitz-Schönauer. JOHANN ŠTĚRBA (*Jahrb. Radioaktiv. Elektronik.*, 1911, **8**, 23—34).—The sediments of the various thermal springs of Teplitz-Schönauer, and the sediments from the drinking-water reservoirs, are all radioactive in the inverse proportion to the activity of the waters themselves. From the nature of the emanation, the activity is due to radium in some cases, thorium or radiothorium in others, and in some cases to a mixture of both.

A chemical examination revealed the presence of the same elements, but uranium could not be detected. F. S.

Conduction of Electricity in Saturated Alkali Metal Vapour. CHRISTIAN FUCHTBAUER (*Physikal. Zeitsch.*, 1911, **12**, 225—228. Compare Abstr., 1909, ii, 537).—By means of an improved form of apparatus, the author has investigated the electric conductivity of saturated cæsium vapour at temperatures between 155° and 205° in presence of helium. This gas was introduced with the object of increasing the resistance friction of the ions. For the above variations of temperature the conductivity increases about fifteen times. For small potential differences the current which passes through the vapour is approximately that required by Ohm's law, but for greater potentials the current increases much more rapidly than the applied voltage. The conduction exhibits a pronounced unipolarity, which is reversed when the applied potential difference exceeds a certain value.

In explanation of the observations, it is supposed that the ions are produced in the neighbourhood of the electrodes. Whether, in addition, the mass of the vapour is ionised to a small extent, has not yet been determined. H. M. D.

Electrical and Mechanical Properties of Alloys of the Noble Metals. II. WILHELM GEIBEL (*Zeitsch. anorg. Chem.*, 1911, **70**, 240—254. Compare this vol. ii, 10).—The alloys of palladium and silver behave as a continuous series of solid solutions, with a minimum conductivity and thermo-electric power and a maximum tensile strength at 40 atomic % of silver. The temperature-coefficient of the conductivity of this alloy is exceedingly low. Alloys of platinum with palladium behave similarly, but the thermo-electric power is throughout positive against palladium, and with the exception of those containing more than 90 atomic % Pd, also against platinum. The alloys of platinum and iridium have only been investigated up to 35 atomic % Ir, alloys richer in iridium being too brittle to be drawn into wire. The form of the curves obtained indicates that the alloys consist of solid solutions. The thermo-electric power, which is positive against platinum, reaches a constant maximum value at 20 atomic % Ir. Annealing these alloys increases the strength of the alloys richer in iridium, a temperature of 750° giving the maximum effect, whilst at higher temperatures the strength diminishes. The ductility is increased by annealing.

Alloys of platinum and gold can only be satisfactorily drawn into wire when the platinum does not exceed 20%. Solid solutions are present. The thermo-electric power is negative towards platinum, and becomes greater on repeated heating, a constant value not being attained even after heating for two hours at 900°.

Platinum–silver alloys can only be drawn into wire when the proportion of platinum is low. The strength increases with the temperature of annealing up to 400°, and then rapidly falls. The thermo-electric power varies with repeated heating, but the differences are smaller than in platinum–gold alloys. C. H. D.

Conductivity and Dissociation of Sodium Hyposulphite and Hyposulphurous Acid in Comparison with Analogous Sulphur–Oxygen Compounds. Dissociation of Ternary Electrolytes. KARL JELLINEK (*Zeitsch. physikal. Chem.*, 1911, **76**, 257—354).—The electrical conductivity of aqueous solutions of sodium hyposulphite, $Na_2S_2O_4$, was measured at 0°, 18°, and 25°, and the results compared with those for other oxygen–sulphur salts. All these salts dissociate in stages. A full account of the present knowledge of the dissociation of ternary electrolytes is given, and on this basis the degree of dissociation of the sodium salts of the acids in question in the two stages is calculated. The mobility of the S_2O_4'' ion is 69 at 25°.

The conductivity curve of the very unstable hyposulphurous acid was obtained by adding to a solution of sodium hyposulphite an equivalent of hydrochloric acid and subtracting from the observed conductivity that due to the sodium chloride. The constant, k_1, for first stage of the dissociation is at least 0·45 at 25° (the same as that for sulphuric acid); k_2, the constant for the second stage of the dissociation, is 0·0035 at the same temperature. These results are compared with those for the other sulphur oxyacids, and in this connexion some fresh measurements and calculations have been made. The value of k_1 for sulphurous acid is about 0·017, and k_2 is 0·000005. The value of k_2 for thiosulphuric acid is 0·0104. The mobility of the HSO_3' ion is 52 at 25°, as determined from conductivity measurements with solutions of sodium hydrogen sulphite. G. S.

Dissociation of Electrolytes in Non-aqueous Solvents as Determined by the Conductivity and Boiling-point Methods. HENRY R. KREIDER and HARRY C. JONES (*Amer. Chem. J.*, 1911, **45**, 282—324).—A brief review is given of the investigations of Jones and his co-workers on conductivity and viscosity in mixed solvents (Abstr., 1903, ii, 55, 634; 1905, ii, 8, 73; 1906, ii, 66, 737, 827; 1907, ii, 438; 1908, ii, 259, 260; 1909, ii, 539, 717, 957).

The conductivity at 0° and 25° of potassium iodide, ammonium bromide, potassium thiocyanate, lithium nitrate, sodium iodide, copper chloride, calcium nitrate, and cobalt chloride has been determined in methyl and ethyl alcohols at very high dilutions, and also in mixtures of these alcohols with water. In many cases, the values of μ_{∞} were found, which generally occurred at concentrations between $V = 3200$ and $V = 51,200$. A constant ratio was found between the values of μ_{∞} for lithium nitrate, sodium iodide, and ammonium bromide in methyl and ethyl alcohols, and the corresponding value for cobalt chloride was calculated. The results show that there is one constant for binary electrolytes and another for ternary electrolytes, and that there is probably a definite relation between these two constants.

Minima were found in most of the curves for mixed solvents.

The dissociation values obtained by the conductivity method are higher than those obtained by the b.-p. method in both methyl and ethyl alcohols. This may be due to polymerisation of the non-dissociated molecules in the solvent. The results obtained by the b.-p. method would thus be too low, since this method takes both the molecules and ions into account, whilst the conductivity method deals with the ions only. E. G.

The Photo-electric Effects of Colloidal Alkali Metals. Robert Pohl and P. Pringsheim (*Ber. Deut. physikal. Ges.*, 1911, **13**, 219—223. Compare Elster and Geitel, Abstr., 1910, ii, 379, 1031).—The relatively high photo-electric sensitiveness of the alkali metals in the colloidal condition is probably not due entirely to increased absorption of light, but is influenced by the relationship between the penetrating power of the electrons which are set free and the form of the boundary surface of the metal. If the diameter of a colloidal metal particle is less than the range of the electrons, the whole of these will escape from the surface. In the case of larger particles a certain proportion of the electrons will, however, be unable to reach the exterior.

Observations of the photo-electric effect on potassium and sodium in the ordinary and colloidal conditions have been made, which show that the colloidal metals are relatively much more photosensitive for long-waved rays. The photo-electric currents obtained for the exciting rays $\lambda = 254$ and 546 gave a mean ratio of 27 and 1·9 for ordinary and colloidal potassium respectively, and a mean ratio of 173 and 18·5 for ordinary and colloidal sodium. H. M. D.

The Law of Babo and the Electron Theory of Metallic Mixed Crystals. August L. Bernoulli (*Ber. Deut. physikal. Ges.*, 1911, **13**, 213—218).—It is shown that Schenck's formula (compare Abstr., 1910, ii, 1030) for the thermo-electric difference of potential between a metal and a solid solution containing a second metal can be obtained quite readily by application of the equation connecting the relative lowering of the vapour pressure with the molar ratio of solute and solvent if it is assumed that the same relationship holds between the pressure of the electrons in the pure metal and its solid solutions. H. M. D.

Measurements of the [Electric] Charge on Fog Particles. Karl Przibram (*Physikal. Zeitsch.*, 1911, **12**, 260—261)—The relatively large number of fog particles which, according to previous measurements (*ibid.*, 62), appear to carry electric charges which differ from unity or from multiples of the unit charge, has been found to be largely due to the form of the apparatus used in the investigation.

With an improved form of condensor, new determinations have been made of the charges carried by particles of phosphorus and sulphur. The calculated mean charges, corrected by Cunningham's method, are respectively $6{\cdot}25$ and $6{\cdot}23 \times 10^{-10}$. H. M. D.

Rapid Measurement of the Concentration of the Hydrogen Ions in Liquids. Wilhelm E. Ringer (*Chem. Weekblad,* 1911, **8**, 293—295. Compare Hasselbalch, this vol., ii, 182).—By experimental determination of the concentration of the hydrogen ions in a slightly acid solution of sodium chloride, phosphoric acid, and sodium hydroxide, the author finds that Hasselbalch's rapid method yields satisfactory results. A. J. W.

Employment of an Electrode of the Third Type to Measure the Potential of the Thallium Ion. JAMES F. SPENCER (*Zeitsch. physikal Chem.*, 1911, **76**, 360—366).—Luther (compare Abstr., 1899, ii, 5) has described so-called electrodes of the third type by means of which the concentration of ions of metals which decompose water can be measured. The author has made use of such an electrode to measure the concentration of thallium ions. In this case it consists of mercury in contact with a solution of a thallium salt saturated with mercurous and thallium iodides. It is shown that the equation, applicable to all electrodes of the third kind, is of the form :

$$\epsilon = EP - \frac{RT}{nF}\log_e(c+i),$$

where ϵ is the observed *E.M.F.*, *E.P.* the hypothetical potential for *N*/1-thallium ion, *c* the ion concentration of the solution to be measured, *i* the concentration of the common ion formed by the depolariser, and the other symbols have the usual significance. Measurements were made with solutions of thallium nitrate, carbonate chloride and sulphate. As a mean of the four series, which are in good agreement, the values $\epsilon_c = +0·5355$ or $\epsilon_h = +0·2585$ are obtained for the hypothetical *N*/1-thallium ion solution. G. S.

The Potential of the Chlorine Electrode. GILBERT N. LEWIS and FRANK F. RUPERT (*J. Amer. Chem. Soc.*, 1911, **33**, 299—307).—Measurements have been made of the potential of the chlorine electrode at pressures ranging from 0·2 to 0·003 atmosphere, air being used as the inert diluting gas. At these low pressures the complications which result from hydrolysis of chlorine in the aqueous solution are eliminated. By arranging the chlorine electrode in series with a calomel electrode in which the potassium chloride solution was replaced by a solution of hydrochloric acid, errors resulting from changes in the potential difference at the liquid surfaces were eliminated, and it was found that accurately reproducible values could be obtained. The separate values of the potential for chlorine at atmospheric pressure, calculated from the observations at the different partial pressures, agree very well with one another, the average deviation from the mean being less than 0·0002 volt. The *E.M.F.* for chlorine at atmospheric pressure in contact with a solution containing chlorine ions in normal concentration when placed in series with the normal calomel electrode is − 1·0795 volts, which differs appreciably from the values given by previous observers. H. M. D.

Thermodynamic Calculation of Electromotive Forces. II. FRANZ HALLA (*Zeitsch. Elektrochem.*, 1911, **17**, 179—182. Compare Abstr., 1908, ii, 755).—The *E.M.F.*'s of the galvanic elements, Ag | AgBr or AgI (saturated solution), $PbBr_2$ or PbI_2 (saturated solution) | Pb, are measured at different temperatures. Four elements of each kind were examined; the agreement between them was exceedingly close in the case of the bromides, but with the iodides differences of 7 or 8 millivolts were observed, and the results are regarded as uncertain. The bromide element gave 0·3708 volt at 0°, 0 3611 volt at 12°, 0·3566 volt at 19°, 0·3521 volt at 27°, 0·3410 volt at 45°, 0·3362 volt at 53°, 0·3320 volt at 59°, and 0·3237 volt at 71°. The heat of the reaction calculated from the individual measurements lies between 12,519 and 12,583 cals., whilst Thomsen found 12,275 cals. The iodide element was measured at seven temperatures; its *E.M.F.* decreases from 0·2338 volt at − 71° to 0·1965 volt at + 62°. The calculation by Nernst's theorem cannot be carried out until the specific heats of the salts have been determined at different temperatures. T. E.

The Influence of Electrolytes on the Maximum Voltage of Electrolytic Valve Action. GÜNTHER SCHULZE (*Ann. Physik*, 1911, [iv], **34**, 657—710. Compare Abstr., 1909, ii, 371).—Measurements of the potential of electrolytic valve action show that, with a constant current, the potential line curves exhibit pronounced breaks. The first break in the curve corresponds with the commencement of spark discharge, and from this point onwards, the potential rises less rapidly than during the preceding interval. The second break corresponds with a new type of spark discharge, and when this sets in, the potential attains a maximum value.

The influence of a large number of different electrolytes on the valve potential has been investigated in the case of tantalum. From these experiments it is found that the maximum voltage is dependent on the concentration of the free anions. Complex anions containing a metal atom exhibit a characteristic maximum potential, which is determined by the nature of the metallic constituent. In general, the maximum potential for such anions is much smaller than for the non-metallic anions.

When the maximum valve potentials for such metallic anions are compared, the metals can be arranged in a series, the first member being palladium, with a very small (20 volts), and the last member, aluminium, with a very large, valve potential (660 volts). For non-metallic anions the maximum valve potentials vary from 440 to 500 volts.

The valve action is independent of the cations in the solutions, but the metals, which lower the valve potential as components of anions, are also effective when present as components of undissociated molecules.

Experiments were also made with anodes of aluminium, antimony, and bismuth. These show a true valve effect when they are not dissolved by the electrolytic solution, and the maximum potentials are very nearly the same as in the case of tantalum. In dilute sulphuric acid, aluminium exhibits an apparent valve potential of 20 volts, but in fuming sulphuric acid the real valve effect is observed, and the maximum potential amounts to 425 volts. H. M. D.

Electrolytic Potential of Hyposulphite Reactions. KARL JELLINEK (*Zeitsch. Elektrochem.*, 1911, **17**, 157—176).—The *E.M.F.*'s of combinations of a hydrogen electrode and a platinised platinum electrode immersed in well stirred solutions containing sodium hyposulphite, sulphite, and hydrogen sulphite are first measured. The *E.M.F.*'s are hardly affected by polarisation, and are quite reproducible. The concentrations of the ions in the solutions are calculated by means of the author's measurements of the conductivity (this vol., ii, 362), and it is shown that the *E.M.F.*'s measured (after correction for the small potential differences between the solutions in the cell) are well represented by the equation: $\pi = -0{\cdot}245 + 0{\cdot}029 \log[S_2O_4''][SO_3'']^2/[HSO_3']^4$ at 20° for the $0{\cdot}1N$-hydrogen electrode. This indicates that the electromotive reaction is $S_2O_4'' + 2SO_3'' + 2H_2O + 2F \rightleftarrows 4HSO_3'$. In order to calculate the potential of the reaction $S_2O_4'' + 2H_2O + 2F = 2H^{\cdot} + 2HSO_3'$, the dissociation constant of the reaction $HSO_3' \rightleftarrows H^{\cdot} + SO_3''$ is required. The author's determinations (*loc. cit.*) gave approximately

$$K = [H^{\cdot}][SO_3'']/[HSO_3'] = 5 \times 10^{-6};$$

introducing this into the above equation, after recalculating it for the N-hydrogen electrode, gives $\pi = -0{\cdot}009 - 0{\cdot}029 \log[S_2O_4'']/[H^{\cdot}]^2[HSO_5']^2$ at 20°.

From this it is calculated that a solution containing hyposulphite and hydrogen sulphite ions in normal concentration should be in equilibrium with gaseous hydrogen at two atmospheres pressure, and therefore that the reducing power of such a solution is very nearly the same as that of gaseous hydrogen.

The *E.M.F.* of the combination measured above increases by 2·27 millivolts per degree rise of temperature. From these data the heat of the reaction is readily calculated; it is $S_2O_4'' + 2SO_3'' + 2H_2O + 2H^{\cdot} = H_2 + 4HSO_3' - 13920$ cals. Subtracting the known value, $HSO_3' = H^{\cdot} + SO_3'' - 700$ cals., gives $S_2O_4'' + 2H_2O = H_2 + 2HSO_3' - 15{,}300$ cals. The heat of formation of hyposulphurous acid is also calculated with the help of Thomsen's data, $2S + 3O + H_2O = H_2S_2O_4 + 105{,}000$ cals. Consideration of the free energy of the reaction between hyposulphites and water leads to the conclusion that they become much less stable as the temperature rises, a rise of 10° increasing the equilibrium pressure of hydrogen two and a-half times.

In alkaline solutions of hyposulphite and sulphite a fairly definite potential is established at a platinum electrode, but the author could not discover the nature of the reaction on which it depends. In solutions of hyposulphite and thiosulphate, or of thiosulphate and sulphite, no definite potential could be observed. The potentials measured were unaffected by the concentration of the thiosulphate.

T. E.

Transference Experiments with Mixtures of Potassium Chloride and Sulphate in Aqueous Solution. George M. J. Mackay (*J. Amer. Chem. Soc.*, 1911, 33, 308—319).—It has been shown by different observers that, in a solution containing two salts with a common ion, each salt has a degree of ionisation equal to that which it has when present alone in a solution in which its ions have a concentration equivalent to that of the common ion in the mixed solution. To test this empirical principle the author has made transference measurements with solutions containing potassium chloride and sulphate, using the apparatus described by Washburn (Abstr., 1908, ii, 805). From these measurements the conductances of the ions in the mixture can be separately determined.

In a solution containing chloride and sulphate in 0·2009*N*-concentration, the quantity of chlorine transferred per farad was found to be 0·289 ± 0·001. On the assumption that the transference number of the chlorine in the potassium chloride in this mixture is the same as in dilute potassium chloride solutions, the proportion of the current carried by its ions is found to be 0·573, and that carried by the ions of potassium sulphate, 0·427. When these values are multiplied by the conductivity of the mixture, the partial conductivities of the component electrolytes are obtained. The partial conductivity of the potassium chloride obtained in this way is 2·0% larger, and that of the potassium sulphate 5·2% smaller, than the corresponding values, which are calculated on the basis of the above empirical rule. H. M. D.

Magneton in Solid Paramagnetic Substances. PIERRE WEISS (*Compt. rend.*, 1911, **152**, 688—691. Compare this vol., ii, 91, 183).—The value 1122·7 has been calculated for the aliquot part (gram-magneton) common to the absolute molecular saturations of four rare earths, employing Urbain's determinations of their coefficients of magnetisation. Results differing very slightly from these were also obtained from the results of Mlle. Feytis for salts of iron, manganese, and chromium (following abstract). Curie's results for metallic iron are explained by supposing that the molecule of β-iron contains three atoms rigidly united, whilst γ-iron has two and δ-iron is monatomic. This being the case, γ-iron contains 19·95 magnetons, β_1- and β_2-iron 12·08 and 10·04 magnetons per atom respectively; allowing for experimental errors these may be taken as whole numbers. Europium gave abnormal results, the atom appearing to contain 18·398 magnetons; this becomes 13·02, however, if it is assumed that two atoms are rigidly united. W. O. W.

Magnetism of Some Complex Salts. Mlle. E. FEYTIS (*Compt. rend.*, 1911, **152**, 708—711).—The magnetic susceptibilities of thirty metallic salts, mostly complex cobaltammines, have been determined by means of the Curie balance. The solid substances were employed to avoid the uncertain influence of solvents. No sharp distinction was found to exist between the coefficients for simple and complex salts. Pascal (Abstr., 1908, ii, 756; 1909, ii, 487) has shown that in solutions a parallelism exists between the variations of the coefficient of magnetisation with constitution and the variations in chemical properties. The same holds good in the case of the solid substances.

The experimental results are shown in tabular form. W. O. W.

Magneto-chemical Researches on the Atomic Structure of the Halogens. PAUL PASCAL (*Compt. rend.*, 1911, **152**, 862—865. Compare Abstr., 1909, ii, 487, 788, 859; 1910, ii, 100, 179).—Measurements have been made of the magnetic susceptibilities of thirty compounds containing more than one halogen atom united to the same atom of carbon, or of boron, silicon, phosphorus, antimony, or tin. The diamagnetic deficits for the whole molecule vary from 29×10^{-7} for tetrachloroethylene to $615{\cdot}5 \times 10^{-7}$ in the case of antimony pentachloride. The specific susceptibilities contain an aliquot part equal to $0{\cdot}2468 \times 10^{-7}$, and this is common to the three halogens; it is explained on the assumption that the halogen atom contains smaller elements having a definite relationship to the subsidiary valencies; mutual saturation of these between neighbouring atoms in the same molecule leads to a fall in diamagnetism by a constant fraction. W. O. W.

Calculation of Temperatures, Especially Below the Boiling Point of the Helium. H. Kamerlingh Onnes (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 441—446).—The author has evaporated helium at a pressure of 0·15—0·25 mm., as compared with 2·2 mm. in 1909, and has calculated by the aid of the vapour-tension formula of van der Waals, that the temperature attained is below 1·9°, and is probably 1·8°, absolute. A. J. W.

Relations between Critical Temperature, Boiling Point, and Expansion Coefficient of Phosphorus Pentachloride. Edmund B. R. Prideaux (*Trans. Faraday Soc.*, 1911, **6**, 155—159).—The thermal expansion of phosphorus pentachloride in sealed glass tubes (Trans., 1907, **91**, 1715) is expressed by the formula $V_t = V_{160}[1 + 0{\cdot}00107(t - 160)]$. The critical temperature, found both with rising and with falling temperature, is 373°. The ratio of the boiling point to the critical temperature is 0·67, showing that the dissociation does not cause any abnormality in this respect. The product of the coefficient of expansion and the critical temperature of phosphorus pentachloride is 0·46, that of nitrogen peroxide being 0·458, and the mean value for undissociated substances being 0·494 (Walden, Abstr., 1909, ii, 122). The product is also calculated for a number of associated liquids, and is found to be high in many cases.
C. H. D.

The Molecular Heat Conduction of Gases and the Accommodation Coefficient. Martin Knudsen (*Ann. Physik*, 1911, [iv], **34**, 593—656).—The fact that the thermal conductivity of gases at low pressures is appreciably smaller than that which is anticipated by the kinetic theory, has led the author to enquire into the cause of the discrepancy. The experiments made with this object show that the thermal conductivity of a gas is largely dependent on the degree of roughness of the surfaces of the hot and cold plates between which the gas is confined. This is supposed to be a consequence of the mode of partition of energy between the gas molecules and the surfaces on which they impinge, and in taking account of this effect the author introduces the conception of "accommodation coefficient." It is shown that the observations can be satisfactorily explained in terms of this modified kinetic theory. H. M. D.

Specific Heat at Low Temperatures. III. Walther Nernst (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 306—315).—Using the method previously described (Abstr., 1910, ii, 263), the author has determined the specific heats of lead, silver, zinc, copper, aluminium, iodine, potassium chloride, and mercurous chloride between the absolute temperatures 23° and 100°.

The curves showing the relation between atomic heat and temperature are all similar in character, and between the atomic heats 2 and 5·6 their course is in agreement with Einstein's formula for the atomic heat (*Ann. Physik*, 1907, [iv], **22**, 184). At very low temperatures the curves fall more slowly than according to Einstein's formula, tending to become tangential to the temperature axis; this supports the author's heat-theorem, whereby at $T = 0$, $lim. dU/dT = 0$.

The curve for potassium chloride is similar to those of the elements, whereas that of mercurous chloride is dissimilar. This agrees with the fact that the characteristic frequencies of potassium and chlorine, according to Lindemann's formula (*Physikal. Zeitsch.*, 1910, **11**, 609), are approximately the same, whereas those of mercury and chlorine are quite different. Since potassium chloride, and also the diamond, behave similarly to the metals, doubt is thrown on the electronic theory of electrical resistance.

It is found empirically that there is a parallelism between the temperature-coefficient of the electrical resistance of a metal and the atomic heat, and theoretical considerations show that Planck's radiation formula may be adapted for calculation of the variation of the electrical resistance with temperature. For example, the electrical resistance of lead between the temperatures 14·39° and 273·09° abs. is given by the expression $(0{\cdot}1626/e^{38/T} - 1) + 0{\cdot}0007$. In this formula the value of the constant in the exponential term is independent of the purity of the metal when only traces of impurity are present, whilst the value of the additive constant increases with the amount of impurity.

From further considerations it is shown how the electrical resistance of any one sample of metal at different temperatures may be calculated from the results obtained for another sample of the metal, a result which is very important in the measurement of low temperatures. T. S. P.

Specific Heats at Low Temperatures. IV. F. A. LINDEMANN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 316—321).—Assuming that relatively few free electrons exist in a metal, and, further, that the sphere of action of the atomic nuclei, with which the free electrons collide, increases with the amplitude of the heat vibrations, a formula is deduced for the relation between the electrical resistance of a metal and the temperature. This formula has the form:

$$R = A^2/(\epsilon^{\beta\nu/T} - 1) + 2AB/\sqrt{\epsilon^{\beta\nu/T} - 1} + B^2,$$

where R is the resistance, β a universal constant $= 4{\cdot}86 \times 10^{-11}$, ν the characteristic frequency of the atoms, and A and B are constants. It gives good results for silver and lead. T. S. P.

Heats of Fusion of Substances Melting Near the Atmospheric Temperature. WLADIMIR F. LUGININ and GEORGES DUPONT (*Bull. Soc. chim.*, 1911, [iv], **9**, 219—224).—The heats of fusion of a number of substances have been determined with a view to (*a*) verifying van't Hoff's law, as expressed in the form $F=0\ 02T^2/k$, where F is the heat of fusion and k the cryoscopic constant, and (*b*) determine or verify the values of k for these substances.

The experimental conditions for the determination of F and the errors incidental to these are discussed, and the apparatus and method used are described in detail. The substances used were acetic acid ($F=43{\cdot}102$, calc. 43·1), acetophenone ($F=33{\cdot}12$, calc. 30·3), *p*-bromotoluene ($F=21{\cdot}33$, calc. 21·9), anethole ($F=25{\cdot}80$, calc. 27·3), veratrole ($F=27{\cdot}75$, calc. 27·3), phenylhydrazine ($F=36{\cdot}31$), paracetaldehyde ($F=25{\cdot}02$), sulphuric acid monohydrate ($F=38{\cdot}97$, calc. 33). These results indicate that the law can be verified for relatively mobile liquids, but for viscous liquids the agreement between "found" and "calculated" values of F is less satisfactory, due to the fact that the experimental value of k for such substances is generally too high. Paracetaldehyde appears to be a promising solvent for cryoscopic determinations. T. A. H.

Cryoscopic Anomalies of Elements of the Fourth Periodic Group. PIETRO FALCIOLA (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. X., 159—161).—Cryoscopic measurements with titanium tetrabromide dissolved in stannic bromide, in a Beckmann apparatus for excluding the entrance of moisture, show that the freezing point of the solvent is raised. Zirconium tetrabromide is very sparingly soluble in stannic bromide, but a slight elevation of freezing point is observed. C. H. D.

Monovariant Systems Admitting of a Gaseous Phase. GEORGES URBAIN and C. SCAL (*Compt. rend.*, 1911, **152**, 769—772).—A mathematical demonstration of the fact that in such systems three determinations are sufficient to enable the vapour pressure to be calculated for any temperature whatever. W. O. W.

Vapour Pressures in Binary Systems with Partial Miscibility of the Liquids. PHILIPP KOHNSTAMM and J. TIMMERMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 865—880, 957).—Certain deductions from van der Waals' theory in reference to the form of the pressure temperature and pressure concentration curves for binary systems containing two liquid phases have been investigated in the case of the following pairs of substances: phenol and water, *cyclo*hexane and aniline, hexane and nitrobenzene, hexane and aniline, *iso*pentane and nitrobenzene.

Contrary to van der Waals' supposition, it is found that the vapour pressure curve for the co-existing liquid phases does not touch the plait-point line in the critical end-point, and this result is shown to be theoretically justified. In opposition to the view that the partial pressures of the components are proportional to the liquid concentrations, it is found that mixtures of normal substances sometimes give rise to pressure concentration curves with points of inflexion as required by van der Waal's theory. H. M. D.

Causes Producing at Constant Temperature Variation in the Vapour Pressure of a Liquid. Félix Michaud (*Compt. rend.*, 1911, **152**, 849—851).—A theoretical discussion of the subject.
W. O. W.

Heat Content of the Various Forms of Sulphur. Gilbert N. Lewis and Merle Randall (*J. Amer. Chem. Soc.*, 1911, **33**, 476—488).—This investigation was undertaken in order to obtain the data required for calculating the free energy of sulphur. Wigand (Abstr., 1908, ii, 677) has calculated the heat associated with the change from Sλ to Sμ, but it is shown that this calculation must be erroneous.

The total heat change has been determined between rhombic sulphur at 23° and liquid sulphur (in a state of equilibrium) at 100°, 140°, 184°, and 390°, and the results have enabled the following data to be calculated, which are expressed in small calories per gram of sulphur. The heat of fusion at 100° to form liquid sulphur in a state of equilibrium is 14·9 from the rhombic and 11·5 from the monoclinic form. The heat of fusion to form pure liquid Sλ is 14·5 from rhombic sulphur and 11·1 from the monoclinic form. The heat of transformation in the liquid state from Sλ to Sμ is about 13. The specific heat of pure liquid Sλ is about $0·21 + 0·00016t$. A diagram is given showing the approximate values of the specific heat of liquid sulphur in a state of equilibrium from 100° to 450°. E. G.

The Heat of Mixture of Substances and the Relative Distribution of the Molecules in the Mixture. Richard D. Kleeman (*Phil. Mag.*, 1911, [vi], **21**, 535—553).—From the law of attraction between molecules which has been obtained in a previous paper (Abstr., 1910, ii, 493), the author deduces formulæ for the heat changes which occur on admixture of two or more substances. The formulæ for special cases, such as the formation of a saturated solution of a salt in a liquid and of one liquid in another, are discussed.

The calculated heats of solution of ammonia, hydrogen fluoride, bromide, and iodide in water are in rough agreement with the experimental values, but there is a much greater divergence in the case of chlorine, hydrogen chloride, and carbon dioxide. It is supposed that this is due to the formation of hydrates or dissimilarity in the positions occupied by solute and solvent molecules. H. M. D.

Influence of Catalysts in Determinations of Vapour Density. André Kling (*Compt. rend.*, 1911, **152**, 702—704; *Bull. Soc. chim.*, 1911, [iv], **9**, 276—281. Compare Abstr., 1904, i, 545).—The method previously described for differentiating between primary, secondary, and tertiary alcohols by determining their vapour densities is only trustworthy when the V. Meyer tube contains 0·4—0·5 gram of washed and calcined sand. The asbestos pad usually placed at the bottom of such tubes is less satisfactory. The method depends for its success on the decomposition of a secondary or tertiary alcohol, giving a low result for the vapour density, and it has been found that such decomposition does not occur as a rule unless a catalyst such as sand is present.

Determinations of the vapour density of a substance, such as *iso*-propyl alcohol at the temperature of boiling naphthalene, furnish a method for comparing quantitatively the catalytic activity of metallic oxides, since they measure the extent to which decomposition has been effected. The following coefficients obtained in this way represent the ratio of the theoretical density to the actual value: ThO_2 2·3, ZnO 2·0, Al_2O_3 1·9, Fe_2O_3 1·3, SnO_2 1·2, TiO_2 1·03.

W. O. W.

The Nature of Adhesiveness. MAURICE HANRIOT (*Compt rend.*, 1911, **152**, 704—706. Compare this vol., ii, 118, 208, 258).—The property of adhesiveness to which attention has been drawn previously in connexion with brown gold is only exhibited when this is brought into contact with the yellow variety at the temperature at which the former is metastable. The contraction that occurs when brown gold is heated may be the result of adhesion between contiguous particles.

W. O. W.

The Weight of a Falling Drop and the Laws of Tate. III. An Apparatus for Rapid and Accurate Determination of the Weight of a Falling Drop of Liquid. J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1911, **33**, 349—362. Compare Abstr., 1908, ii, 356, 668).—A detailed description is given of an apparatus for measuring accurately the relative surface tensions of liquids by means of the weights of drops of the various liquids formed at straight-edged tips under such conditions that the speed of formation of the newly-formed drop is very small. For this purpose, the apparatus permits of perfect control of the speed at which the drops are formed, and any loss of liquid by evaporation from either the hanging drop or from drops which have already fallen is eliminated. The apparatus permits of measurements being made up to within a few degrees of the boiling point of the liquid, and it ensures constancy of temperature during the drop formation. The apparatus can be readily cleaned without disturbing the setting. For a description of the mechanical details, the original must be consulted.

H. M. D.

Rôle of Affinity in Dyeing. AUGUSTE ROSENSTIEHL (*Bull. Soc. chim.*, 1911, [iv], **9**, 224—231).—The argument begun in the previous paper (this vol., ii, 99) is continued and extended to a number of apparently anomalous cases of the application of dyes to fibres, and it is concluded that cohesion plays the principal part in dyeing. Even when the coloured layer is formed by combination between dye and fibre, cohesion ensures the adherence of this coloured layer to the bulk of the fibre.

T. A. H.

Viscosity and Fluidity of Matter in the Three States of Aggregation and the Molecular Weight of Solids. EUGENE C. BINGHAM (*Amer. Chem. J.*, 1911, **45**, 264—281).—A theoretical paper on the viscosity of gases, liquids, and solids. It is pointed out that in gases the viscosity depends primarily on the momentum of the molecules, whereas in liquids it is mainly dependent on the volume of the molecules. With regard to solids, the amount of damping of the vibration of a wire is usually regarded as a measure of the viscosity, but it is now shown to be rather a measure of the fluidity.

The author has shown (Abstr., 1909, ii, 382) that the molecular weights of liquids can be determined by means of their viscosities, and it is now considered probable that the molecular weights of solids could also be determined by viscosity measurements. E. G.

The Viscosity of Colloidal Solutions. REGINALD O. HERZOG (*Zeitsch. Chem. Ind. Kolloide,* 1911, 8, 210—211).—In reference to Einstein's deduction that the difference between the viscosity of a colloidal suspension and that of the dispersive medium is determined by the relative volume occupied by the suspended phase, the author points out that the frequently observed diminution in the viscosity of a colloidal solution may in some cases be due to the liberation of the dispersive medium in the ageing of the suspended particles. Experiments with an arsenious sulphide sol are recorded, in which the time of flow through a viscometer tube diminished from 43′9″ to 41′29″ after twenty-five days. At the same time the density fell from 1·0069 to 1·0011. H. M. D.

Influence of the Acidity of Aqueous Solutions on the Surface Tension of the System Water and Oil. WILLEM REINDERS (*Gedenkboek aangeboden aan J. M. van Bemmelen,* 1910, 333—341. Compare Ringer, Abstr., 1909, ii, 660, and Meyeringh, this vol., ii, 78).—An investigation of the surface tension of mixtures of various oils with dilute aqueous solutions of primary, secondary, and tertiary sodium phosphates. A. J. W.

Fluidity of Binary Mixtures. KARL DRUCKER and R. KASSEL (*Zeitsch. physikal. Chem.,* 1911, 76, 367—384).—The variation of viscosity with composition has been measured for the following eleven binary mixtures: tetrachlorethane–acetophenone, tetrachlorethane–nitrobenzene, bromoform–nitrobenzene, *i*-amyl alcohol with nitrobenzene, formamide, diethylaniline and paracetaldehyde respectively, acetic anhydride with paracetaldehyde and with acetic acid, and sulphuric acid with acetic acid and with methyl sulphate at a relatively low temperature (0—15°) and a relatively high temperature (76—80°). In most cases the results do not correspond with the mixture rule.

The authors agree with Bingham (Abstr., 1909, ii, 382) that the results are best represented in terms of fluidity rather than of viscosity, and curves are given in which fluidity, ϕ, is plotted against composition expressed as the fraction by weight, a, of one of the components in the mixture. It is assumed that miscibility is chemical combination, and that linear curves are obtained only when complete reciprocal substitution of complexes or components takes place, whilst deviations from a straight line are due to incomplete substitution. On this basis the formula $\phi = \phi_1 a + \phi_2(1-a)$, where ϕ_1 and ϕ_2 represent the respective fluidities of the pure compounds, is derived, and is shown to represent the experimental results at least as well as any formula so far proposed. The deviations from this formula are ascribed to chemical influences.

These considerations cannot be expected to represent entirely satisfactorily the behaviour of a liquid in motion as opposed to a liquid at rest, and in this connexion it is suggested that there must be a relationship between fluidity and compressibility. G. S.

The Adsorption of Electrolytes by Sols. WOLFGANG OSTWALD (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 267—274).—By addition of a colloid to a solution of an electrolyte, the electric conductivity of the solution is diminished if adsorption of the electrolyte takes place. From Dumanski's data (*Zeitsch. Chem. Ind. Kolloide*, 1906, **1**, 281) for solutions of ammonium chloride to which a constant quantity of colloidal ferric hydroxide was added, the author shows that the dependence of the quantity of adsorbed electrolyte on the concentration of the solution can be expressed satisfactorily by means of an exponential equation. The formula no longer holds good when the concentration of the electrolyte is such as to cause coagulation of the sol. This behaviour is in agreement with Freundlich's theory of the coagulating effect of electrolytes; according to this, the coagulation is intimately connected with the adsorption of electrolytes by the colloidal substance. H. M. D.

The Adsorption of Methylene-blue and Crystal-ponceau by Carbon in its Dependence on the Temperature. LOUIS PELET-JOLIVET and HANS SIEGRIST (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 158—162).—Measurements of the adsorption of methylene-blue and crystal-ponceau from aqueous solutions by animal charcoal have been made at temperatures of 15°, 50°, and 70°. In both cases the coefficients β and m of the exponential formula $x/a = \beta . c^m$ increase as the temperature rises. The sign of the temperature-coefficient of the adsorption is therefore the same for both the basic and acid colouring matters. H. M. D.

Adsorption in a Solution of Several Substances. HERBERT FREUNDLICH and M. MASIUS (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 88—101).—The phenomena accompanying the simultaneous adsorption of two substances from aqueous solution by animal charcoal have been examined. Solutions of oxalic and succinic acids and of oxalic and benzoic acids were chiefly investigated.

Both substances are adsorbed from the mixed solutions to a smaller extent than from the corresponding solutions of the single substances. The mutual influence is such that the diminution in the adsorption of a given substance in presence of a second substance increases with the extent to which the latter is adsorbed. If the adsorption of one of the two substances is not altered to any large extent, the adsorption of this takes place in accordance with the exponential formula.

For the three acids in pure aqueous solution the constants a and $1/n$ in the formula $x/m = ac^{1/n}$ were found to be respectively: oxalic acid, $a = 5{\cdot}403$, $1/n = 0{\cdot}4501$; succinic acid, $a = 4{\cdot}426$, $1/n = 0{\cdot}274$; benzoic acid, $a = 12{\cdot}23$, $1/n = 0{\cdot}2848$. H. M. D.

Dissociation of Hydrated Salts. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1911, [v], **20**, 112—119).—It is known that below a certain temperature the dissociation pressure of magnesium sulphate heptahydrate is less, and above this temperature greater, than that of ferrous sulphate heptahydrate. The author finds that the equilibrium temperature, determined directly by the tensimeter, is 44·01°, as compared with the value 45·70° calculated by a thermodynamical method fully described in the paper. The dissociation tension of the mixed salts, $MgSO_4,xFeSO_4,7(1+x)H_2O$, has been measured at the equilibrium temperature for different values of x; the results will be communicated in a later paper. G. S.

Relation of Osmotic Pressure to Temperature. II. The Manometers. HARMON N. MORSE, WILLIAM W. HOLLAND, and J. L. CARPENTER (*Amer. Chem. J.*, 1911, **45**, 237—263).—In the previous paper on this subject (this vol., ii, 191) the method of manufacturing the osmotic cells was described. A detailed description is now given of the construction and calibration of the manometer, and the method of obtaining and applying the correction for meniscus (compare Morse and Lovelace, Abstr., 1908, ii, 1020). The instrument is not yet entirely satisfactory in certain respects, but improvements have been devised and will be carried out in future work. E. G.

Rate of Diffusion and Relative Size of Dissolved Molecules. THE SVEDBERG and ANDREA ANDREEN-SVEDBERG (*Zeitsch. physikal. Chem.*, 1911, **76**, 145—155).—According to the Sutherland-Einstein formula connecting the rate of diffusion with the size of the diffusing particles, the rate of diffusion is under comparable conditions inversely proportional to the diameter of the molecules. This consequence of the theory has been tested by comparing the relative rates of diffusion of organic substances of similar type in methyl alcohol as solvent, the relative sizes of the molecules being deduced approximately on the basis of their structural formulæ. In this way benzene, naphthalene, diphenyl and triphenylmethane, and also pyridine and quinoline, were compared, and the results were in qualitative agreement with the theory. The values found for the diffusion coefficients at 14—15° are as follows: benzene 1·85, naphthalene 1·38, diphenyl 1·34, triphenylmethane 0·75, pyridine 1·37, quinoline 1·13. G. S.

The Dialytic Capacity of the Colouring Matters. WILHELM BILTZ and F. PFENNING (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 108—120).—Dialysis experiments have been made with a large number of colouring matters in order to ascertain the factors on which the dialytic capacity depends. From the measurements, which were made with a collodion membrane, the conclusion is drawn that the dialysing power of a colouring matter is dependent on the number of atoms in the molecule. If this is less than forty-five, dialysis takes place quickly, but the rate diminishes as the number of atoms increases beyond this number. Between fifty-five and seventy, the dialytic capacity is very small, and substances containing more than seventy atoms in the molecule do not dialyse at all. This relationship is, however, influenced to some extent by the composition and constitution of the substance. In particular, it is found that the presence of sulphonic groups increases the dialytic capacity to a marked extent. For example, the colouring matters of the malachite-green series which contain two or three sulphonic groups dialyse quite readily, although the number of atoms in the molecule is greater than seventy. On the other hand, it appears that substances having the "alizarin constitution" dialyse less readily than would be expected from the number of atoms in the molecule.

H. M. D.

The Amorphous and Crystalline States. CORNELIO DOELTER (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 232—239. Compare Abstr., 1910, ii, 696, 834).—The author considers that many freshly precipitated substances must be regarded as amorphous, although many of these undergo transformation into crystalline forms under suitable conditions. In this connexion the author has examined the gel forms of silicic acid and sodium chloride, precipitated zinc sulphide, and silver obtained by vaporisation in an electric arc.

After prolonged agitation, the zinc sulphide was found to have become distinctly crystalline, but no change was evident in the silicic acid or sodium chloride. These gels and the vaporised silver are therefore considered to be amorphous. H. M. D.

Abnormal Dependence of the Velocity of Crystallisation on the Temperature. GUSTAV TAMMANN (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 297—302).—It has been found previously that for substances which crystallise quickly, the velocity of crystallisation attains a maximum value at 20—30° below the melting point, and then remains constant until the supercooling amounts to about 70°. Further experiments have shown that this behaviour is not quite general. In the case of dinitrophenol, acetanilide, antipyrine, and erythritol, the velocity of crystallisation increases with the supercooling in this region, whereas it decreases in the case of *m*-chloronitrobenzene, *m*-bromonitrobenzene, benzophenone, and sodium thiosulphate pentahydrate.

This abnormal behaviour is attributed to differences in the molecular complexity of the liquid and solid substances. If the liquid is to some extent associated, this association will increase as the temperature is lowered, and if the reconversion of the polymerised molecules is comparatively slow, the molecular condition of the liquid at the crystallisation surface will vary with the extent of the supercooling. According to this, observations of the dependence of the velocity of crystallisation on the degree of supercooling may, in certain cases, be utilised as a means of determining whether the liquid consists of simple or polymerised molecules. If the equilibrium between the two kinds of molecules is established with great rapidity, the method cannot afford information relative to the molecular condition, for the velocity of crystallisation in this case will be independent of the temperature. H. M. D.

The Degree of Dispersity and its Influence on the Chemical Composition and the Firmness of the Combination of Water of Hydration. P. P. von Weimarn (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910. 50—54).—The crystallisation process is analysed, and it is shown that the increase in the water content of crystalline hydrates, which is observed when the degree of dispersity of the precipitated substance increases, is consistent with the author's view that these so-called amorphous precipitates are crystalline. On account of the action of special forces at the surface of a crystal, the surface layer approximates in a way to the molecular condition which is characteristic of highly compressed liquids. This layer is, moreover, of different composition from the crystalline nucleus, and on this account increased dispersity of the crystals is accompanied by increased hydration. The water contained in gelatinous precipitates, which owes its origin to the excessive development of the surface layers, is only very loosely combined, as has been shown by the experiments of van Bemmelen, and this observation is consistent with the author's views of the origin of this water of hydration. H. M. D.

Certain Arbitrary Distinctions which are made in Theoretical Chemistry. Giovanni Malfitano (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 368—379).—The author maintains that the grounds on which a distinction is drawn between chemical compounds and solutions are more or less arbitrary. It is also claimed that the grounds for differentiating between adsorption and chemical combination are insufficient. H. M. D.

The Electrolytic Dissociation Theory. Niels Bjerrum (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. X., 58—60).—It is suggested that when the colour of a solution changes with dilution, the cause is combination of the ions. The decrease in molecular conductivity with increasing concentration is due to retardation of the movement of the ions. The anomalies of strong electrolytes are attributed to electrolytic friction. C. H. D.

Chemistry of Colloids. Eduard Jordis (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 214—225).—In support of the author's view that the hydrosol and hydrogel forms of various substances are characterised by the presence of more or less definite quantities of electrolytes, experiments are described in which the conditions necessary for the production of the hydrosols of ferric and aluminium hydroxides and of silicic acid from the precipitated substances have been determined. H. M. D.

Colloids and Permanent Chemical Modifications. Pierre Duhem (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 1—6).—A comparison is made between the changes in the properties of colloidal substances which accompany the absorption or emission of water-vapour and changes which have been found to occur in amorphous carbon when its tendency to undergo oxidation is measured at successive time intervals, between which the carbon is subjected to a slow variation of temperature.

In the author's opinion, the introduction of terms, which take account of the action of capillary forces, into the thermodynamical equations which express the conditions of equilibrium in heterogeneous systems cannot give a satisfactory account of the behaviour of colloidal substances (solutions). H. M. D.

Electrolytic Colloids. WILLIAM B. HARDY (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 180—193).—Colloidal solutions may be considered as special cases of molecular solution, in which there is a wide departure from thermodynamic reversibility in consequence of the operation of a large internal frictional constraint which owes its origin to the limited mobility of one of the constituents. Electrolytic colloids are those in which the relatively immobile constituent of the colloidal solution is an ion. Such colloids will exhibit electrolytic phenomena at internal surfaces.

These electrolytic phenomena are considered from the point of view of Nernst's solution tension theory and the observations of Burton relative to the charges of colloidal metals produced by cathodic disintegration. Whereas, according to Nernst's theory, these colloidal particles should be negatively charged, it has been found that the non-noble metals are positively, and the noble metals negatively, charged.

This can be explained by assuming that the non-noble metals react with water to form a film of hydroxide which ionises, hydroxyl ions passing into the water and leaving the metal positively charged. The noble metals, on the other hand, form hydrides which ionise, and the particles are left negatively charged. This is supported by the fact that the noble metals do not yield colloidal solutions in methyl or ethyl alcohol, whereas the non-noble metals behave as in water. In ethyl malonate, on the other hand, the behaviour of the two groups is exactly reversed.

This view is developed in detail and applied to other substances which give rise to colloidal solutions. H. M. D.

Simultaneous Coagulation of Two Colloids. F. W. TIEBACKX (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 198—201).—The coagulation of solutions containing gelatin and gum arabic on the addition of acids leads to the separation of both colloids. Experiments showing the influence of different amounts of hydrochloric, sulphuric, acetic, and citric acids, of the relative proportions of the colloids and of the absolute concentration are described. The phenomena observed on addition of salts are very similar. H. M. D.

Some Reactions in Gels. EMIL HATSCHEK (*J. Soc. Chem. Ind.*, 1911, **30**, 256—258).—The formation of a number of insoluble precipitates from solutions containing gelatin has been studied, stratified layers being obtained. The micro-crystalline precipitates composing these layers have been photographed. Spherulitic forms are obtained in most cases, lead salts giving large spherulites, especially from agar solutions. Barium silicofluoride yields remarkably perfect and transparent, although smaller, spherulites. The only compound which was not found to assume this form is lead ferrocyanide, which forms long crystallites, terminating in rhombohedra. C. H. D.

The Theory of Swelling. KARL SPIRO (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 261—266).—Experiments are described which indicate that the swelling or contraction of plates of solidified gelatin or agar jelly is to some extent determined by forces acting at the surface of the jelly which tend to contract it.

Both the swelling and contraction which occur when the jelly is immersed in certain solutions are dependent on the original gelatin or agar content of the solidified jelly. Isosmotic solutions of sodium and calcium chlorides are found to give rise to swelling or contraction effects of different magnitudes. The importance of the phenomena in connexion with changes in plant and animal cells is referred to.

H. M. D.

"Pyrosols." Colloidal Phenomena in Molten Solids. RICHARD LORENZ (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 395—398).—The coloured turbid liquids which are obtained when metals are heated in contact with their fused salts are supposed to represent colloidal solutions of the metal, and for these the name "pyrosol" is suggested. H. M. D.

Separation on the Appearance of a Solid Phase. ANDREAS SMITS (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 434—440). —A theoretical paper on the equilibrium with solid phases.

A. J. W.

Heterogeneous Equilibrium in Dissociating Compounds. III. F. E. C. SCHEFFER (*Zeitsch. physikal. Chem.*, 1911, **76**, 161—173). —The three-phase equilibrium in the system NH_3-H_2S has been redetermined by a more accurate method; the results correspond very closely with those previously obtained (Abstr., 1910, ii, 278). On the basis of these results the properties of the system at relatively low temperatures (about 30°) are more accurately stated. The work of Briner (compare Abstr., 1909, ii, 124) is adversely criticised in some respects. G. S.

Equilibria in the System Sulphuric Acid, Ammonia, and Water at 30°. G. C. A. VAN DORP (*Chem. Weekblad*, 1911, **8**, 269—273).—An application of Schreinemakers's graphic method, with special reference to the possibility of the formation of primary ammonium sulphate in the manufacture of ammonium sulphate.

A. J. W.

Equilibrium between Sodium Carbonate, Sodium Hydrogen Carbonate, and Water. II. HERBERT N. McCOY and CHARLES D. TEST (*J. Amer. Chem. Soc.*, 1911, **33**, 473—476).—In an earlier paper (McCoy, Abstr., 1903, ii, 413) an account was given of a study of the equilibrium between sodium carbonates, carbon dioxide, and water in solutions of *N*/10- to *N*-concentration. The work has now been extended to solutions in equilibrium with solid phases at 25°. Sodium hydrogen carbonate (40 grams) and water (about 200 c.c.) were rotated in a thermostat until equilibrium was reached. About 15 grams of sodium carbonate decahydrate were then added to the mixture of saturated solution and sodium hydrogen carbonate, and the mixture was again rotated until a new state of equilibrium was attained. The results obtained by continuing this method are plotted as a curve in which the ordinates represent the number of grams of sodium per c.c. of solution, and the abscissæ the percentages of total sodium in the solution in the form of sodium hydrogen carbonate.

At the point at which 12·9% of the sodium is in solution as sodium hydrogen carbonate and 87·1% as sodium carbonate, a new solid phase, $Na_2CO_3,NaHCO_3,2H_2O$, appears in the form of long needles. Between this point and that at which 5·92% of the sodium is present as sodium hydrogen carbonate, only this one solid phase exists, but at the latter point another solid phase, $Na_2CO_3,10H_2O$, appears.

E. G.

Equilibrium between Alkali-Earth Carbonates, Carbon Dioxide, and Water.

HERBERT N. McCOY and HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1911, **33**, 468—473).—This investigation was undertaken in view of the fact that previous workers had not used modern methods and had not made measurements at higher pressures than 6 atmospheres.

Experiments have now been made with calcium carbonate with pressures of carbon dioxide between 0·06 and 25 atmospheres. It has been found that the maximum solubility of the calcium salt is 0·485 normal molecular, and corresponds with a pressure of about 15 atmospheres. The solubility of calcium hydrogen carbonate is thus equal to 4·2 grams per litre at 25°. The mean value of the equilibrium constant k at pressures less than 15 atmospheres was 0·0234. The solubility product $Ca \times CO_3 = 9{\cdot}3 \times 10^{-9}$.

In the case of strontium carbonate, experiments have been made at pressures between 0·05 and 1·1 atmospheres. The equilibrium constant $k = 1{\cdot}29 \times 10^{-2}$, and the solubility product,

$$Sr \times CO_3 = 1{\cdot}567 \times 10^{-9}.$$

Experiments have also been made with barium carbonate at pressures between 0·2 and 30 atmospheres. A maximum solubility, 0·028, is reached at a carbon dioxide pressure of about 22 atmospheres. The solubility of barium hydrogen carbonate is 7·3 grams per litre at 25°. The equilibrium constant $k = 2{\cdot}24 \times 10^{-2}$, and the solubility product, $Ba \times CO_3 = 8{\cdot}1 \times 10^{-9}$.

E. G.

The Ternary System Potassium Sulphate, Copper Sulphate, and Water below 50°.

P. A. MEERBURG (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 356—360. Compare Trevor, Abstr., 1891, 973).—A criticism of Trevor's work on solutions of potassium sulphate and copper sulphate. The author employs Schreinemakers's graphic method, and disputes Trevor's statement that his solid phases were pure salts and not mixtures. A. J. W.

Equilibria in the System Water–Ammonium Chloride–Lead Chloride. J. N. Brönsted (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. X., 110—111).—The solubility of lead chloride in solutions of ammonium chloride has been examined at 22°. The solubility curves of lead chloride and of the double salt $2PbCl_2,NH_4Cl$ intersect at a concentration of 0·52*N*-ammonium chloride, at which point both solid salts are in equilibrium with the solution. C. H. D.

Equilibria in the System Sodium Chloride, Sodium Sulphate, Cupric Chloride, Cupric Sulphate, and Water at 25°. Frans A. H. Schreinemakers and (Miss) W. C. de Baat (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 361—367).—An application of Schreinemakers's graphic method. At 25° the solid phases of the quaternary system are: $NaCl,Na_2SO_4$; $Na_2SO_4,10H_2O$; $CuSO_4,5H_2O$; $Na_2Cu(SO_4)_2,2H_2O$, and $CuCl_2,2H_2O$. A. J. W.

Nature of Disperse Systems. P. P. von Weimarn (*Zeitsch. physikal. Chem.*, 1911, 76, 212—230).—A theoretical paper. In the systems liquid–solid and liquid–liquid there are three types of disperse systems, the first being characterised by the gradual diminution and the second by the progressive increase in the degree of dispersion of the disperse phase. The third type occurs near the point of transition of the one-phase to a two-phase system; for example, in disperse systems near the critical point. The different types are discussed in detail. G. S.

The Composition of Eutectic Mixtures. Cecil H. Desch (*Trans. Faraday Soc.*, 1911, 6, 160—166).—The methods of predicting the position of the eutectic point in binary systems are discussed, and the rules proposed by Flawitzky (Abstr., 1906, ii, 152) and Gorboff (Abstr., 1910, ii, 111) are tested by application to a large number of binary mixtures, being found to have only a limited validity. C. H. D.

Temperature-coefficient of Chemical Reaction Velocities. V. Reaction Path and Nascent State. The Upper Limit of Chemical Reaction-Velocity and the Temperatures at which it is Reached. Max Trautz (*Zeitsch. physikal. Chem.*, 1911, 76, 129—144).—A further theoretical discussion of the temperature-coefficient of chemical reaction velocities on the lines of the author's recent communications (compare Abstr., 1910, ii, 24, 114, 1051). The formula already referred to leads to the conception of an upper limit for the speed of reactions and the temperatures at which they are attained. From the available thermal data, and making use of Nernst's theorem, it is calculated that the temperature of maximum velocity for the thermal decomposition of nitric oxide is 5468° abs., and the time taken for the decomposition of 99·9% of the gas is 0·66 second when the initial pressure is one atmosphere. On the same lines the rate of combination of nitric oxide and oxygen has been calculated at a readily attainable temperature. This reaction is now being investigated by Bodenstein, and it will be possible to test the formula when the experimental data are available. G. S.

The Hypohalogenous Acids and the Hypohalogenites. III. Influence of Electrolytes on the Velocity of the Hypoiodite Reaction. Anton Skrabal (*Monatsh.*, 1911, **32**, 167—184).—In continuation of the author's investigations on the kinetics of the decomposition of hypoiodites (Abstr., 1907, ii, 448), the influence of electrolytes on the velocity of reaction has been studied. Electrolytes accelerate the reaction, but their influence is much less than in the analogous hypobromite reaction (Abstr., 1909, ii, 224). The acceleration is not a simple function of the electrolyte concentration $[E]$, but a complex function of $[E]$, $[OH']$, and $[I']$.

With large concentrations of iodide ions and small concentrations of hydroxide ions, the course of the reaction is best represented by the equation: $-d[IOH]/dt = K[IOH]^2[I']/[OH']$, whereas with small concentrations of iodide ions and large concentrations of hydroxide ions the equation which best represents the reaction is: $-d[IOH]/dt = K'[IOH]^2\{[I'] + e[E]\}/[OH']$; e is only approximately constant, its value being of the order 0·01. The second equation best represents the course of reaction under the most varying conditions.

The temperature quotient (for 10°) of the reaction is 2·1.

If the concentrations are expressed in gram-formula-weights per litre, the time in minutes, and the temperature in absolute degrees, the velocity of the formation of iodate according to the equation: $3IOH + 3OH' = 2I' + IO_3' + 3H_2O$, at temperatures in the neighbourhood of room temperature, is expressed by the equation:

$$-d[IOH]/dt = 2{\cdot}2 \times 10^{-8} \times 10^{0{\cdot}0322T}\{[I'] + 0{\cdot}01[E]\}[IOH]^2/[OH'].$$

By means of this equation the velocity of formation of iodate from alkali hydroxide and iodine, or from alkali hydroxide, iodine, and potassium iodide solutions, can be accurately calculated for all attainable concentrations. T. S. P.

The Hypohalogenous Acids and the Hypohalogenites. IV. The Influence of Electrolytes on the Velocity of the Hypobromite Reaction. Anton Skrabal (*Monatsh.*, 1911, **32**, 185—196).—The equation previously put forward (Abstr., 1909, ii, 224) to represent the velocity of formation of bromate from hypobromite, namely, $-d[BrOH]/dt = K'[BrOH]^2\{[Br'] + e[E]\}/[OH']$, has been further tested. The value of e is found to be 0·5, but it can be taken as constant only as a first approximation, since its value depends on the conditions of experiment. When the ratio $[OH'] : [Br']$ is very great, e becomes greater than 1.

The temperature quotient of the hypobromite reaction is 1·7.

If the concentrations are expressed in gram-formula-weights per litre, the time in minutes, and the temperatures in absolute degrees, the velocity of the formation of bromate according to the equation: $3BrOH + 3OH' = 2Br' + BrO_3' + 3H_2O$, at temperatures in the neighbourhood of room temperature, is expressed by the equation: $-d[HOBr]/dt = 2{\cdot}7 \times 10^{-11} \times 10^{0{\cdot}02350T}\{[Br'] + 0{\cdot}5[E]\}[HOBr]^2/[OH']$. Owing to the inconstancy and high numerical value of e, this equation is not valid for so large a range of concentrations as the corresponding equation for the hypoiodite reaction.

At 25°, and in solutions free from electrolytes, the hypoiodite reaction proceeds 440,000 times as fast as the hypobromite reaction; this ratio is somewhat smaller in the presence of electrolytes. The calculated ratios and those experimentally determined are in good agreement with each other. T. S. P.

Rate of Reaction between Potassium Dichromate and Iodide in the Presence of Hydrochloric Acid and of Catalysts.

GIUSEPPE KERNOT and F. PIETRAFESA (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii*A*], **16**, 275—287).—The rate of reaction between potassium dichromate, potassium iodide, and hydrochloric acid is proportional to the concentration of each of the reacting substances. Under corresponding conditions, the speed of the reaction is more influenced by the iodide than by the dichromate, and most of all by the acid. The authors find by the method of Noyes that the reaction is of the fifth order.

Colloidal platinum accelerates the reaction proportionally to its concentration, but the effect falls off as the reaction proceeds. Ferrous sulphate also accelerates the reaction to an extent proportional to its concentration. The effect of a mixture of colloidal platinum and ferrous sulphate is rather greater than the sum of the separate effects. G. S.

The Rate of Dissolution of Metallic Copper in Aqueous Ammonia.

EÜCHI YAMASAKI (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. X., 172—178).—In the preparation of Schweizer's reagent by the action of ammonia on copper in presence of air, the velocity increases regularly from a certain initial value to a maximum and then decreases. The measurements are made in a thermostat at 24·8°, the partial pressures of ammonia and oxygen being kept constant. The copper plates used, which are rotated in the solution, are weighed at intervals. The initial velocity of dissolution is independent of the concentration of the ammonia. The velocity increases proportionally to the concentration of copper already in solution, and the maximum velocity is reached at a concentration of copper which is smaller the smaller the concentration of ammonia. The total concentration of copper dissolved in time t may be calculated from the equation: $ln(c+k_0/k) = kt/A + lnk_0/k$; k_0 is found to be $4{\cdot}48 \times 10^{-6}$, and k, $2{\cdot}24 \times 10^{-3}$. The accelerating action of copper may be explained by the reactions: $Cu(NH_3)_x^{\cdot\cdot} + Cu + yNH_3 = 2Cu(NH_3)^{\cdot}_{(x+y)/2}$ and

$$2Cu(NH_3)^{\cdot}_{(x+y)/2} + (x-y)NH_3 + O + H_2O = 2Cu(NH_3)_x^{\cdot\cdot} + 2HO'.$$

The first reaction proceeds slowly, whilst the second is very rapid. The acceleration is thus proportional to the concentration of the complex $Cu(NH_3)_x^{\cdot\cdot}$. When pure oxygen is used instead of air, the initial velocity is considerably increased, whilst the acceleration is not affected, the actual values found being k_0 $12{\cdot}86 \times 10^{-6}$ and k $2{\cdot}126 \times 10^{-3}$, which is approximately in accordance with the changed partial pressure of the oxygen. The addition of sodium hydroxide diminishes the velocity. Rise of temperature accelerates it, but k_0 and k are only increased by 15% by a rise of 10°. C. H. D.

Action of Bromine on Formic Acid. ALFRED F. JOSEPH (*Zeitsch. physikal. Chem.*, 1911, **76**, 156—160. Compare Bognar, Abstr., 1910, ii, 282).—The rate of reaction between bromine and formic acid is retarded by mineral acids, as well as by chlorides and bromides, but is accelerated by sodium sulphate. The effect of the same substances on the vapour pressure of dissolved bromine and on its solubility is parallel to that on the rate of reaction. G. S.

Catalysis. JACOB BÖESEKEN (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 386—391).—The author discusses the formation of by-products in catalytic actions, and the relation between the amount of the catalyst employed and the velocity of the reaction induced. A. J. W.

Specific Stereochemical Behaviour of Catalysts. LEOPOLD ROSENTHALER (*Zeitsch. physikal. Chem.*, 1911, **76**, 255. Compare Abstr., 1910, ii, 840; Fajans, *ibid.*, 599).—Polemical. G. S.

Modification of the Mechanism of Flame by Convergent Combustion. JEAN MEUNIER (*Compt. rend.*, 1911, **152**, 706—708. Compare Abstr., 1910, ii, 407).—A description, illustrated by a diagram, of a burner suitable for observing the flame of convergent combustion. An Auer burner, from which the cylinder has been removed, carries a central metallic stem supported by the wire gauze. The lower third of this is surrounded by a conical spiral of platinum wire terminating in a narrower platinum cone. The burner is lighted to heat the platinum, and the gas momentarily cut off by compressing the tube. On allowing gas to pass again, the platinum becomes incandescent, and on applying a light to the upper part of the central stem, a flame of air burning in coal gas appears at the point. It is protected from draughts by an inverted lamp cylinder held in a wire support. W. O. W.

A Sublimation Apparatus. R. WRIGHT (*Chem. News*, 1911, **103**, 138).—The apparatus consists of a narrow bell-jar, fitted with a cork through which passes the delivery tube of a small glass retort, the tube being cut off fairly short. The substance to be sublimed is placed in the retort, which is then connected with the bell-jar, and the whole inverted over a watch glass or small porcelain dish resting on a few thicknesses of moist filter-paper laid on a tile.

On gently heating the retort bulb, the substance sublimes into the dish. Slow heating is necessary, otherwise the substance may be deposited on the sides of the jar.

By placing the jar on a ground glass plate and connecting with a pump by means of an extra tube through the cork, sublimations may be carried out in a vacuum. T. S. P.

A Simple Constant-Temperature Bath for Use at Temperatures both Above and Below that of the Room. J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1911, **33**, 344—349).—By means of the movement of mercury in the regulator, which is immersed in the bath, an electrical circuit is completed. This contains a small relay which is so arranged that the house circuit can be either made or broken in a large telegraph sounder. This is so placed as to act on a rod, which by means of a suspended weight presses tightly on a piece of rubber tubing, through which hot or cold water can be automatically delivered to the thermostat. It is said that any temperature between 0·1° and 90° can be maintained with an accuracy of a few hundredths of a degree. H. M. D.

Crucible Furnace. NORMAN ROBERTS and F. ALEX. MCDERMOTT (*J. Amer. Chem. Soc.*, 1911, **33**, 507—510).—A small crucible furnace is described which is heated by gas, the flame entering at the bottom. It consists of an outer container and an inner lining both made of sheet-iron, the intermediate space being filled with a non-conducting, refractory powder, such as light magnesia, kaolin, or sifted ashes. The inner lining is more durable if made of clay or graphite, but these materials are less satisfactory than sheet-iron, since the latter can be more easily replaced, is free from risk of breakage, and is more quickly heated than a more massive lining. The crucible is supported either by a pipe-clay triangle, the wire exposed at the bends being coated with asbestos, or by a ring of graphite, clay, or iron. The lid consists of a circular disk of sheet-iron with a hole in the middle, or may be made of asbestos board or clay. Such a furnace with both iron and graphite linings has been found capable of melting copper, brass, and even cast-iron.

The furnace is superior to those with solid walls of clay or some similar substance, since it is lighter, less expensive, better insulated, can be more rapidly heated, and can be more easily and cheaply repaired. The insulating layer can be made of any desired thickness. E. G.

Pulsating Ultrafiltration. HEINRICH BECHHOLD (*Gedenkboek aangeboden ann J. M. van Bemmelen*, 1910, 430—433).—In reference to the possible influence of the pulsations of the blood pressure on the velocity of blood secretion processes, the author has compared the rates of filtration through a collodion membrane under continuous pressure and under conditions in which the pressure was periodically removed and allowed to act for thirty seconds. The results indicate that filtration takes place more quickly under the influence of the pulsating pressure. H. M. D.

A New Separating Funnel. A. BOLLAND (*Chem. Zeit.*, 1911, **35**, 373).—To an ordinary spherical-shaped separating funnel is added an extra tubulure in the upper quadrant of the sphere. Through this tubulure pass two tubes, fitted with stopcocks, and so arranged that the upper layer in the funnel can be removed without first running out the lower layer. Time and trouble are thus saved when a liquid has to be repeatedly extracted with a lighter solvent. T. S. P.

Lecture Experiment on the Extinction of Burning Light Petroleum, etc. P. RATHGEN (*Chem. Zeit.*, 1911, **35**, 308).—A wide-necked bottle contains sodium carbonate solution to which liquorice extract has been added. A tube with a thin bulb, containing hydrochloric acid, passes through the cork. On breaking the bulb by pushing down the tube, foam escapes from a delivery tube, and is directed on to the burning light petroleum. C. H. D.

Inorganic Chemistry.

Polymerised Water and Water of Crystallisation. Temperature and Conditions of Dehydration. Water of Crystallisation. AUGUSTE ROSENSTIEHL (*Bull. Soc. chim.*, 1911, [iv], **9**, 281—283, 284—291, 291—295).—Much uncertainty still exists as to the exact degree of polymerisation of water, although the balance of evidence seems to be in favour of water being a ternary mixture of the molecules H_2O, $(H_2O)_2$, and $(H_2O)_3$ (compare Abstr., 1910, ii, 842). The author suggests that definite evidence may be obtained from an examination of the water of crystallisation of different salts and the effect of temperature on their dehydration, the idea being that the state of polymerisation of the water in solutions from which the salts separate will be reflected in the amount of water of crystallisation taken up by the salts and the way in which it is bound. Such an examination shows that salts with water of crystallisation may be divided into three classes. The *first* class contains salts of the formulæ: R,H_2O; $R,2H_2O$, and $R,3H_2O$. All the water of crystallisation in each case is lost in one step. The *second* class contains salts with 3, 6, 9, 12, 15, 18, and 24 molecules of water of crystallisation, and, when dehydrated, the water of crystallisation is lost as $3H_2O$, or in multiples of $3H_2O$. The *third* class includes salts with 4, 5, 7, 8, and 10 H_2O. The manner in which such salts undergo dehydration shows that each salt contains two different kinds of water. For example, $CuSO_4,5H_2O$ is $CuSO_4,H_2O + 2(H_2O)_2$; $MgSO_4,7H_2O$ is $MgSO_4,H_2O + 3(H_2O)_2$; $Na_2CO_3,10H_2O$ is $Na_2CO_3,H_2O + 3(H_2O)_3$, etc.

The above considerations support the idea that water is a ternary mixture of H_2O, $(H_2O)_2$, and $(H_2O)_3$. T. S. P.

Oxidation of Iodine by Hydrogen Peroxide. VICTOR AUGER (*Compt. rend.*, 1911, **152**, 712—713).—The well-known decomposition of iodides by hydrogen peroxide in acid solution, whereby iodine is liberated, is followed by further oxidation to iodic acid, which is produced in theoretical amount if precautions are taken to keep the iodine in solution, for example, by the addition of hydriodic acid. The reaction only takes place in presence of hydrochloric or hydrobromic acid, and is represented by the equations: $2HCl + H_2O_2 = 2H_2O + Cl_2$; $I + 3Cl = ICl_3$; $5ICl_3 + 9H_2O \rightleftarrows 3HIO_3 + 15HCl + I_2$.

W. O. W.

The Rectilinear Diameter for Oxygen. ÉMILE MATHIAS and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 939—956. Compare Abstr., 1910, ii, 771, 829).—Between $-210°$ and $-120°$ the mean density of liquid oxygen and its saturated vapour can be represented very satisfactorily by means of the equation: $D = 0{\cdot}1608 - 0{\cdot}002265t$. This gives 0·4299 for the critical density.

The value of $RT_k/p_k.v_k$ for oxygen is 3·346, which is smaller than the values (3·4 to 3·9) for normal substances of higher critical temperature. Oxygen approaches therefore more closely the value (2·67) which is derived from van der Waals' equation. H. M. D.

Separation of Oxygen by Cold. JAMES SWINBURNE (*Trans. Faraday Soc.*, 1911, **6**, 212—224).—A discussion of the energy changes involved in the production of oxygen by the liquefaction of air. C. H. D.

The Nature of the Uppermost Layers of the Atmosphere. II. ALFRED WEGENER (*Physikal. Zeitsch.*, 1911, **12**, 214—222. Compare this vol., ii, 271).—Further observations are cited which afford information relative to the constitution of the outer layers of the earth's atmosphere. In particular, the nature and spectrum of the gases enclosed in meteorites, the spectra of shooting stars and of the polar light, and the nature of the zodiacal light are discussed. H. M. D.

The Production of Ozone at a Low Temperature and the Continuous Measurement of the Yield. ANDRÉ JOB (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. II., 143—145).—If the ozoniser is cooled by means of solid carbon dioxide and acetone, the proportion of ozone is largely increased. In order to determine the yield of ozone at any moment, the oxygen apparatus is provided with a pressure-indicator, and the escaping mixture of gases is caused to pass through a capillary tube. The fall of pressure in the manometer is due partly to the diminution of volume caused by ozonisation and partly to the changes in viscosity. The relation between the relative fall of pressure and the proportion of ozone having been determined by analysis, the reading of the manometer suffices. The viscosity of ozone is slightly less than that of oxygen.

By this means, the working of the coil and the flow of oxygen are readily adjusted to give the maximum yield of ozone. C. H. D.

New Method of Preparing Ozone by Chemical Means. P. MALAQUIN (*J. Pharm. Chim.*, 1911, [vii], **3**, 329—335).—A mixture of 20 grams of ammonium persulphate and 15 grams of nitric acid is placed in a specially designed glass apparatus consisting of a bottle, washing-cylinder, and delivery tube. Air is displaced by carbon dioxide, and the mixture in the bottle is carefully heated to 65—75°, at which temperature the exothermic reaction proceeds spontaneously. The liberated gases, after being washed by not too concentrated potassium or sodium hydroxide in the washing-cylinder, are collected and analysed; they consist of ozone 3—4% (sometimes

5%), nitrogen 4—4·5%, oxygen 94—95%, and carbon dioxide less than 1%. It is not advantageous to use larger quantities than those quoted, or to increase the proportion of nitric acid. The reaction cannot be represented by an equation. As regards security and ease of manipulation, the method exceeds all other chemical processes for the production of ozone. C. S.

Ultra-microscopic Observations. J. AMANN (*Zeitsch. Chem. Ind. Kolloide,* 1911, 8, 197—198. Compare Abstr., 1910, ii, 496, 617, 844).—The ultra-microscopic appearance of solutions of sulphur in carbon disulphide, carbon tetrachloride, benzene, amyl alcohol, and turpentine oil is described. Corresponding with the conversion of soluble ($S\lambda$) into insoluble ($S\mu$) sulphur under the influence of light, it is found that the exposure to light causes considerable changes in the ultra-microscopic character of the solutions. The transition from the amicroscopic to the micellary condition diminishes in velocity as the viscosity of the dispersive medium increases. The adsorption of the particles by the glass walls of the containing vessel decreases simultaneously.

Aqueous solutions of the polysulphides of the alkali and alkaline earth metals behave similarly. A solution of sodium hydrogen sulphide is also photosensitive, but the normal alkali metal sulphides are not influenced by light. H. M. D.

The Preparation of Colloidal Solutions of Sulphur of Different Degrees of Dispersity by Fractional Coagulation. SVEN ODÉN (*Zeitsch. Chem. Ind. Kolloide,* 1911, 8, 186—193).—Experiments on the coagulation of colloidal solutions of sulphur of different degrees of dispersity show that the electrolyte concentration which is necessary for coagulation increases as the suspended phase becomes more highly disperse. This observation is made the basis of a method of fractional coagulation which has been applied in the preparation of colloidal solutions of sulphur of different dispersities from Wackenröder's solution, sodium chloride being used as the coagulating electrolyte. In all, nine fractions were obtained, and the ultra-microscopic characters of the corresponding sols are described. The stability of the sols towards sodium chloride and hydrochloric acid has been examined, and in both cases it is found that the stability increases with the degree of dispersity of the sol, the differences being more marked in the case where hydrochloric acid is added. H. M. D.

Preparation of Pure Tellurium. ROBERT SCHELLE (*7th Intern. Congr. Appl. Chem.,* 1909, Sect. III A, 80—81).—Crude tellurium, containing 30—70% Te, together with copper and antimony, is prepared from Hungarian silver ores by the usual method. Purification by precipitation with sulphurous acid is unsuccessful on the large scale, copper not being completely removed, whilst gold and selenium are also retained.

If the crude tellurium is boiled with sodium sulphide solution and powdered sulphur, and sodium sulphite is added, a greyish-black precipitate of pure tellurium is obtained. Selenium, arsenic, tin, gold, and platinum are not precipitated by this method, whilst copper is removed by the initial treatment with sodium sulphide.

The process may also be applied to the estimation of tellurium, after fusing the ore with sodium carbonate and sulphur or with sodium thiosulphate.

The grey tellurium thus obtained is silvery-white after fusion. If fused under sodium hydrogen sulphate and cooled in carbon dioxide, a crystalline star, resembling that of antimony, is observed.

C. H. D.

The Relative Atomic Weights of Nitrogen and Sulphur. Frank P. Burt and Francis L. Usher (*Proc. Roy. Soc.*, 1911, *A*, **85**, 82—98).—The decomposition of nitrogen sulphide into nitrogen and sulphur has been used to determine the relative atomic weights of nitrogen and sulphur. The nitrogen sulphide was made by passing dry ammonia into a benzene solution of sulphur chloride, and repeated extraction of the product with pure dry benzene in a Soxhlet apparatus. It was then purified by sublimation in a vacuum over a roll of silver gauze at 100°, the product thus obtained consisting of large, orange-coloured, monoclinic crystals, which, when struck, or rapidly heated in the air, detonated violently; $D^{24} = 2{\cdot}24$, the density of the unsublimed sulphide being 2·20.

When sublimed in a vacuum over silver gauze heated at 360°, nitrogen sulphide is decomposed, the sulphur combining with the silver, but discrepant quantitative results were obtained, possibly because nitrogen is occluded by silver sulphide at the moment of its formation. A satisfactory method of decomposition was found, however, to consist in passing the vapours of nitrogen sulphide over quartz wool heated to bright redness in a quartz tube. After allowing for various errors, such as the diffusion of hydrogen from the flame into the quartz tube, the occlusion of air in the quartz wool, and the presence of gases absorbable by potassium hydroxide in the nitrogen, the ratio N/S is found to be $0{\cdot}43687 \pm 0{\cdot}000006$ (mean of seven experiments). Assuming that this ratio is correct, and that $14{\cdot}009 \pm 0{\cdot}001$ is the atomic weight of nitrogen, the atomic weight of sulphur may be taken as $32{\cdot}067 \pm 0{\cdot}002$. T. S. P.

Some Experiments on the Formation of Ammonia from its Elements. F. Alex. McDermott (*J. Amer. Chem. Soc.*, 1911, **33**, 515—517).—In view of recent papers by Lipski (Abstr., 1909, ii, 478) and Haber (*Chem. Zeit.* 1910, **34**, 345) on the direct synthesis of ammonia from its elements, an account is given of some qualitative experiments on the same subject. These consisted (1) of passing mixtures of hydrogen and nitrogen over several catalytic agents at various temperatures and under the ordinary pressure; (2) of passing mixtures of steam and nitrogen at the ordinary pressure over iron filings, zinc dust, and sodium amalgam, and (3) of passing electric sparks between platinum electrodes in a mixture of hydrogen, nitrogen, and hydrogen chloride under both ordinary and higher pressures.

In all cases, traces of ammonia were produced, but the yield was too small to render any of the processes of practical value. E. G.

Law Relating to the Solubility of Ammonia [in Water] at Different Temperatures and Pressures. A. BRICHAUX (*Bull. Soc. chim. Belg.*, 1911, **25**, 145—153).—From a consideration of the available data for the solubility of ammonia in water, the author finds that the ammonia content of a solution under given conditions is determined by what is called the differential temperature. This is the difference between the temperature of an ammoniacal solution of known vapour pressure and the temperature at which pure water boils at the same pressure. The influence of the differential temperature is such that aqueous ammoniacal solutions, saturated at different pressures and temperatures, will contain the same amount of ammonia if their differential temperatures have the same value.

From the tabulated data, this relationship appears to hold with considerable accuracy for solutions containing less than about 12% of ammonia. For more concentrated solutions, deviations are found, but these are comparatively small for solutions of which the vapour pressures are not widely different.

A method is described by means of which the law of differential temperatures can be examined experimentally. H. M. D.

Representation of the Vapour Pressures of Aqueous Ammoniacal Solutions. EDOUARD HERZEN (*Bull. Soc. chim. Belg.*, 1911, **25**, 154—157. Compare preceding abstract).—For solutions containing less than 14% of ammonia, the connexion between the differential temperature, θ, and the concentration, n, can be expressed by $\theta = 40{\cdot}191 - 18{\cdot}634\sqrt{4{\cdot}652 + n}$.

The vapour pressure at temperature t is given by

$$p = \left(\frac{233{\cdot}115 + 1{\cdot}4467t + 26{\cdot}957\sqrt{4{\cdot}652 + n}}{232{\cdot}809 + t + 18{\cdot}634\sqrt{4{\cdot}652 + n}}\right)^{50}.$$

A diagram has been constructed in which vapour pressure, temperature, and percentage concentration are plotted on three parallel lines separated from one another by definite distances. These distances are such that if points on any two of these axes are joined by a straight line, the point of intersection of this line with the third axis gives the value of the variable (pressure, temperature, or concentration) corresponding with this axis. H. M. D.

The Recognition of Solid Arsenic Hydride. HANS RECKLEBEN and JOHANNES SCHEIBER (*Zeitsch. anorg. Chem.*, 1911, **70**, 255—274).—There has been hitherto no agreement as to the composition and properties of solid hydrogen arsenide, the products usually obtained being indefinite mixtures containing arsenic. The formulæ H_2As, H_2As_2, and HAs_2 have been proposed. It is now shown that only one such compound exists, with the composition HAs or H_2As_2.

It is possible to analyse products of this kind by means of ammoniacal silver nitrate, which oxidises arsenic and its compounds according to the following equations: $As_2O_3 + 2Ag_2O = As_2O_5 + 4Ag$;

$As_2 + 5Ag_2O = As_2O_5 + 10Ag$; $2H_3As + 8Ag_2O = As_2O_5 + 16Ag + 3H_2O$; $H_2As_2 + 6Ag_2O = As_2O_5 + 12Ag + H_2O$. The ratio As : Ag is therefore 1 : 5 for metallic arsenic, but is less if the arsenic is combined with oxygen, and greater if it is combined with hydrogen. The solution is boiled out of contact with air, and the precipitated silver is weighed as such or after conversion into chloride.

[With K. STRAUSS.]—The yellow powder obtained when arsenic is sublimed in hydrogen proves to be arsenic, and a hydrogen compound is not formed (compare Retgers, Abstr., 1893, ii, 570; 1894, ii, 314).

The action of an electric discharge on arsenic trihydride in an ozoniser yields the solid compound As_2H_2 with some crystalline arsenic. The decomposition of sodium arsenide also yields the same compound. The action of arsenic trihydride on solid alkali hydroxide, followed by addition of water, yields a mixture of arsenic and the solid hydride. The reaction has been studied quantitatively, and is found to be: $AsH_3 + 3KOH = K_3As + 3H_2O$; $2K_3As + 6H_2O = As_2H_2 + 6KOH + 2H_2$. A similar mixture of arsenic and the solid hydride is obtained from mixtures of oxygen, hydrogen, and arsenic trihydride, whilst the deposit obtained on cooling an arsenic trihydride flame consists only of arsenic.

The solubilities given by Retgers for solid arsenic hydride really apply to yellow arsenic. C. H. D.

Formation of Graphite. WILHELM HEINISCH (*Monatsh.*, 1911, **32**, 225—239).—After a summary of what is known as to the formation of graphite, the author gives an account of the so-called "field-chalk" (Ackerkreide), which is found, for example, at Neubistritz on the borders of South Bohemia and Lower Austria. This field-chalk forms hard, dark grey masses of a graphitic nature, and, by appropriate treatment, graphitic acid is obtained from it. Examination shows it to consist mainly of portions of brick and of earthenware vessels, which may be only a few decades old, but in any case not more than a few centuries old. The graphite has probably been formed from humus substances which have penetrated into the porous material, and then been oxidised by absorbed oxygen. It is considered that this find shows that the graphite has not been formed by allotropic change from amorphous carbon, but directly by the degradation of the carbon compounds in the humus under the molecular forces existent in the fine pores of the "field-chalk." T. S. P.

Theory of the Formation of Graphite in Iron Alloys. E. HEYN (*Zeitsch. Elektrochem.*, 1911, **17**, 182).—Polemical (compare Jeriomin, this vol., ii, 289). T. E.

Action of Water Vapour on Carbon in Presence of Lime. LÉO VIGNON (*Compt. rend.*, 1911, **152**, 871—874*).—When steam is passed over a mixture of lime and carbon at 600—800°, three exothermic reactions occur: $C + CaO + 2H_2O = CaCO_3 + 2H_2$; $2C + CaO + 2H_2O = CaCO_3 + CH_4$; $3C + CaO + 2H_2O = CaCO_3 + C_2H_4$. In this way water is decomposed more rapidly and at a lower temperature than by carbon alone. Carbon monoxide is also formed by interaction of methane and water. In the experiments quoted, the proportion of methane varied from 7·92 to 28·05%, according to the amount and rate of flow of the steam.

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* and *Bull. Soc. chim.*, 1911, [iv], **9**, 420—422.

The bearing of these observations on the question of the formation of natural petroleum is discussed. W. O. W.

Constancy of the Ratio of Helium to Argon in Natural Gaseous Mixtures. Explanatory Hypothesis. CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1911, **152**, 934—937. Compare this vol., ii, 439).—The method recently described has been applied to determine the proportion of krypton to argon in gases from nineteen mineral springs, and one from a volcanic source. The ratio krypton : argon was almost constant in the samples examined ($6·1 \times 10^{-6}$—$9·2 \times 10^{-6}$), and did not differ much from the same ratio for air ($5·2 \times 10^{-6}$). Such constancy was to be expected from inert gases, which can only owe to physical causes local differences in proportion at different parts of the solar system. The wide variations met with in the proportions of helium in natural gases are accounted for by inequalities in the distribution of radioactive material from which it has been produced. W. O. W.

Temperature at which Alkali Metals Attack Water. L. HACKSPILL and ROBERT BOSSUET (*Compt. rend.*, 1911, **152**, 874—876). —The alkali metals were brought into contact with ice in a vacuum at −130°, and the containing vessel slowly allowed to attain the ordinary temperature. Commencement of reaction, detected by alteration of the pressure through liberation of hydrogen, was first apparent at the following temperatures: cæsium, −116°; rubidium, −108°; potassium, −105°; sodium, −98°. It is not possible to determine whether the action is due to water in the solid state or to the vapour from the ice. W. O. W.

An Acid Potassium Sulphate. WILLEM STORTENBEKER (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 329—332. Compare Abstr., 1903, ii, 143).—The primary potassium sulphate previously described has the formula $K_2SO_4,3KHSO_4,H_2O$. It crystallises in the monoclinic system [$a:b:c = 1·708:1:2·748$; $\beta = 113°59'$]. A. J. W.

The Mother Liquors of Salt Gardens (Marais salants). THÉOPHILE SCHLŒSING (*Compt. rend.*, 1911, **152**, 741—746).—The author has established some relationships between the density of the mother liquor from salt gardens in Tunis and the amount of salt crystallising out after a given loss of water by evaporation. The results are chiefly of industrial interest. W. O. W.

Decomposition of Sodium Chloride. ALEXANDER C. VOURNASOS (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. II., 109).—Sodium chloride and powdered lead react at a red heat according to the equation: $2NaCl + Pb = PbCl_2 + 2Na$. A closed furnace is used, and at the end of the operation the sodium is distilled off and either condensed or burnt in air, and the product converted into hydroxide. The lead chloride is fused and electrolysed. C. H. D.

Formation of Double Salts. III. Question of Double Salt Formation between the Alkali Sulphates. Harry W. Foote (*J. Amer. Chem. Soc.*, 1911, **33**, 463—468).—Solutions containing both sodium and potassium sulphates yield homogeneous crystals. Some investigators have claimed that these products are double salts, whilst others have asserted that they are mixed crystals. A study of this question has now been made by the solubility method, which consists of shaking the salts with water and determining the composition of the solution and residue. The results show that a limited series of mixed crystals is present, and that a double salt is not formed (compare van't Hoff and Barschall, Abstr., 1906, ii, 666). The limiting values of the series at 25° are about 78·6% of sodium sulphate and 73·9% of potassium sulphate.

A similar study of mixtures of sodium and cæsium sulphates has shown that in this case neither double salts are formed nor mixed crystals analogous to those of the sodium and potassium sulphates, but that the crystals obtained are a mechanical mixture of the two salts. E. G.

Some New Compounds of Nitrogen and Hydrogen with Lithium. Franz W. Dafert and R. Miklauz (*Ber.*, 1911, **44**, 809—810. Compare this vol., ii, 39).—A reply to Ruff and Goerges (this vol., ii, 280). The authors do not agree with the view that the compounds Li_3NH_4 and Li_3NH_2 are mixtures, for the following reasons: (1) Lithiumimide is easily decomposed on exposure to sunlight, according to the equation: $2Li_2NH = Li_3N + LiNH_2$, at the same time becoming coloured intensely red (Mentrel, *Diss.*, Nancy, 1902). Trilithiumamide is not sensitive to sunlight, and therefore cannot be a mixture of lithiumimide and lithium hydride; (2) the conversion of Li_3NH_4 into Li_3NH_2 is a reversible process, which cannot be accounted for by Ruff and Goerges' explanation, and (3) analogy to tricalciumamide is not in favour of trilithiumamide being a mixture of lithiumamide and hydride. T. S. P.

Ammonium Sulphate and its Instability. The Hydrolytic Dissociation of Ammonium Salts. Watson Smith (*J. Soc. Chem. Ind.*, 1911, **30**, 253—256).—The statement, repeated in most text-books, that ammonium sulphate melts at 140° is erroneous. Powdered ammonium sulphate loses ammonia even below 100°, and at 300° is completely converted into molten ammonium hydrogen sulphate, which melts at 140° after solidification. It is not possible to sublime this salt.

When a solution of ammonium chloride is distilled, the first portions of the distillate are alkaline, but contain small quantities of chloride. When the residue approaches the crystallising point, the distillate becomes acid. Other ammonium salts behave similarly. A solution containing 1 gram-mol. of sodium ammonium phosphate per litre loses 31% of its ammonia at the boiling point, whilst a *N*/500-solution loses

79·4%. In separating lime and alumina by Rose's method, it is necessary to use a delicate indicator, in order to stop boiling at the first appearance of acidity in the solution. Hendrick's method for the estimation of lime in slag (*ibid.*, 1909, **28**, 775) is liable to error from the same cause. C. H. D.

Density of Ammonium Sulphate Solutions. HUGO WIENER (*Zeitsch. physiol. Chem.*, 1911, **71**, 120—124).—The Landolt-Börnstein tables connecting concentration and density of ammonium sulphate solutions, based largely on figures obtained by Schiff by interpolation, are incorrect. The saturated solution, D 1·248, contains 53·2% of ammonium sulphate; the three-quarters saturated solution, D 1·195, contains 39·9%; the half saturated solution, D 1·138, contains 26·6%; the one-quarter saturated solution, D 1·077, contains 13·3%, and the one-eight saturated solution, D 1·039, contains 6·65%. E. F. A.

The Differently-coloured Forms of Silver. LÜPPO-CRAMER (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 143—146).—Experiments are described in support of the view that the differently-coloured forms of colloidal silver are due to differences in the size of the colloidal particles.

To separate portions of a solution containing gelatin and silver nitrate, varying quantities of a 0·05% solution of colloidal silver, obtained by reduction with dextrin, were added as catalyst, and this was followed by the addition of a constant quantity of an alcoholic solution of quinol. In the absence of catalyst, the resulting colloidal solution has a bluish-grey colour, and, as the quantity of catalyst increases, the colloidal silver changes successively to pure blue, bluish-violet, ruby-red, and yellowish-brown. Since the size of the colloidal particles must diminish as the number of the nuclei increases, it follows that these successive changes in colour are due to the gradual diminution in the size of the silver particles. In agreement with this view it is found that the addition of successive quantities of silver nitrate and quinol to the yellowish-brown solution brings about the same series of colour changes. Insolation of the gelatin silver nitrate solutions for different time intervals previous to addition of the reducing agent, gives rise to similar colour differences in the colloidal solutions which are obtained, and this result can be readily interpreted in terms of the above view. H. M. D.

Replacement of Metals in Non-aqueous Liquids and the Solubility of Metals in Oleic Acid. CHARLES BALDWIN GATES (*J. Physical Chem.*, 1911, **15**, 97—146. Compare Sammis, Abstr., 1906, ii, 835).—Silver is precipitated by metallic copper from pyridine solutions of its abietate, citrate, tartrate, and succinate. Copper can be precipitated from dehydrated solutions of many of its organic salts. The amount of copper salt dissolving without decomposition in any of the seventeen purified and dried organic solvents used never exceeded 5%

The conductivity of the nitrobenzene, carbon disulphide, carbon tetrachloride, toluene, pentane, ethyl benzoate, ethylene dibromide, ether, pinene, and oleic acid, was less than 2×10^{-10} mhos. Benzaldehyde, amyl alcohol, acetone, ethyl alcohol, pyridine, acetaldehyde, and acetonitrile had conductivities ranging from 35×10^{-8} to 71×10^{-7}. The conductivities of the copper solutions were of the same order of magnitude, and usually somewhat higher than the conductivity of the pure solvent.

Copper may be precipitated by the metals lead, zinc, cadmium, tin, bismuth, antimony, mercury, silver, iron, nickel, cobalt, aluminium, magnesium, sodium, potassium, and calcium, but whether action will occur in any particular combination depends on the specific nature of the acid radicle and the solvent, the latter being the more important factor.

In some trials, precipitated copper could be noticed within ten minutes, but the experiments usually extended over several days. The general conclusions were unaffected when specially purified solvents of less conductivity than the above were used, and the solutions were heated for twenty-five days.

Undoubted deposition of copper was observed 169 times, and in a large number of trials some interaction of less pronounced character was indicated. Often the immersed sheet of metal assumed a brassy appearance, supposed to be due to formation of alloy. Neglecting the doubtful cases, benzaldehyde appears to be the most favourable solvent and carbon disulphide the least. Of the salts, copper camphorate reacted most frequently and hexoate least. The order of activity of the metals is cadmium, lead, zinc, bismuth, magnesium, cobalt, tin, iron, aluminium, silver, antimony, and nickel. Mercury should probably be placed between tin and iron, but owing to its solvent properties the deposition of metallic copper was never observed on it. The order of the metals is entirely different from the electrochemical series. Many of the experiments were duplicated in sealed tubes to exclude atmospheric moisture without any difference in the result.

Copper palmitate, stearate, and margarate melt without decomposition at 200°, 240°, and 255° respectively, giving non-conducting liquids which are presumably anhydrous. Copper is immediately deposited from these fused salts on lead, zinc, tin, and bismuth, more slowly on cadmium, antimony, mercury, cobalt, nickel, magnesium, and sodium, and is not deposited on aluminium, silver, platinum, and iron. The order of the metals is again anomalous. In the case of fused inorganic salts the replacement phenomena are in general agreement with the electrochemical series.

Oleic acid dissolves many metals at room temperature with evolution of hydrogen, although its conductivity is less than 2×10^{-10} mhos. In two years, 0·1875 gram of copper was dissolved by 3 c.c. of oleic acid.

Sodium, potassium, and calcium are rapidly dissolved at room temperature, and copper, zinc, lead, and cadmium at 100°. With prolonged heating, tin, magnesium, iron, bismuth, and mercury are appreciably dissolved, whilst antimony, nickel, gold, platinum, silver, chromium, aluminium, and cobalt amongst others are unattacked.

The solvent action of oleic acid on zinc–tin alloys increases with the zinc content. R. J. C.

Decomposition of Calcium Carbide by Heat. GEORG ERLWEIN, C. WARTH, and REINHARD BEUTNER (*Zeitsch. Elektrochem.*, 1911, **17**, 177—179).—When calcium carbide is heated, the quantity of acetylene evolved by treating it with water gradually diminishes. For example, a sample which contained 63% of carbide after heating for three hours at 500°, only contained 36·6% after thirty hours at 1000°. The substance becomes black during the heating, and the decomposition is accelerated by the addition of calcium salts or sodium chloride; calcium fluoride is especially active, for example, a mixture containing 10% of this salt gave no acetylene after three hours' heating at 1260°. Notwithstanding the decomposition of the carbide, the heated substances are still able to absorb nitrogen. The last-mentioned sample, after adding 10% more calcium fluoride, absorbed 12·5% of nitrogen, and similar results were obtained in other cases. The heated material evolves no hydrogen when treated with water, and it is therefore free from calcium. T. E.

Action of a Solution of Sodium Hydroxide on Tricalcium Phosphate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 10—11).—Calcium phosphate is not acted on by a strong solution of sodium hydroxide on heating for eighty-seven hours at 97—98°. Some sodium silicate is dissolved from the glass of the flask, and the filtrate from the calcium phosphate gives a slight precipitate of silicic acid on the addition of ammonium oxalate.

There is a tendency for the calcium phosphate to assume temporarily the colloidal state. T. S. P.

Action of Sodium Carbonate on Calcium Carbonate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1911, 10).—A solution of pure sodium carbonate has no action on pure precipitated calcium carbonate (compare Abstr., 1910, ii, 846). T. S. P.

Gases Disengaged from the Walls of Tubes of Glass, Porcelain, and Silica. MARCEL GUICHARD (*Compt. rend.*, 1911, **152**, 876—879).—The liberation of gases from the walls of heated tubes was followed by determining variations in pressure by means of the MacLeod guage. A Jena glass tube, area 100 sq. cm., gave about 0·05 mg. of gas at 600°. A porcelain tube, heated area 117 sq. cm., gave, on prolonged heating at 1170°, 2·1 c.c. of gas at 746 mm., composed of 0·3 c.c. CO_2, 0·3 c.c. O_2, 1·5 c.c. N_2. This appeared to come from minute bubbles in the enamel. A silica tube at 1040°, with an area of 130 sq. cm., gave 2·45 c.c. of gas containing equal volumes of carbon monoxide and hydrogen with a little carbon dioxide. W. O. W.

Monohydrate of Barium Chloride. AAGE KIRSCHNER (*Zeitsch. physikal. Chem.*, 1911, **76**, 174—178).—The monohydrate is prepared by shaking barium chloride dihydrate with 99% methyl alcohol, and filtering at once through a Buchner funnel to remove the small amount of undissolved salt; after a few minutes the monohydrate separates from the solution in colourless, rhombic plates. It cannot be completely dried by suction, as in these circumstances the dihydrate forms, but can be dried readily over calcium chloride in a vacuum. At 14°, 100 c.c. of methyl alcohol dissolve about 2·5 grams of the monohydrate. G. S.

Cadmium Sulphate and the Atomic Weight of Cadmium. W. L. PERDUE and GEORGE A. HULETT (*J. Physical Chem.*, 1911, **15**, 155—165).—Purified cadmium sulphate was obtained in hydrated crystals of the formula $CdSO_4,\frac{8}{3}H_2O$. To avoid included mother liquor, the clearest crystals were picked out and rapidly wiped with thin rubber sheet. The hydrate appears to be stable in a dry atmosphere. On heating, the water is removed, and there is a loss of cadmium sulphate by dissociation (into $SO_3 + CdO$, both being volatile). The percentage of water was found to be 18·733 as the mean of nine determinations by heating at 700° in a current of air containing sulphur trioxide to prevent dissociation. Although this value is very near the calculated, it was found that there had been a loss of 0·011% of cadmium sulphate, so that dehydration was not complete. Cadmium was determined by the authors' electrolytic method (compare this vol., ii, 433).

Seven determinations gave the value 43·799 as the mean percentage of cadmium in the crystalline hydrate.

The atomic weight, $Cd = 112{\cdot}30$ ($H = 1{\cdot}008$), requires 43·797%, whereas the value at present in currency, namely, 112·40, requires 43·819% of cadmium in the crystalline hydrate. R. J. C.

Mercuric Oxychlorides. DRIOT (*Compt. rend.*, 1911, **152**, 958—960).—Only four oxychlorides of mercury are stated to exist. The product obtained by heating mercuric oxide with mercuric chloride in sealed tubes has the composition $HgCl_2,2HgO$. The four salts are all formed when mercuric oxide is boiled with the chloride in aqueous solution for eight hours. When the latter is in 0·5—4% solution, the compound $HgCl_2,3HgO$ separates on cooling, in yellow to black needles. Solutions containing 4—8% of mercuric chloride yield $HgCl_2,2HgO$ in small, black rhombohedra. A 30% solution yields a mixture of the foregoing, separable by levigation from the pale yellow substance, $2HgCl_2,HgO$. The compound $HgCl_2,HgO$ is prepared by heating the oxide for six days with a 30% solution of mercuric chloride at 100°. W. O. W.

Formation of Double Salts. II. Double Cæsium Mercuric Chlorides Forming from Acetone. HARRY W. FOOTE and F. L. HAIGH (*J. Amer. Chem. Soc.*, 1911, **33**, 459—462).—In the earlier paper (Abstr., 1910, ii, 505) it has been shown that when a double salt is formed containing the solvent, the latter is an essential constituent, and that on substituting one solvent for another, an entirely different type of salt may be produced, or the formation of a double salt may be prevented.

In the case of double salts which do not contain the solvent, it would be expected that the same salt would be produced whatever the solvent employed. In order to test this, an investigation has been made of the five anhydrous cæsium mercuric chlorides described by Wells (Abstr., 1892, ii, 68) and also studied by Foote (Abstr., 1903, ii, 728). The solubility method was employed as in previous work. The results show that the same anhydrous double salts are produced when acetone is used as the solvent as when water is used.

E. G.

Dimercurammonium Compounds. HENRI GAUDECHON (*Ann. Chim. Phys.*, 1911, [viii], **22**, 145—247. Compare Abstr., 1907, ii, 621, 667; 1908, ii, 85, 188, 383; 1909, ii, 670; 1910, ii, 296).—A résumé of work already published.

The only compound of dimercurammonium chloride with mercuric chloride is stated to be that having the constitution $2NHg_2Cl,HgCl_2$. This is formed when a hot concentrated solution of mercuric chloride is treated with an equimolecular amount of ammonia, or by the action of mercuric chloride on the monohydrate of dimercurammonium chloride. It is slightly decomposed by water and readily by potassium hydroxide, but attempts to prepare the corresponding base in this way were not successful. Measurement of the heat of dissolution in aqueous potassium cyanide confirmed the formula ascribed to the compound. Aqueous ammonia gives rise to a mixture of NHg_2Cl,NH_4Cl and NHg_2Cl,H_2O.

The corresponding bromine derivative, $2NHg_2Br,HgBr_2$, has been obtained as a yellow powder, converted by hot water into the compound $4NHg_2Br,HgBr_2$. The existence of the hydrate, NHg_2Br,H_2O, is doubtful. Unlike the chlorine compound, it is not formed by the action of the halogen hydride on the base, $(NHg_2)_2O,4H_2O$, the product obtained in this way being anhydrous. When dimercurammonium bromide is treated with gaseous ammonia under pressure, it changes into a red compound, $2NHg_2Br,NH_3$, which is much less stable than the corresponding chlorine derivative. When allowed to remain over phosphoric oxide, it loses ammonia and forms the compound, $4NHg_2Br,NH_3$. The latter has a great affinity for water, and on exposure to the air changes into a hydrate, $4NHg_2Br,NH_3,H_2O$.

W. O. W.

Alterability of Aluminium. HENRI LE CHATELIER (*Compt. rend.* 1911, **152**, 650—652).—The spontaneous crumbling of hammered aluminium is accompanied by very slight chemical change. Microscopically, an altered specimen shows a network of minute fissures, giving the surface a cellular appearance. The paper is illustrated with four microphotographs. W. O. W.

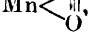
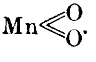
Thermic Reactions in a Vacuum. I., II., and III. FRANK E. WESTON and H. RUSSELL ELLIS (*Trans. Faraday Soc.*, 1911, **6**, 144—147, 148—150, 151—154).—Mixtures of the nature of thermit have been ignited electrically in an exhausted vessel. Mixtures of aluminium powder and sodium peroxide ignite violently when moistened in air, but only a slow evolution of gas is observed in an exhausted vessel. The reduction of silica by magnesium in absence of air yields a mixture containing magnesium, magnesium silicides, silica, and free silicon. It has not been found possible to make a complete analysis. C. H. D.

Manganese Arsenides. G. Arrivaut (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. II., 100—103).—Arsenic combines with manganese at 500° with incandescence. The arsenide Mn_2As, stable at high temperatures, is grey and non-magnetic. At 700—800°, in a current of hydrogen, the arsenide obtained has the composition Mn_3As_2, and is highly magnetic. The highest arsenide, stable only below 400—450°, has the formula MnAs, and is highly magnetic. This compound is also obtained by the action of arsenic chloride on manganese, incandescence taking place at 500°. C. H. D.

Colloidal Manganese Dioxide and its Behaviour towards Hydrogen Peroxide. Georg Bredig and A. Marck (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 342—355).—Colloidal solutions of manganese dioxide can be conveniently prepared by the action of hydrogen peroxide on a neutral solution of potassium permanganate. The hydrogen peroxide solution should not contain more than 3% and the permanganate solution not more than 16 grams per litre. The resulting brown solution is then subjected to dialysis until the electric conductivity reaches a constant value.

Colloidal solutions prepared in this way exhibit large numbers of ultramicroscopic particles. Coagulation takes place on addition of salts, although potassium permanganate is without effect. Acids also bring about coagulation, but small quantities of alkali hydroxides have apparently no influence on the stability of the solutions. The stability is dependent on the conditions of preparation, and increases with the dilution of the hydrosol. In presence of gelatin, flocculation by neutral salts is not brought about so readily. The colloidal particles move toward the anode in an electric field.

Hydrogen peroxide is decomposed rapidly by colloidal manganese dioxide in strongly alkaline solution, but the rate of decomposition diminishes rapidly with the concentration of the alkali. In the absence of free alkali, no catalytic decomposition is observed, and the solution obtained in these circumstances is quite colourless.

In the further investigation of the cause of the disappearance of the brown colour, it has been found that freshly precipitated manganese dioxide dissolves to an appreciable extent in concentrated hydrogen peroxide solution cooled to − 20°. At the ordinary temperature the resulting solution evolves oxygen very readily. It is supposed that a manganous salt of hydrogen peroxide is present in the colourless solution; this salt,  $\mathrm{Mn}{<}\begin{smallmatrix}\mathrm{O}\\|\\\mathrm{O}\end{smallmatrix}$, is isomeric with manganese dioxide,  $\mathrm{Mn}\begin{smallmatrix}=\mathrm{O}\\=\mathrm{O}\end{smallmatrix}$.

Further experiments relate to the kinetics of the catalytic decomposition in its dependence on the concentrations of the colloidal manganese dioxide, the hydrogen peroxide, and alkali hydroxide. Substances, such as hydrogen sulphide, hydroxylamine, mercuric cyanide, potassium cyanide, iodine, carbon monoxide, and mercuric chloride, which act as "poisons" in the decomposition of hydrogen peroxide by colloidal metals, exert no depressing influence on the activity of manganese dioxide. On the other hand, disodium hydrogen phosphate reduces appreciably the rate of the reaction, and this is attributed to the formation of manganese phosphates. In presence of mercuric chloride, the hydrogen peroxide is more rapidly decomposed, and this is probably due to the simultaneous action of the colloidal mercury which is formed by reduction of the mercuric chloride by the hydrogen peroxide, in which reaction, also, the colloidal manganese dioxide acts as a catalyst. H. M. D.

The Thermal Formation of Manganates. IV. OTTO SACKUR (*Ber.*, 1911, **44**, 777—787).—From the results of previous investigations (Abstr., 1910, ii, 214, 215) the author had come to the conclusion that the compound formed when an oxide of manganese is fused with potassium carbonate in a current of air has the composition $Mn_5O_{13},5K_2O$. Having since found, however, that a mixture of manganic oxide and potassium carbonate evolves a small amount of carbon dioxide when heated to a dark red heat without any manganate being formed, it was necessary to repeat the experiments, since the former ones depended on the measurement of the evolved carbon dioxide. Different mixtures of well dried potassium carbonate and manganic oxide were rapidly fused in a platinum crucible, and heated for varying lengths of time in a current of air, the evolved carbon dioxide being absorbed and weighed; the contents of the crucible were extracted with water, and the amounts of manganese and active oxygen in the solution determined. The results show that there is no very definite relation between the oxygen absorbed and the amount of carbon dioxide evolved, but they point to the formation of a compound $Mn_5O_{13},8K_2O$. This compound is supposed to be formed according to the successive reactions: $5Mn_2O_3 + 10K_2CO_3 + 11O = 2(Mn_5O_{13},5K_2O) + 10CO_2$, and

$$2(Mn_5O_{13},5K_2O) + 6K_2CO_3 = 2(Mn_5O_{13},8K_2O) + 6CO_2.$$

The evidence in favour of the formation of the compound

$$Mn_5O_{13},5K_2O$$

is obtained from the author's former results (*loc. cit.*) and from those of Askenasy and Klonowsky (Abstr., 1910, ii, 297), and by further experiments in which it is shown that at 900—950° manganic oxide and potassium carbonate interact in an atmosphere of nitrogen according to the equation: $19Mn_2O_3 + 5K_2CO_3 = Mn_5O_{13},5K_2O + 11Mn_3O_4 + 5CO_2$. Further evidence in favour of the formula

$$Mn_5O_{13},8K_2O$$

was obtained by analysis of a fusion (in air) from known weights of manganic oxide and potassium carbonate, the amount of manganese, active oxygen, and carbon dioxide being determined. If this compound is looked on as an additive compound of quadri- and sexa-valent manganese, it may be formulated as $2(MnO_2,K_2O),3(MnO_3,2K_2O)$, that is, a potassium mangani-manganate.

Similar experiments in which potassium carbonate was replaced by sodium carbonate point to the formation of a compound

$$Mn_2O_5,4Na_2O$$

or $(MnO_2,2Na_2O),(MnO_3,2Na_2O)$, an intermediate sodium manganite, $MnO_2,2Na_2O$, being formed.

It is noteworthy that sodium and potassium carbonates give such different results, and also that such complex molecules are formed at high temperatures, the usual tendency under such conditions being for the complex molecules to break down into simpler ones.

T. S. P.

The Passivity of Metals. WLADIMIR A. KISTIAKOWSKY (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. X., 56—57).—Dilute solutions of nitric acid, chromic acid, or potassium permanganate have a periodic action on iron, chromium, and magnesium, the metal becoming, under certain conditions, alternately active and passive (compare Abstr., 1908, ii, 249). The phenomena are explained by the formation of a thin passive film of oxide, which then becomes torn. C. H. D.

The Corrosion of Iron. A Historical Correction. J. NEWTON FRIEND (*Chem. News.*, 1911, **103**, 138).—Crum Brown is generally referred to as the originator of the acid theory of the corrosion of iron, although in his original paper he, himself, does not make the claim. Historical investigation shows that the formulation of the theory was one of gradual development up to the time of Crace Calvert, and that this investigator was the first to give clear expression to the same, in a paper read before the Manchester Phil. Soc., Jan. 24th, 1871. T. S. P.

The Chemical Physics Involved in the Precipitation of Free Carbon from the Alloys of the Iron-Carbon System. WILLIAM H. HATFIELD (*Proc. Roy. Soc.*, 1911, **85**, *A*, 1—13).—Graphite is formed by the decomposition of cementite after solidification, and its arrangement depends on the original structure. Annealing carbon is a mixture of finely-divided iron and carbon occupying the position of the original cementite. Silicon and manganese are not uniformly distributed through the iron, the cementite containing relatively more manganese and less silicon than the matrix. In the case of iron rich in sulphur, the silicon in the cementite is abnormally low. Silicon renders the carbide less stable, and manganese and sulphur more stable, but at 1050° even 3% of manganese or 0·45% of sulphur fail to render the carbide stable. The separation of carbon in steel, forming " black steel," only occurs in steels containing free cementite.

C. H. D.

Guignet's Green. LOTHAR WÖHLER and W. BECKER (*Zeitsch. angew. Chem.*, 1911, **24**, 484—487).—Eibner and Hue have recently criticised (*Farbenzeit.*, 1910, **15**, 2106, 2157, 2213, 2268, 2319) the authors' views as to the constitution of Guignet's Green (compare Abstr., 1908, ii, 765).

The authors maintain their thesis that the differences observed by them are simply due to hydration isomerism. At the same time a correction is made, in that the densities of both isomerides are now found to be 2·9, instead of 3·3 as stated originally. T. S. P.

The Electrolytic Reduction of Tungstic Acid.

ARTHUR ROSENHEIM and R. BERNHARDI-GRISSON (*7th Intern. Congr. Appl. Chem.*, 1911, Sect. X., 120—127).—The electrolytic reduction of tungstic acid has hitherto given unsatisfactory results, on account of the very sparing solubility of tungstic acid in such acid solvents as do not, like phosphoric acid, form complexes with it.

Tungstic acid dissolves in 50% hydrofluoric acid to the extent of 44·7% at 25° and 55·3% at 50°. It dissolves in hydrochloric acid at 80°, hydrogen chloride being passed into the solution until 100 grams contain 0·68 gram. Alcoholic hydrogen chloride, saturated at 75°, dissolves 9·8%. Alcoholic solutions of hydrogen bromide and iodide are without solvent action. The alcoholic hydrogen chloride solution may be diluted with fuming aqueous hydrochloric acid without precipitation taking place. Using a graphite anode, reduction only proceeds as far as quinquevalent tungsten with a platinum cathode. If the cathode is of mercury or lead, the extent of the reduction varies with the current density, whilst with a zinc cathode reduction rapidly proceeds as far as the tervalent stage, as determined iodometrically. The change of colour is through blue and green to brown. Metallic tungsten is not obtained.

Hydrofluoric acid solutions may be electrolysed in a V-tube, of which the anode limb is made of lead, and the cathode limb of cardboard impregnated with celluloid. The cathode is mercury, and the anode a platinum wire. Much ozone is liberated. Reduction only proceeds as far as the blue quinquevalent compound. This solution is very unstable in air, whilst the brown quadrivalent compound is stable, but gradually deposits a black decomposition product.

The original acid solution of tungstic acid yields crystalline precipitates with pyridine and quinoline hydrochlorides, having the composition WO_2Cl_2,C_5NH_5,HCl and WO_2Cl_2,C_9NH_7,HCl respectively. The blue reduced solutions yield a deep blue, crystalline powder or green needles, of variable composition, but if reduced until green, the precipitate consists of golden-brown, glistening needles, of the composition $W_6O_7Cl_{18},6(C_5NH_5,HCl)$. C. H. D.

The Constitution of the Metatungstates.

HIPPOLYTE COPAUX (*Zeitsch. anorg. Chem.*, 1911, **70**, 297—300).—The loss of water by barium metatungstate on heating is not consistent with the formula, $M_2\left[WO\begin{cases}(WO_4)_3\\(H_2O)_3\end{cases}\right]$, proposed by Rosenheim and Kohn (this vol., ii, 116), but accords with the formula proposed by the author (Abstr., 1909, ii, 318), namely, $6M_2O,3H_2O,24WO_3$. The uncertainty of dehydration measurements, however, makes other methods of determining constitution preferable, and the isomorphism with other complex salts of which the constitution is known favours the second formula.

C. H. D.

The Formula of Uranium Carbide. PAUL LEBEAU (*Compt. rend.*, 1911, **152**, 955—958).—Moissan's formula for uranium carbide, U_2C_3, is rejected owing to the possibility of errors in the analytical method adopted. By determining the amount of free graphite and of uranium in a specimen of the substance containing but little uncombined carbon, the author has arrived at the formula UC_2, which brings it into line with the carbides of the rare earth metals. To avoid the presence of hydrocarbons in the graphite, the sample analysed was triturated under vaselin, washed with anhydrous ether, and then decomposed by dilute nitric acid. W. O. W.

Determination of the Molecular Weight of Uranous Oxide. WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1911, **152**, 711—712). —Uranyl chloride was heated to dull redness in a current of hydrogen. The mean of five determinations gave 270·07 as the molecular weight of uranous oxide, adopting 238·5 as the atomic weight of uranium.
W. O. W.

The Hydrates of Uranyl Nitrate. PAUL LEBEAU (*Bull. Soc. chim.*, 1911, [iv], **9**, 298—300. Compare Abstr., 1909, ii, 736; 1910, ii, 1072).—Uranyl nitrate trihydrate, $UO_2(NO_3)_2,3H_2O$, is obtained by the dehydration of the hexahydrate over concentrated sulphuric acid at the ordinary temperature and pressure. The same salt is obtained by dehydration in a vacuum with a small quantity of calcium oxide.

Uranyl nitrate dihydrate, $UO_2(NO_3)_2,2H_2O$, is obtained by evaporation, at the ordinary temperature, of an ethereal solution of uranyl nitrate hexahydrate which has been dried with calcium nitrate. It is soluble in dry ether to the extent of 52·39% at 7° and 54·25% at 10°. T. S. P.

Two New Compounds of Stannous Chloride with Ammonia. ATH. J. SOFIANOPOULOS (*Compt. rend.*, 1911, **152**, 865—867).—The nature of the compounds of stannous chloride with ammonia depends on the temperature at which the two substances are allowed to combine. When the dry materials are cooled in a freezing mixture, a yellow powder is produced, having the composition $SnCl_2,2NH_3$. This substance blackens on exposure to light, and is decomposed by moisture into stannous oxide and ammonium chloride. If ammonia and stannous chloride react at the ordinary temperature, a mixture of the foregoing with Persoz's compound, $SnCl_2,NH_3$, is formed (*Ann. Chim. Phys.*, 1830, [ii], **44**, 315). The latter is the sole product at 100°. At 120—300° a third substance, $3SnCl_2,2NH_3$, is formed. This occurs as a brownish-red, crystalline mass, D^{12} 3·94, showing strong double refraction. It is the most stable of the three compounds, but is slowly decomposed by water.
W. O. W.

Preparation of Arsenic Amalgam. ERNEST DUMESNIL (*Compt. rend.*, 1911, **152**, 868—869).—Ten grams of arsenious oxide dissolved in 100 grams of concentrated hydrochloric acid are treated with 40·65 grams of mercuric chloride in 700—800 grams of dilute hydrochloric acid (1 : 5). After filtration, 60 grams of sodium hypophosphite are added, the mixture is shaken from time to time, and allowed to remain for several hours. On heating to boiling, a black precipitate of microscopic, mamellated crystals appears. These approximate in composition to the formula Hg_3As_2. W. O. W.

Thorium Peroxide. F. Calzolari (*Atti R. Accad. Sci. Torino*, 1911, **46**, 195—202. Compare Pissarjewski, Abstr., 1902, ii, 565).—The author has investigated the composition of the hydrated thorium peroxide which is precipitated when hydrogen peroxide acts on solutions of thorium salts. The method adopted consisted in the estimation of the excess of hydrogen peroxide and of the liberated acid present in an aliquot portion of the clear solution after the precipitate had settled. The precipitate obtained by the action of hydrogen peroxide on thorium nitrate contains for every two atoms of thorium, three atoms of active oxygen and two equivalents of combined nitric acid. The precipitate which separates from solutions of thorium chloride contains for every two atoms of thorium, three atoms of active oxygen and one equivalent of hydrogen chloride. From solutions of thorium sulphate, precipitates are obtained which contain for every two atoms of thorium, two equivalents of combined sulphuric acid and either two or three atoms of active oxygen, according to the conditions. In no case do the active oxygen and liberated acid reach the proportions given by Pissarjewski.

When to a dilute (about 2%) solution of thorium chloride an excess of 1% hydrogen peroxide solution is added, no precipitate forms, but thorium peroxide is present in the liquid in colloidal form. The pure colloidal solution may be prepared by dialysis. It evolves oxygen on warming, but remains clear; addition of an electrolyte (ammonium chloride) causes precipitation. R. V. S.

The Recognition of a Solid Antimony Hydride. Hans Reckleben and Johannes Scheiber (*Zeitsch. anorg. Chem.*, 1911, **70**, 275—281. Compare this vol., ii, 390).—Deposits containing antimony and hydrogen may be analysed iodometrically, the ratio Sb : I being 1 : 5 for antimony, less if an oxide is present, and greater if the antimony is combined with hydrogen. No evidence has been found for the existence of a solid antimony hydride.

[With K. Strauss.]—The action of the silent electric discharge on antimony trihydride yields only antimony and hydrogen, and metallic antimony is obtained when alkali antimonides are decomposed. Explosive antimony does not contain hydrogen, and is free from any but traces of chlorine (compare Cohen and Strengers, Abstr., 1905, ii, 532). C. H. D.

The Action of Hydrogen and Sodium Peroxides on Bismuth Salts. Josef Hanuš and O. Kallauner (*Zeitsch. anorg. Chem.*, 1911, **70**, 232—239).—When a solution of bismuth nitrate is precipitated by means of ammoniacal hydrogen peroxide, a yellow product is obtained, which sets free iodine from potassium iodide, and gives a transient red coloration with manganous sulphate and nitrous acid. If the precipitate is heated in a tube connected with a second tube containing copper gauze, in a stream of carbon dioxide, the oxygen present as active oxygen and as nitrate is estimated by the increase in weight of the gauze, whilst nitrogen is collected over potassium hydroxide and measured.

None of the preparations obtained give constant results on analysis. The proportion of active oxygen is increased by greater alkalinity of the solution, higher temperature, and excess of the oxidising agent. The yellow product is decomposed by sulphuric acid, liberating oxygen, and dissolves slowly in cold nitric acid. The brown product obtained when sodium peroxide is used is not decolorised by boiling for five minutes with water. C. H. D.

Some Definite Bismuthides. ALEXANDER CH. VOURNASOS (*Compt. rend.*, 1911, **152**, 714—715.)—The freezing-point curves for alloys of bismuth and sodium reveal the existence of *sodium bismuthide*, $BiNa_3$. This substance was isolated as small, grey lamellæ by adding bismuth to excess of sodium fused beneath paraffin, the excess of alkali metal being removed with liquid ammonia. *Potassium bismuthide*, BiK_3, was prepared in the same way; the reaction was strongly exothermic.

The alkali bismuthides are readily oxidised on exposure, and burn in air, forming red bismuthates. They absorb hydrogen at 350°, and the product, on treatment with water, yields an unstable solid, probably bismuth hydride. W. O. W.

Definite Bismuthides. PAUL LEBEAU (*Compt. rend.*, 1911, **152**, 874. Compare Abstr., 1900, ii, 276).—Sodium bismuthide has already been prepared by a method simpler than that employed by Vournasos (preceding abstract). W. O. W.

Metallography of the Gold-Tellurium System. MAURICE COSTE (*Compt. rend.*, 1911, **152**, 859—862).—Microscopic examination of gold-tellurium alloys, as well as determinations of the electromotive force on solution in nitric acid, reveal the existence of a compound $AuTe_2$. No other compound could be recognised, and no evidence was obtained for the existence of Margottet's Au_2Te (*Thesis*, 1873); moreover, a repetition of the author's experiments failed to produce this substance. The results are in agreement with those of Pelabon (Abstr., 1909, ii, 584). W. O. W.

Mineralogical Chemistry.

Serpentines of Krebet-Salatim (North Urals). Louis Duparc and M. Wunder (*Compt. rend.*, 1911, 152, 883—885).—A description of a band of serpentinised rocks bounded on one side by crystalline schists, on the other by basic schists with granites and gneiss rich in epidote. It is rich in highly serpentinised harzburgites, represented by olivine, picotite, and enstatite, the latter sometimes twinned with diopside.

I, Dunite; II, harzburgite; III, serpentinised harzburgite; IV, fibrous antigorite:

	SiO_2.	TiO_2.	Al_2O_3.	Cr_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO.	H_2O.	Total.
I.	35·70	0·21	0·75	0·58	4·29	5·38	0·26	43·34	9·35	99·86
II.	38·00	—	1·33	0·21	3·05	4·46	0·23	41·92	11·18	100·38
III.	39·80	0·21	2·11	—	5·47	2·49	0·50	36·86	12·34	99·78
IV.	41·30	0·18	2·17	0·59	1·87	4·72	0·37	37·17	11·90	100·27

W. O. W.

Allophane, Halloysite, and Montmorillonite are Mixtures of Colloidal Alumina and Silica. H. STREMME (*Centr. Min.*, 1911, 205—211. Compare Abstr., 1908, ii, 1041).—A reply to Thugutt (this vol., ii, 210). L. J. S.

Veined Lodes of Peridotites in New Caledonia. ALFRED LACROIX (*Compt. rend.*, 1911, **152**, 816—822).—About one-third of the soil is composed of more or less serpentinised peridotites, chiefly durites and harzburgites containing magnesiochromite. A description is given of the constituents of veins by which the larger masses are traversed. Gabbros are represented by anorthite and diopside, distinguished by their large grains from a new type, recalling beerbachite in structure, and for which the name *ouenite* is proposed. Chemically it is related to the ariegites:

SiO_2.	Al_2O_3.	Cr_2O_3.	FeO.	MgO.	CuO.	Na_2O.	K_2O.	H_2O.	Total.
46·81	19·25	0·21	1·85	14·23	16·80	0·57	0·13	1·00	100·85

Analyses (by Boiteau) of bronzitite, norite, anorthosite, diallagite, hornblendite, and three diorites are also given. W. O. W.

A Felspar Aggregate from Nelson Co., Virginia. WILLIAM M. THORNTON, jun. (*Amer. J. Sci.*, 1911, [iv], **31**, 218—220).—Analysis I is of the extreme acidic phase of a pegmatite composed essentially of felspar and blue quartz. The felspar is light bluish-grey, D 2·68, and under the microscope it is seen to consist of a mixture of orthoclase and plagioclase. The proportions calculated from the analysis are 18·96% orthoclase and 81·04% plagioclase ($Ab_{10}An_7$).

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	Na_2O.	K_2O.	H_2O (110°).	H_2O (>110°).	TiO_2.	P_2O_5.	F.	S.	Total (less O for F).
I.	59·92	24·23	0·29	0·24	0·23	6·47	5·03	2·93	0·08	0·28	0·22	0·09	—	trace	100·01*
II.	0·67	—	2·87	5·04	0·15	12·16	—	—	0·09	0·11	69·67	9·41	0·70	0·34	100·82†

* Also CO_2, MnO, traces. † Also Cl, trace.

The pegmatite is intersected by a narrow dyke of a peculiar type of rock called nelsonite (anal. II); this consists essentially of rutile and apatite, with accessory ilmenite, pyrites, and quartz. L. J. S.

A Scandium-rich Orthite from Finland and its Alteration. RICHARD J. MEYER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 379—384).—The mineral was found as irregular masses in a felspar quarry at Impilaks on Lake Ladoga. The fresher material is black with a pitchy lustre (anal. I.), but when weathered, it is brown and friable (anal. II.):

	SiO_2.	Al_2O_3.	Fe_2O_3.	Ce_2O_3, etc.	Sc_2O_3.	ThO_2.	FeO.	CaO.	MnO.	MgO.	K_2O.	H_2O.	CO_2.	Total	Sp. gr.
I.	30·52	12·88	10·01	16·45	0·80	1·32	6·02	10 25	trace	3·80	0·22	7·34	0·90	100·51	3·20
II.	23·53	15·21	12·05	16·80	1·00	1·10	—	4·72	trace	4·39	0·51	14·01	6·90	100·22	2·84

These analyses correspond with the formulæ:

Unaltered orthite	$6SiO_2,3R_2O_3,4RO,H_2O$.
Slightly altered orthite (anal. I) ...	$5SiO_2,2\frac{1}{2}R_2O_3,3\frac{1}{2}RO,4H_2O$.
Much altered orthite (anal. II) ...	$4SiO_2,3R_2O_3,2RO,8H_2O$.

The alteration of the mineral is accompanied by the addition of water and carbon dioxide, the oxidation of the iron, and the abstraction of calcium and some silica. Wiikite, also from Impilaks, is the only other mineral in which so large an amount of scandium has been found. The occurrence of this element in a mineral of the cerium earths, rather than in one of the yttrium earths, is of interest.

L. J. S.

Ilmenite from Brazil. L. Azéma (*Bull. Soc. franç. Min.*, 1911, **34**, 29—32).—The material, from Pelotas, Rio Grande do Sul, consists of rounded grains, 2 cm. in diameter, with a yellow weathered exterior: inside, these show a conchoidal fracture with iron-black colour and semi-metallic lustre. Analysis gave:

SiO_2.	TiO_2.	FeO.	MnO.	CaO.	MgO.	Fe_2O_3.	Total.	Sp. gr.
5·30	48·88	25·44	2·60	2·38	6·26	8·94	99·80	4·44

Deducting 16·74% of sphene present in the weathered crust, these results give the formula $(Fe,Mn,Mg)O,TiO_2,Fe_2O_3$. L. J. S.

Meteorite Studies. III. Oliver C. Farrington (*Field Museum of Nat. Hist. Chicago, Geol. Ser.*, 1910, **3**, 165—193).—*Leighton Meteorite.*—This stone was seen to fall on January 12th, 1907, eight miles south of Leighton, in Colbert Co., Alabama. It weighed 877 grams, and the structure is that of a breccia-like grey chondrite (Cgb). A partial analysis by H. W. Nichols gave:

SiO_2.	Al_2O_3.	Cr_2O_3.	NiO.	CoO.	CaO.	Na_2O.	K_2O.	P.	S.	Fe.	Ni.	Co.	Total.*
35·69	1·03	0·12	1·04	0·08	1·93	0·95	0·47	0·40	2·11	10·48	1·59	0·21	56·10

* The remaining 44% is almost wholly FeO and MgO in approximately equal proportions.

Quinn Canyon Meteorite.—This large mass of iron, weighing 3275 lb (1450 kg.), was found in 1908 near the Quinn Canyon mountains, Nye Co., Nevada. The structure is that of a medium octahedrite (Om). Analysis by H. W. Nichols gave:

Fe.	Ni.	Co.	Cu.	Au, Pt, etc.	S.	P.	Si.	Total.
91·63	7·33	0·73	trace	nil.	nil.	0·20	0·02	99·91

An analysis of the black crust on the meteorite shows it to consist of magnetite.

Composition of Taenite.—Twenty-two published analyses are tabulated ; these range from Fe_7Ni to FeNi.

Times of Fall of Meteorites.—Three hundred and fifty recorded falls are tabulated according to year (1800—1909), month, day, and hour. These times differ considerably from the times of meteors, and are not noticeably related to any well-known star-showers. The rate of supply of meteorites to the earth has been remarkably uniform.

List of United States Meteorites.—These are arranged according to States. They include 65 stones, 11 iron-stones, and 129 irons, a total of 205, of which 47 have been observed to fall. L. J. S.

Physiological Chemistry.

The Amount of Metabolism Produced by the Breathing of Town and Country Air, and of Dry and Damp Air as Measured by the Carbon Dioxide Expired. William Thomson (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VIII A, 154—160).—The expired air, tested in the case of several individuals, is found to contain 4% of carbon dioxide in Manchester, but an average of 5% in country districts, and 5·2 to 5·4% on high ground near Buxton. These results are confirmed by experiments on a guinea-pig and a mouse. Heating the air before inhalation increases the carbon dioxide. The metabolism is also increased by substituting dry air for moist. It is not increased when pure oxygen is substituted for air. In a few cases of phthisis and anæmia examined, the proportion of carbon dioxide in the expired air is much diminished. C. H. D.

Effects on Men at Rest of Breathing Gas Mixtures Rich in Oxygen. Francis G. Benedict and Harold L. Higgins (*Amer. J. Physiol.*, 1911, **28**, 1—28).—In experiments on men at rest, performed twelve hours since the last meal, breathing air containing 40, 60, and 90% of oxygen, there is no noticeable difference in their gaseous metabolism or in the character, depth, or frequency of respiration. The only difference is that the higher the percentage of oxygen breathed, the lower is the pulse rate. These experiments suggest that some systematic attempt should be made to ascertain what really occurs in oxygen therapy. W. D. H.

A Respiration Apparatus for the Estimation of Carbon Dioxide Produced by Small Animals. Francis G. Benedict and John Homans (*Amer. J. Physiol.*, 1911, **28**, 29—48).—This is a resuscitation of the closed chamber method, and lends itself well to the determination of carbon dioxide output in such animals as dogs. Samples of the air were analysed by Haldane's method. Arrangements are also provided for getting the dog to do work, the amount of which can be recorded. W. D. H.

Oxidation in the Blood. MORIZO ONAKA (*Zeitsch. physiol. Chem.*, 1911, 71, 193—199).—The oxidation which occurs in shed blood is usually attributed to respiratory changes occurring in the surviving corpuscles. It is shown in the present research that these changes are greater the more thoroughly the integrity of the blood-platelets is preserved, and that they diminish with the destruction of the platelets. It is to this form of corpuscular element then that the greater part of the using up of oxygen is assigned. W. D. H.

Physiology of Blood-Sugar. III. The Residual Reduction in the Blood after Fermentation. E. FRANK and A. BRETSCHNEIDER (*Zeitsch. physiol. Chem.*, 1911, 71, 157—167).—The whole blood or the serum in man in the state of health and diabetes, or in dogs rendered hyperglycæmic by phloridzin, was investigated. In the great majority of cases no residual reducing substance remains after the sugar has been removed by fermentation; in cases of hyperglycæmia, a trace of sugar was left behind in a few instances. Bertrand's method was employed. W. D. H.

Changes in Blood and Muscle Following Bilateral Nephrectomy and Double Ureteral Ligation. HOLMES C. JACKSON (*Proc. Amer. Soc. Biol. Chem.*, 1910, xxvii; *J. Biol. Chem.*, 9).—Animals survive the operation of double kidney removal longer than that of ligature of both ureters. The analyses of the blood showed no differences to account for this. The changes in the blood noted are increased molecular concentration, increased venosity and viscosity due to carbon dioxide, and increased coagulation time. No vicarious elimination of uric acid and purine bases occurs into the intestine. Hydræmia does not occur, and œdema very seldom; true uræmic convulsions developed in some cases where the ureters were tied; the muscles have a tendency to lose water. W. D. H.

Influence of Antipyretics on the Proteins of Blood-Serum. CARLO CERVELLO (*Arch. exp. Path. Pharm.*, 1911, 64, 403—406. Compare Abstr., 1910, ii, 515).—In medicinal doses antipyrine has little or no influence in dogs on the amount or proportion of the serum proteins, on the viscosity, or on the course of metabolism. W. D. H.

Passage of the Nucleo-protein Anticoagulase of the Liver into the Blood. Comparative Action of Atropine According to the Manner of Introduction. MAURICE DOYON, ALBERT MOREL, and A. POLICARD (*Compt. rend.*, 1911, 152, 793—794. Compare this vol., ii, 216).—After injection of peptone into dogs, the blood becomes non-coagulable, owing to passage from the liver of a phosphorus-containing nucleo-protein having the chemical characteristics of the antithrombin previously described. Atropine acts in the same way, but only if the injection is made into the bile duct or mesenteric vein. When introduced into the general circulation, it is without action. W. O. W.

Serological Studies by the Optical Method. XIII. Emil Abderhalden and Ludwig Pincussohn (*Zeitsch. physiol. Chem.*, 1911, 71, 110—119).—This research was directed to determine whether during the anaphylactic period following a second parenteral administration of a foreign protein, the serum or plasma shows any difference in its power to split polypeptides, or in its optical behaviour. No differences, quantitative or qualitative, were found. W. D. H.

The Sulphur Balance in Metabolism. Alonzo E. Taylor (*Proc. Amer. Soc. Biol. Chem.*, 1910, ix—x; *J. Biol. Chem.*, 9).—The peroxide method applied to foods gives results which are too low, and for this purpose the method of Carius must be used in metabolic experiments. W. D. H.

The Dependence of Calcium Metabolism on the Organic Constituents of the Food in a Grown Dog, with Some Observations on Phosphoric Acid and Magnesium Metabolism. Martin Kochmann (*Biochem. Zeitsch.*, 1911, 31, 361—376).—It was found that even with foodstuffs which are very rich in calcium compounds, such as dog-biscuits, it is not always possible to bring about a retention of calcium when the animal is in nitrogen equilibrium. When the ratio of calcium to nitrogen is 1 : 4·5, the calcium metabolism is partly influenced by the nitrogen, but it is influenced far more by some other unknown organic constituent of the food, which causes a withdrawal of calcium from the organism. Only when the ratio of calcium to nitrogen reaches 1 : 3 can the influence of this second factor be eliminated. The magnesium and phosphoric acid metabolism cannot be sharply characterised. S. B. S.

Utilisation of Ingested Fat under the Influence of Copious and Moderate Water Drinking with Meals. H. A. Mattill and Philip B. Hawk (*Proc. Amer. Soc. Biol. Chem.*, 1910, xx; *J. Biol. Chem.*, 9).—Copious and moderate water drinking with meals leads to a great reduction of the unused fat in the fæces. W. D. H.

Formation of Glycogen from Formaldehyde. Karl Grube (*Pflüger's Archiv*, 1911, 139, 428—434).—Polemical against Schöndorff and Grebe (this vol., ii, 306). Fresh experiments are cited which in many cases show an increase of glycogen after perfusion with formaldehyde in Ringer's solution, but attention is drawn to the differences, often great ones, which occur between the amounts of glycogen in the different lobes of the liver without any treatment. W. D. H.

Mucic Acid and Carbohydrate Metabolism. Lafayette B. Mendel and William C. Rose (*Proc. Amer. Soc. Biol. Chem.*, 1910, xii; *J. Biol. Chem.*, 9).—If mucic acid is given to rabbits and dogs, some appears unaltered in the urine, but equivalent amounts of lactose and galactose are completely oxidised. Mucic acid is, therefore, presumably not an intermediary oxidation product in the metabolism of galactose-yielding carbohydrates. The urinary oxalic acid is very slightly increased after the ingestion of large amounts of mucic acid, but this is not so large as one would expect if mucic acid were a precursor of oxalic acid. W. D. H.

Creatinine Metabolism. CARL VOEGTLIN and C. TOWLES (*Proc. Amer. Soc. Biol. Chem.*, 1910, xi—xii; *J. Biol. Chem.*, **9**).—In birds, creatine is an end-product of metabolism; no creatinine is found in the urine. If creatine or creatinine are given, both are excreted as such. There is no evidence cf creatinase or creatininase in birds' organs. If dogs receive creatine, the output of creatinine is increased. The presence of an Eck fistula has little or no effect, and so the liver can hardly occupy an important place in creatinine metabolism
W. D. H.

Influence of Alcohol on Protein Metabolism in Dogs. WILLIAM SALANT and J. B. RIEGER (*Proc. Amer. Soc. Biol. Chem.*, 1910, xii—xiii; *J. Biol. Chem.*, **9**).—Small doses of alcohol exerted a sparing influence on protein, but larger amounts increased protein metabolism, the urea and ammonia being specially increased.
W. D. H.

Protein as a Factor in the Nutrition of Animals. I. A Study of the Physical Constants of Fats from Swine. A. D. EMMETT and E. C. CARROLL (*Proc. Amer. Soc. Biol. Chem.*, 1910, xxiii—xxiv; *J. Biol. Chem.*, **9**).—There are differences in some of the physical constants in the fat from different parts of the pig, but no differences were produced by the amount or nature of the protein mixed with the food. W. D. H.

The Action of Animal Proteins on Vegetarians. PIETRO ALBERTONI and FELICE ROSSI (*Arch. exp. Path. Pharm.*, 1911, **64**, 439—455).—The investigation was conducted on four Italian peasants, aged respectively 30, 42, 47, and 76. Meat and, in other experiments, eggs were added to their customary vegetarian diet. Full details of the caloric value and chemical composition of the diet are given, also particulars of the nitrogen and phosphorus balance, the loss of protein in fæces, etc. The loss of animal protein in the fæces is very small. Improvement in health, digestive power, amount of hæmoglobin in blood, and increase of body-weight were among the effects noted. W. D. H.

Fasting Studies. II. Catalase Content of Tissues and Organs after Prolonged Fasting. PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1911, **33**, 425—434).—Further experiments have been made in connexion with the author's study of the alterations in catalytic power which accompany fasting (Abstr., 1910, ii, 728; this vol., ii, 304). It was found that the tissues of an adult dog, which had been subjected to two fasts of 117 days and 104 days respectively, possessed catalytic powers which were more comparable with those of normal tissues than with those of the tissues of another adult dog which had only been subjected to a single fast of 48 days.
E. G.

Fasting Studies. III. Nitrogen Partition of Two Men through Seven-day Fasts Following the Prolonged Ingestion of a Low Protein Diet; Supplemented by Comparative Data from the Subsequent Feeding Period. PAUL E. HOWE, H. A. MATTILL, and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1911, **33**, 568—598).—An account in full detail of the effect on two men of a fast of seven days; a preliminary statement has already appeared (Abstr., 1910, ii, 729). E. G.

Catalase Content of Tissues and Organs after Prolonged Fasting. PHILIP B. HAWK (*Proc. Amer. Soc. Biol. Chem.*, 1910, xxi—xxii; *J. Biol. Chem.*, **9**).—The catalase value of organs and tissues estimated by the volume of oxygen liberated from neutral hydrogen peroxide is much lower after fasting. W. D. H.

Ash Constituents in Ordinary Diets of Human Beings. ROBERT TIGERSTEDT (*Skand. Archiv. Physiol.*, 1910, **24**, 97—112).—The total ash, phosphoric acid, calcium, and magnesium in the diets used by children at various ages, and adults of both sexes in Finland are given in a table, and the results compared with each other, and with similar figures previously published by Sundström. Observations are given altogether on sixty-four different individuals. W. D. H.

The Nuclease Content of Different Organs of Man and Animals. A. J. JUSCHTSCHENKO (*Biochem. Zeitsch.*, 1911, **31**, 377).—The method generally adopted was to determine the amount of acid eliminated as inorganic phosphorus when a solution of sodium nucleate was treated with the extracts. In a few cases, which gave similar results to the phosphoric acid method, the purine bases eliminated by the enzyme were estimated. The relative amounts of nuclease from the various organs were in the following (descending) order: liver, kidneys, spleen, pancreas, and thyroid (all relatively rich in enzyme); brain, suprarenals, lungs, and lymphatic glands (smaller quantities); heart, blood, muscles, and serum (small quantities only). In most organs of a young dog, the content is smaller than in an older animal. The organs of man are relatively rich in nuclease, and the content of the enzyme does not appreciably diminish if the organs be kept for some time after death. S. B. S.

The Oxidation of Citric, Malic, and Fumaric Acids by Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1911, **31**, 478—505).—The authors investigated by the methods already employed for other substances the action of the tissues on these acids, which they find increase in cases of all tissues the respiratory quotient to 1·33, which indicates the complete combustion to carbon dioxide and water. The substance causing the oxidation cannot be extracted by water from the tissues. The optimum temperature of the enzyme action is 40°, and the action takes place most readily in slightly acid or alkaline media. Hydrocyanic acid, salicylaldehyde, formaldehyde, and bile act deleteriously even in low concentrations. S. B. S.

Chemical Composition of the Nervous System. N. ALBERTO BARBIERI (*7th. Intern. Congr. Appl. Chem.*, Sect. IV. A 2, 63—65).—The author has examined the products obtainable from nervous tissue by means of various solvents. White matter contains cerebrin, cholesterol, and traces of cerebroin. Grey matter contains cerebroin, cholesterol, oil, and neurochromatin. From nerves and optic nerves, cerebrin, cholesterol, and traces of cerebroin are obtained, whilst the retina yielded cerebrin and cholesterol. Lecithin, nuclein, and protagon were not found, and the conclusion is drawn that these substances do not exist in the nervous system.

Cerebroin is a white substance, m. p. 176°, and contains C 66·9, H 10·9, N 3·9, P 0·7, S 0·5, O 17·10. When hydrolysed with 2% hydrochloric acid, it gives no sugar. *Cerebrin* is a white substance, m. p. 170°, and has the composition: C 69, H 11, N 3·8, O 16·20. When hydrolysed with 2% hydrochloric acid it yields a *sugar*, m. p. 142°, which gives an *osazone*(?), m. p. 140°. R. V. S.

Relation between the Physical, Chemical, and Electrical Properties of Nerves. IV. Potassium, Chlorine and Potassium Chloride. NATHANIEL H. ALCOCK and G. ROCHE LYNCH (*J. Physiol.*, 1911, 42, 107—112. Compare Abstr., 1910, ii, 323).—In both medullated and non-medullated nerves there is a considerable amount of potassium not combined with chlorine. The following maximum possible amounts (%) are probably in excess of the true values:

	In connective tissue.	In medullated nerve-fibres.	In non-medullated nerve-fibres.	In axis cylinder.
K	0·043	0·284	0·301	1·17
Cl	0·333	0·176	0·154	0·722
KCl	—	0·370	0·324	1·52

W. D. H.

Replacement of Calcium in Certain Neuro-muscular Mechanisms by Allied Substances. GEORGE R. MINES (*J. Physiol.*, 1911, 42, 251—266).—Calcium, strontium, and barium show a gradation of physiological activity in relation to the following neuro-muscular mechanisms in the frog: (1) on the movements of skeletal muscles immersed in solutions of sodium or lithium salts; (2) on the excitability of muscle towards electric currents of long duration; (3) in their power to antagonise the contractions produced by potassium chloride; (4) on the tone of cardiac muscle; and (5) on the transmission of excitation from motor or inhibitory nerves to muscles. In the first three respects, magnesium behaves like calcium, but is slightly inferior in activity; in the two last-named actions, it is entirely unable to replace calcium, barium, and strontium. It is evidently some chemical property, and not their electric charge, which determines the behaviour of these cations. W. D. H.

Reactions of Surviving Arteries. DOUGLAS COW (*J. Physiol.*, 1911, 42, 125—143).—The coronary and cerebral arteries are dilated by adrenaline; all other arteries are constricted; the pulmonary artery, however, is only constricted in the portion outside the lung;

the parts inside the lung are either not affected or dilated. The gastric, hepatic, and splenic arteries are dilated by pituitary extract, and this decreases progressively from the viscus to the origin of the vessel, where it may give place to constriction. The renal artery is dilated by pituitary extract, and this increases progressively from its origin to its branches within the kidney. The results were obtained by taking graphic records of the lengthening or shortening of rings of the arteries in question. W. D. H.

The Combined Action of Muscle Plasma and Pancreas Extract on Glucose and Maltose. PHŒBUS A. LEVENE and GUSTAVE M. MEYER (*J. Biol. Chem.*, 1911, **9**, 97—108).—The present experiments amplify the views of Cohnheim and of Hall. The reducing power of a sugar solution lowered by the combined action of muscle plasma and extract of pancreas was restored to its original height by boiling in a reflux apparatus for two hours in the presence of 1% hydrochloric acid. The disappearance of sugar is therefore apparently caused, not by degradation, but by condensation of the dextrose molecule. Further, from a sugar solution which had lost part of its reducing power through the action of muscle and pancreas, an osazone was isolated having the properties of a biosazone; this is mixed with glucosazone. Pancreatic extract alone causes no change in the reducing power of maltose; muscle plasma alone causes a rise, and the two together cause more vigorous hydrolysis, and so a greater rise in reducing power. W. D. H.

Action of Caffeine on Muscle. FRED RANSOM (*J. Physiol.*, 1911, **42**, 144—155).—The rigor produced by caffeine in frog's muscles is attended by lactic acid formation, which passes into the saline solution in which the muscles were suspended; in the presence of oxygen the acid formed disappears from the solution. The solution also gives the biuret reaction after the muscles have passed into rigor. If the skinned hind limbs of frogs are immersed in saline solution at room temperature, the solution contains diastase in one or two hours. Neither the diffusion of diastase nor the amount of sugar formed on the addition of glycogen are influenced by the presence of caffeine.

W. D. H.

The Utilisation of Different Sugars for the Formation of Glycogen in the Liver. HANS MURSCHHAUSER [with H. HAFFMANS] (*Pflüger's Archiv*, 1911, **139**, 255—277).—The main results from these experiments on dogs are given in the following table; taking the amount of hepatic glycogen in the control animal as 1, the other figures express the amounts found after feeding on various kinds of sugar: in column 1, eight hours after feeding; in column 2, sixteen hours after feeding, and in column 3, after eight days' feeding, the sugar being in each case added to a flesh diet.

	1.	2.	3.
Sucrose	2·83	5·16	4·08
Lactose	1·25	3·18	1·39
Dextrose	4·06	4·84	3·63
Maltose	1·47	2·55	—
Galactose	1·43	1·77	—
Lævulose	2·99	1·51	—

W. D. H.

Autolysis of Liver Tissue as Affected by Thyroid Administration. ELIZABETH COOKE and S. P. BEEBE (*Proc. Amer. Soc. Biol. Chem.*, 1910, xv; *J. Biol. Chem.*, 9).—Schryver stated that administration of thyroid causes an increased rate of autolysis in the liver. In the present research, administration of thyroid (and also of parathyroid) caused no change in the rate of autolysis. W. D. H.

Behaviour of Glycogen after Extirpation of the Suprarenal Capsules. R. H. KAHN and EMIL STARKENSTEIN (*Pflüger's Archiv*, 1911, 139, 181—195).—Schwarz's statements, that in rats extirpation of the suprarenals causes a reduction in the amount of glycogen and supersensitiveness towards adrenaline, are confirmed. Rabbits were found to survive extirpation of the suprarenals without ill effects, and to contain the normal amount of glycogen. During the short time dogs survive the operation, there is a loss of glycogen, but this is mainly attributed to the severity of the operation. W. D. H.

Mode of Production of Lactose in the Mammary Gland. D. NOËL PATON and E. PROVAN CATHCART (*J. Physiol.*, 1911, 42, 179—188).—In a goat, phloridzin produced but little increase in the amount of urine, and the amount of milk secreted fell; the lactose in the milk also fell, the lowest output coinciding with the largest output of sugar in the urine. This it held to indicate that the blood sugar is used in the formation of lactose; the source of galactose, the other constituent of lactose, is still unsolved. The milk fat was increased in some of the experiments. W. D. H.

A Glucose-protein Compound in Ascaris Lumbricoides. FRANCIS H. MCCRUDDEN (*Proc. Amer. Soc. Biol. Chem.*, 1910, viii; *J. Biol. Chem.*, 9).—*Ascaris* contains considerable quantities of a substance soluble in dilute alcohol which, on cleavage, yields a sugar (probably dextrose), a protein (in which tryptophan is absent), and a volatile substance (probably an aromatic oil). W. D. H.

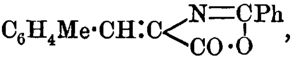
Albumin and Globulin in the Ovaries of Barbus fluviatus and the Pike. FRANCIS H. MCCRUDDEN (*Proc. Amer. Soc. Biol. Chem.*, 1910, viii; *J. Biol. Chem.*, 9).—The albumin and globulin from the ovaries of the fishes mentioned were separated and examined. All contain phosphorus and sulphur, none contain iron. The albumins yielded a reducing substance on hydrolysis, the globulins did not. The two proteins from the *Barbus* gave Millon's reaction, those from the pike did not. Tryptophan was absent in all cases. The absence of iron, reducing substance, and tryptophan shows that the globulins of these eggs differ considerably from those of bird's eggs.
W. D. H.

Output of Ammonia in Normal Urine. ALONZO E. TAYLOR (*Proc. Amer. Soc. Biol. Chem.*, 1910, x—xi; *J. Biol. Chem.*, 9).—In Californian urines the amount of ammonia (Folin's method) is much lower than in Philadelphian. The cause attributed is some factor in diet or water. An excess of magnesium and preformed phosphoric acid might, for instance, have resulted in the ammonia being eliminated as ammonium magnesium phosphate in the fæces.
W. D. H.

The Partition of the Urinary Nitrogen after Enteral and Parenteral Feeding on Protein. Sigmund von Somogyi (*Zeitsch. physiol. Chem.*, 1911, 71, 125—133).—Protein was administered to a dog enterally and parenterally, and the urine examined for total nitrogen, urea, ammonia, total purine bases, uric acid, and creatinine. In the enteral period, the total nitrogen, the urea, and the ammonia are increased. In the other constituents the differences are slight.

W. D. H.

Chemical Nature of Alcaptonuria. Henry D. Dakin (*J. Biol. Chem.*, 1911, 9, 151—160).—The author has studied the behaviour of *p*-tolylalanine and *p*-methoxyphenylalanine in the normal and alcaptonuric organisms. In both cases the substances were oxidised and no excretion of homogentisic acid was observed. It appears probable, therefore, that alcaptonuria represents a condition in which the formation of homogentisic acid is abnormal as well as the failure to effect its katabolism when formed. When *p*-tolylalanine was fed to an alcaptonuric, a small amount of d-p-*tolylacetylalanine* (m. p. 170—171°, $[\alpha]_D^{20}$ +34·6°) was formed, and cats, when fed with the same substance, excreted *p*-tolylacetic acid and *α*-carbamido-*β*-*p*-tolylpropionic acid.

The *azlactone*,  $C_6H_4Me\cdot CH{:}C<\begin{matrix}N{=}CPh\\ \vert \\ CO\cdot O\end{matrix}$, prepared by condensing *p*-tolualdehyde with hippuric acid (see following abstract), crystallises in yellow needles, m. p. 141—142°, and on hydrolysis it gives *α-benzoylamino*-p-*tolylacrylic acid*, $C_6H_4Me\cdot CH{:}C(NHBz)\cdot CO_2H$, which forms rosettes of colourless needles, m. p. 226—227° (decomp.). On reduction with sodium amalgam this yields p-*tolylbenzoylalanine* (not analysed), and this on hydrolysis furnishes p-*tolylalanine*,

$$C_6H_4Me\cdot CH_2\cdot CH(NH_2)\cdot CO_2H,$$

which forms colourless prisms, m. p. 277—279° (decomp.). The *hydrochloride* is crystalline.

α-Carbamido-β-p-*tolylpropionic acid*,

$$C_6H_4Me\cdot CH_2\cdot CH(NH\cdot CO\cdot NH_2)\cdot CO_2H,$$

prepared by heating *p*-tolylalanine with aqueous potassium cyanate, crystallises in small prisms, m. p. 195—196° (decomp.). W. D. H.

Katabolism of Phenylalanine, Tyrosine, and of Their Derivatives. Alfred J. Wakeman and Henry D. Dakin (*J. Biol. Chem.*, 1911, 9, 139—150).—Evidence is adduced to show that the condition of alcaptonuria does not simply represent a failure to oxidise homogentisic acid. The formation of this acid from phenylalanine or tyrosine is probably abnormal. If simple derivatives of these substances (*p*-methylphenylalanine and *p*-methoxyphenylalanine) are given to an alcaptonuric patient, these amino-acids apparently undergo complete oxidation. Such a person has not lost his ability to katabolise simple derivatives of phenylalanine and tyrosine provided their structure is such that formation of substances of the type of homogentisic acid is excluded.

p-*Tolylpyruvic acid*, $C_6H_4Me\cdot CH_2\cdot CO\cdot CO_2H$, is prepared by condensing *p*-tolualdehyde with hippuric acid by means of sodium acetate and acetic anhydride to the *azlactone*, m. p. 141—142° (see preceding abstract), and boiling this with 40% sodium hydroxide. The acid crystallises in prismatic needles, m. p. 178—180°. p-*Methoxyphenylpyruvic acid*, $OMe\cdot C_6H_4\cdot CH_2\cdot CO\cdot CO_2H$, similarly prepared from the condensation product of anisaldehyde and hippuric acid, crystallises in opaque needles, m. p. 190—192°. W. D. H.

General Metabolism with Special Reference to Mineral Metabolism in a Patient with Acromegaly complicated with Glycosuria. FLORENTIN MEDIGRECEANU and L. KRISTELLER (*J. Biol. Chem.*, 1911, **9**, 109—120).—The glycosuria in the case described followed the usual course, and was not affected by injection of extracts of the anterior lobe of the pituitary body. The injection, however, caused a general rise of metabolism, accompanied with certain peculiarities in salt metabolism which could not be interpreted as due to the general rise in metabolism. W. D. H.

Bence-Jones Protein, and the Metabolism in Three Cases of Bence-Jones Proteinuria. F. GOWLAND HOPKINS and HORACE SAVORY (*J. Physiol.*, 1911, **42**, 189—250).—The characteristic solubility at 100° of the heat coagulated protein is due to the influence of associated substances, especially electrolytes, in solution. Much of the present paper is occupied with a consideration of the influence of various factors on the solvent influence of salts on protein-salt comcomplexes at various temperatures. In the case of the Bence-Jones protein its behaviour is due to the stability of its compounds with neutral salts increasing rapidly with the temperature.

The general characters, elementary analysis, and yield of amino-acid suggest that the protein was identical in the three cases examined. It contains all the amino-acids characteristic of a typical protein, and the proportion of the aromatic groupings is high. No protein with the same characters could be detected in the tissues or tumours. It is less powerful than serum proteins as a precipitinogen, but its solutions reacted slightly with an anti-human serum.

The three individuals differed in the grade of their total metabolism; the protein excreted was proportional to this. The protein-nitrogen on an unrestricted diet amounted to nearly one-third of the total nitrogen excreted. The study of metabolism indicates that the protein arises endogenously. W. D. H.

Renal Glycosuria. LEO POLLAK (*Arch. exp. Path. Pharm.*, 1911, **64**, 415—426).—By previously treating rabbits partly with adrenaline, partly with cantharidine, a state was produced in which poisons that excite glycosuria (adrenaline, diuretin) caused hyperglycæmia, but no sugar in the urine. In this state poisoning with uranyl nitrate caused glycosuria, whilst the amount of sugar in the blood was but little, if at all, increased. This was not merely the result of diuresis, but a specific increase in the permeability of the kidney to sugar.
W. D. H.

The Colloido-chemical Analysis of Nephritis. MARTIN H. FISCHER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 201—208).—The morphological changes which accompany nephritis are examined from the point of view of colloidal chemistry. It is shown that the primary cause of nephritis is to be found in the abnormal production or accumulation of acid in the cells of the kidney. Under conditions in which turbid swelling occurs as the result of this production of acid, the kidneys undergo morphological changes accompanied by the development of the diagnostic epithelial, granular, and hyaline cylinders. These three forms can be successively produced by increase in the acid concentration. Conversely, the hyaline cylinders can be transferred into the granular elements by the addition of neutral salt to the acid solution. The presence of acid in the kidney cells causes coagulation of albumin, and is therefore to be regarded as the primary cause of albuminuria. H. M. D.

The Schardinger Enzyme in the Milk of Cows with Diseased Udders. RICHARD REINHARDT and ERNST SEIBOLD (*Biochem. Zeitsch.*, 1911, **31**, 385—396).—The milk from cows with mastitis shows great variations in the Schardinger enzyme reaction. When the secretion is of normal appearance, the enzyme reaction is normal, but when there are marked changes in the properties, the reaction is weak or even negative. Owing to the variations, however, the Schardinger reaction is of no value for diagnosis of udder diseases.

S. B. S.

Pancreatic Lipase. IV. The Action of Serum of Mice Inoculated with Malignant Mouse Tumour. JOHN A. SHAW-MACKENZIE (*Proc. physiol. Soc.*, 1911, xi—xvi; *J. Physiol.*, **42**).—The power of the serum to accelerate the lipoclastic power of pancreatic lipase is increased in various phases of tumour inoculation and growth in mice, in cases of spontaneous recovery, in mice negative to inoculation, and in mice presumably rendered immune to inoculation by previous inoculation with normal mouse tissues. The same power of the serum was noted in cases of human cancer in which recovery was apparently complete, and also during the course of the disease. The same property is, however, also found in other pathological conditions. It is suggested that lipoclastic acceleration is one factor in the natural defensive processes of the body. W. D. H.

New Method for Introducing Radium into the Tissues. HARET, DANNE, and JABOIN (*Compt. rend.*, 1911, **152**, 800—802).—The method consists in introducing radium ions by electrolysis, employing as electrode gauze dipped in a very dilute solution of a pure radium salt. After treatment, radium was found in the adjacent skin, aponeurosis, muscular fibre, and bone, and also in the urine. Clinical experience shows that this mode of application has a sedative effect, and brings about the rapid diminution of certain tumours.

W. O. W.

Colloidal Metals in Relation to their Physio-chemical Properties and their Pharmacological Action. OSKAR GROS and JAMES M. O'CONNOR (*Arch. exp. Path. Pharm.*, 1911, **64**, 456—467).—

The experimental results agree with those of Portig in showing that collargol can form silver compounds in the organism. The colloidal metals have certain actions in common, which is explained on the physico-chemical condition of their solutions; these are (1) hyperleucocytosis if the metals enter the circulation; (2) adsorption phenomena, so that many poisons act less rapidly and intensely if they are mixed with the colloidal solutions before injection; (3) elevation of body temperature if the solutions are injected intravenously. The experiments were performed on rabbits. W. D. H.

The Behaviour of Antimony Preparations in the Body and the "Accustoming" to the Same. MAX CLOETTA (*Arch. exp. Path Pharm.*, 1911, **64**, 352—361).—In chronic poisoning with preparations of antimony there is, in contradistinction to arsenic poisoning, not only no diminution of absorption, but an absolute and relative increase, which grows with the length of time the administration lasts and with the strength of the dose. W. D. H.

Influence of the Vapours of Formaldehyde, Acetaldehyde, and Acraldehyde on the Organism. N. IWANOFF (*Arch. Hygiene*, 1911, **73**, 307—340).—The aldehydes were estimated by Romyn's process in the case of formaldehyde, and by Ripper's process in the case of the other two. Cats were exposed to vapour containing varying quantities of these substances, and the toxic effects were noted and described in detail. Of these, acraldehyde is the most toxic, doses of 1·5 mg. per litre being so toxic that the animal dies after eighteen hours after remaining for two and a-half hours in an atmosphere with this content of the aldehyde. Formaldehyde is more toxic than acetaldehyde. S. B. S.

The Fate of Benzoylacetic Acid in the Animal Body. HENRY D. DAKIN (*J. Biol. Chem.*, 1911, **9**, 123—128).—Sodium benzoylacetate was administered to cats either intravenously or subcutaneously; the urine contained cinnamoylglycine and *l*-β-hydroxy-β-phenylpropionic acid: the presence of the latter compound was indicated by Friedmann (Abstr., 1910, ii, 795), but the author has now succeeded in isolating it. This acid and benzoylacetic acid are mutually interconvertible in the animal body by means of reversible reactions involving oxidation and reduction respectively. A small yield of cinnamoylglycine may follow the intravenous injection of sodium cinnamate and glycine. W. D. H.

Picrotoxinin and Some of its Derivatives. CARLO CERVELLO (*Arch. exp. Path. Pharm.*, 1911, **64**, 407—414).—Picrotoxinin acts like the picrotoxin of commerce; acetylpicrotoxinin produces the same effects, but in frogs smaller doses produce the characteristic convulsions than are necessary in the case of picrotoxinin. Picrotin, which differs in composition from picrotoxinin by H_2O, is less effective. The greater intensity of the action of picrotoxinin is probably due to the existence of a double linking and to its strong reducing properties. The increased action by the introduction of an acetyl group is analogous to what occurs in the case of other drugs. W. D. H.

Action of Phloridzin. KARL GRUBE (*Pflüger's Archiv*, 1911, **139**, 165—180).—Fresh experiments on dogs (with and without kidneys) confirm the author's previous contention that phloridzin diabetes is not a pure kidney diabetes, but that the drug acts directly on the liver cells. The recent work of Schöndorff and Sukrow (this vol., ii, 306) is regarded as a confirmation, not a contradiction, of this view.

W. D. H.

Pharmacological Investigations on Dicentrine, the Alkaloid of Dicentra pusilla. K. IWAKAWA (*Arch. exp. Path. Pharm.*, 1911, **64**, 369—382).—The plant from which dicentrine is obtained (compare Asahina, Abstr., 1909, i, 601) is known as Koma-kusa in Japan, and is much prized by the populace as a drug. It belongs to the Fumariaceæ, a sub-group of the Papaveraceæ. In cold- and warm-blooded animals the alkaloid produces slight narcosis in small doses; in larger doses it stimulates the medullary centres and produces convulsions. It weakens the heart and the motor apparatus generally. It paralyses the respiratory centre, and in warm-blooded animals this is preceded by excitation.

W. D. H.

The Behaviour of Indole in the Human Organism. MAX KAUFFMANN (*Zeitsch. physiol. Chem.*, 1911, **71**, 168—173).—If indole is given in large quantities by the mouth, only part is recoverable in the urine as urinary indican on the same day. The increased excretion of this substance may continue for as long as two months.

W. D. H.

The Antagonism in the Toxic Action of Potassium and Sodium Salts. JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, **31**, 450—477).—The experiments were carried out on a marine fish (*Fundulus*) which is relatively insensitive to changes in the osmotic pressures of solutions. Both pure sodium and potassium chloride solutions are toxic to this fish, which can live for almost indefinite periods in pure solutions of calcium and magnesium chlorides. Sodium chloride acts, however, antagonistically to potassium chloride, and the amounts of the former necessary to deprive different amounts of the latter salt of toxicity were quantitatively determined. It was shown that the ratio of the concentration of the potassium salt to that of the sodium salt necessary to produce a non-toxic mixture was about 1:17, and this ratio C_{KCl}/C_{NaCl} is termed by the author the "coefficient of antagonism" (Entgiftungs-koeffizient). In higher concentrations of potassium chloride (more than 6·6 c.c. $M/2$-chloride per 100 c.c.) it could not be antagonised by sodium chloride. The coefficient of antagonism is also slightly higher (1/5—1/16) in the more concentrated solutions of potassium chloride (concentrations of 4·4—6·6 c.c. $M/2$-salt to 100 c.c.). The actions are due to the cations and not the anions, as shown by comparison of the antagonistic action of other sodium salts. Very small quantities of sodium salts increase the toxic action of potassium salts, instead of acting antagonistically.

S. B. S.

The Toxic Action of Certain Fish Ovaries. FRANCIS H. MCCRUDDEN (*Proc. Amer. Soc. Biol. Chem*, ix ; *J. Biol. Chem.*, 9).—The ovaries of *Barbus fluviatus* and the pike contain a toxic substance ; small quantities of the aqueous extract injected under the skin of rabbits cause severe convulsions and death in a few minutes. When the albumin and globulin were separated, the toxic action appeared always in the albumin fraction. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Consumption of Malic Acid and Formation of Lactic Acid During Fermentation. Independence of the Two Phenomena. W. MESTREZAT (*7th Intern. Congr. App. Chem.*, 1909, Sect. VI B, 94—97).—Most wine musts contain malic acid, which disappears during fermentation. Yeast water solutions, containing 4 grams of malic acid per litre, were fermented with a variety of yeasts, all of which consumed the acid, *Saccharomyces pombe* removing 75%. During fermentation small quantities of lactic acid are formed, but the amount of this bears no relation to the malic acid consumed; lactic acid is also formed when no malic acid is present.

The formation of lactic acid during fermentation appears to be quite general, but it is not always found in wines. E. F. A.

The Juice of Beer Yeast. E. KAYSER (*Compt. rend.*, 1911, **152**, 975—977. Compare Lebedeff, this vol., i, 248).—If yeast is macerated with water at 35—40°, according to Lebedeff's process, the filtered solution is quite inactive as a ferment. If the operation is effected at 4°, the preparation is more active than when it is conducted at 1° or 25°. The preparation readily decomposes sucrose, maltose, dextrose, lævulose, galactose, and raffinose. Its action on sugar is influenced by concentration in the same way as that of Buchner's zymase.

W. O. W.

Loss of Nitrogen During the Purification of Water by Bacterial Beds. ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1911, **152**, 822—826. Compare Abstr., 1909, ii, 423).—The loss of nitrogen occurring in the septic tanks, to which attention has previously been drawn, is attributed chiefly to direct oxidation of ammonia and organic nitrogenous matter. There is also, however, a direct reduction of nitrates with liberation of nitrogen, but unaccompanied by formation of nitrites, unless air is excluded during the process. W. O. W.

Joint Influence of Zinc and Manganese on the Development of Aspergillus niger. GABRIEL BERTRAND and MAURICE JAVILLIER (*Compt. rend.*, 1911, **152**, 900—902. Compare Abstr., 1908, ii, 124; this vol., ii, 222).—Simultaneous addition of zinc and manganese salts to the nutrient medium increases the yield to a greater extent than when either metal is present alone. W. O. W.

Elective Power of Vegetable Cells for Dextrose and Lævulose. Léon Lindet (*Compt. rend.*, 1911, **152**, 775—777).—Yeast which has been cultivated in dextrose solutions shows greater zymatic and reproductive activity than a similar culture from lævulose solutions when the two are compared by their behaviour towards the same sugar. If, on the other hand, the two yeasts are allowed to grow, one in a nutritive medium containing dextrose, and the other in a similar solution with lævulose, it is found that whilst the amount of sugar consumed is the same, the production of yeast is more rapid in the latter than in the former. Experiments on invert sugar and with germinating barley, *Aspergillus*, *Penicillium*, etc., lead to similar results.

These observations point to the possibility that the organism accustomed to dextrose decomposes the sugar more rapidly than it can assimilate it, as a consequence of which lævulose is more closely connected with tissue formation, and dextrose more intimately associated with the functions of fermentation and respiration.

W. O. W.

Action of Some Hydrolysable Salts and of Some Colloids on the Higher Plants. Ach. Grégoire (*Bull. Soc. chim. Belg.*, 1911, **25**, 85—103. Compare Abstr., 1910, ii, 644).—Barley behaves very similarly to rye (Abstr., 1910, ii, 644); it was selected as giving an ash of acid reaction. Growth, in culture solutions containing the desired additions, is accelerated by silica, analcime, and heulandite, slightly retarded by aluminium hydroxide, and more so by calcium palmitate, laurate and carbonate, and also by straw gum. Calcium humate is directly deleterious, killing the plants.

The amount of silica absorbed by the growing barley in presence of silica, analcime, and heulandite is large, amounting in the case of silicic acid to 44% of the total ash, whereas the control plants contained only 4·86%. This amount is apparently in excess of that required for the maximum development of the barley plant, as analcime produced a larger crop than silicic acid, although its ash only contained 13% of silica. The proportion of alumina in the ash is decreased slightly in presence of silicic acid, and augmented when aluminium hydroxide or zeolites were used. Plants are able to absorb both aluminium and silica from the glass of the culture vessel. It is considered that silica plays some essential part in the metabolism of barley.

The relatively greater fertilising action of ammonium sulphate than sodium nitrate in the case of the graminæ is attributed to the acid salt rendering more silicic acid available.

Beet, of which the ash gives an alkaline reaction, behaves entirely differently. Calcium humate very greatly accelerates development, which is also increased by aluminium hydroxide. Growth is retarded by the calcium salts, by silica, and by gum. The amount of silica in the ash increases when the beet is grown in presence of silica, analcime, or heulandite; plants grown in aluminium hydroxide, analcime, and calcium humate contain an increased proportion of alumina. The behaviour towards calcium humate is in agreement with the effects of stable manure on the beet. E. F. A.

Vegetable Assimilation and Respiration. VIII. New Method for Estimating the Gaseous Exchanges of Submerged Plants. F. FROST BLACKMAN and A. M. SMITH (*Proc. Roy. Soc.*, 1911, *B*, 83, 374—388).—The usual method for evaluating assimilation in submerged plants, which consists in counting or measuring the evolution of bubbles of gas, fails at both extremes of the conditions (light, temperature, and the supply of carbon dioxide) which chiefly control the magnitude of assimilation.

In the method now described, a continuous current of water flows over the assimilating plant; the difference in the amount of carbon dioxide in the water before and after contact with the plant is a measure of the assimilation. Fewer bubbles are found than when the water is stationary, and any gas given off is collected automatically and allowed for.

A sketch of the apparatus is given. N. H. J. M.

Vegetable Assimilation and Respiration. IX. Assimilation in Submerged Water-Plants and its Relation to the Concentration of Carbon Dioxide and Other Factors. F. FROST BLACKMAN and A. M. SMITH (*Proc. Roy. Soc.*, 1911, *B*, 83, 389—412). —Experiments with *Elodea* and *Fontinalis*, in which the light and temperature remained constant, whilst the amount of carbon dioxide varied from 0·0025 to 0·0540 gram per 100 c.c. of water, showed that assimilation increases in proportion to the supply of carbon dioxide, until the amount of carbon dioxide assimilated is about 0·023 gram per hour, when the increase abruptly stops. Without more light the assimilation cannot be increased by an increase of carbon dioxide.

A diagram is given by which it is possible to foretell what value of assimilation in *Elodea* will be attained in any combination of medium magnitudes of the three factors (carbon dioxide supply, temperature, and light) of the environment. All the experiments of previous investigators are more in harmony with the point of view of interacting limiting factors than with the conception of optima. N. H. J. M.

Conservation of Saline Materials by an Annual Plant; Distribution of Dry Material, Total Ash, and Nitrogen. GUSTAVE ANDRÉ (*Compt. rend.*, 1911, 152, 777—780. Compare Abstr., 1910, ii, 334, 442).—A tabular statement shows variations in the weight of dry material, ash, and nitrogen in the roots, leaves, stem, and seeds of pinks at different stages of the plants' growth. In the leaves, the absolute weight of nitrogen increases until flowering occurs, and then diminishes owing to migration to the reproductive organs.

W. O. W.

Conservation of Saline Materials by an Annual Plant; Distribution of Fixed Elements. GUSTAVE ANDRÉ (*Compt. rend.*, 1911, 152, 956—967. Compare this vol., ii, 141, and preceding abstract). —The absolute amount of phosphoric acid is at a maximum when flowering commences, and then diminishes until the end of vegetation, except in the seeds, in which it increases slightly. The amount of potassium varies precisely as the nitrogen, its accumulation in the leaves being especially noticeable. The plant loses potassium more readily by exosmosis from the roots and stomata than the other elements studied. The absolute weight of calcium and magnesium increases continuously throughout vegetation. W. O. W.

Influence on Plant Development of Mineral Substances Accumulating in the Organs as Residues from Assimilation. Absorption of Colloidal Organic Matter by the Roots. PIERRE MAZÉ (*Compt. rend.*, 1911, **152**, 783—785. Compare this vol, ii, 141).—Absorption of sodium and of sulphates in excess by the roots of plants is harmful to their development. When maize is allowed to grow in sterilised solutions containing a colloid, such as starch, peptone, or humus, the roots absorb these substances readily. The absorption of starch appears to be direct, and not to depend on its previous transformation by amylase or sucrase. Contrary to earlier statements by the author, these enzymes do not pass from the roots into solution, the effects previously attributed to their action being due to an increased acidity of the media. W. O. W.

Formation of Chlorophyll in Plants. N. A. MONTEVERDE and V. N. LUBIMENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1911, 73—101).—Since Liro (*Ann. Acad. Sci. Fennicae*, 1908) has controverted their view that the formation of chlorophyll in the plastids of green plants is preceded by that of an intermediate pigment, the so-called chlorophyllogen (*Bull. Imp.* [*St. Petersburg*] *Botanical Gardens*, 1902, **2**; 1909, **9**, parts 2 and 3), the authors have repeated their previous work, and have carried out a new series of investigations with living plants, the general results being as follows.

A whole series of changes, in which light appears to play only a subordinate part, are concerned in the formation of chlorophyll. The first stage which has been observed is the formation, from an unknown colourless chromogen, of chlorophyllogen, which is a very unstable colouring matter, and never accumulates in relatively large quantities; in the region of the red rays, its absorption spectrum exhibits great similarity to that of chlorophyll. In the plastids of living plants, chlorophyllogen undergoes two distinct changes, by which two more stable colouring matters are formed: (1) The first of these changes, which takes place under the influence of chemical agencies alone and proceeds especially readily with the *Cucurbitaceæ*, results in the formation of protochlorophyll, very similar to, but more stable towards light than, chlorophyll; it is converted into the dirty-green protochlorophyllan by the action of light and oxygen, the conversion taking place most readily in blue light. (2) The second change, that of chlorophyllogen into chlorophyll, is brought about by the action of light, or, with plants which become green in the dark, by chemical agencies. Both protochlorophyll and chlorophyll undergo further changes, forming new colouring matters similar to chlorophyll.

A plate, showing the absorption spectra of the various products, accompanies the paper. T. H. P.

Preparation and Properties of an Oxydase Occurring in Fruits. H. P. BASSETT and FIRMAN THOMPSON (*J. Amer. Chem. Soc.*, 1911, **33**, 416—423).—In the course of some fruit analyses, it was observed that when a fruit is injured and afterwards left exposed to the air, a tannin-like substance is rapidly produced which is capable of precipitating proteins.

Experiments which have been carried out with apples, pears, and walnuts show that this change is due to the action of an oxidising enzyme, which is only active in slightly acid solutions and in concentrations above a certain minimum. The function of this enzyme is to inhibit the growth of fungi or bacteria on injured fruits, probably partly by rendering the proteins insoluble and partly by its own germicidal action.

Evidence has been obtained of the presence of another enzyme in fruits which is probably a catalase. E. G.

Chemistry of Fly Agaric (Amanita muscaria). IV. JULIUS ZELLNER (*Monatsh*, 1911, **32**, 133—142. Compare Abstr., 1904, ii, 678; 1905, ii, 550; 1906, ii, 572).—The substance isolated from the fungus and regarded by the author as identical with Tanret's ergosterol (*loc. cit.*) has been separated by hot 90% alcohol into two substances. The less soluble constituent, $C_{26}H_{40}O,H_2O$, m. p. 159°, $[\alpha]_D$ $-121\cdot2°$ in chloroform, is almost certainly proved to be ergosterol by an examination of its acetyl derivative, despite the discrepancies between the m. p.'s and rotations of the two compounds.

The more soluble constituent is obtained as a sandy, indistinctly crystalline powder, m. p. 133°, containing a little nitrogen and a trace of ash; it is probably a cerebrin, but is not identical with the cerebroside isolated by Bamberger and Landsiedl from *Lycoperdon Bovista* (Abstr., 1905, ii, 852).

Scholl has shown that chitin can be obtained in a comparatively simple manner from *Boletus edulis* (Abstr., 1908, ii, 1065). The author has applied Scholl's method to this fungus, and also obtained a product rich in chitin. The method, therefore, seems to be suitable for the isolation of chitin from fleshy fungi, but not from those having coriaceous or leathery membranes. C. S.

Composition of the Pulp of Cassia fistula. CONSTANT GRIEBEL (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 283—288).—Four samples of cassia pulp, free from seeds and tissue, were found to contain: Insoluble substances, 6·32—9·99%; invert sugar, 6·79—16·42%; sucrose, 53·13—66·31%; sugar-free extractives, 20·31—24·32%; mineral substances, 3·98—5·67%. Citric acid, tannins, pectinous substances, and colouring substances were also present. As a rule, the presence of added sugar is not indicated by the sucrose content of a sample, this form of adulteration being detected more readily from the amounts of sugar-free extractives and mineral substances present. A mixture consisting of 75% of pure pulp and 25% of sucrose gave the following results on analysis: Insoluble substances, 6·19%; invert sugar, 7·12%; sucrose, 72·36%; sugar-free extractives, 14·33%; mineral substances, 2·91%. All the figures given are calculated on the dry substance. W. P. S.

Variations in the Composition of the Root of the Gentian during a Year's Growth. MARC BRIDEL (*J. Pharm. Chim.*, 1911, [vii], 3, 294—305).—The principal constituents of the root of the official gentian (*Gentiana lutea*) are the glucoside gentiopicrin and the carbohydrates dextrose, lævulose, sucrose, and gentianose. Gentianose is hydrolysed by invertase, yielding lævulose (1 mol.) and gentiobiose; the latter can be hydrolysed by the gentiobiase in emulsin to 2 mols. of dextrose. For this reason, the amount of gentiopicrin in the root of the gentian cannot be estimated by the aid of emulsin and the polarimeter, because the enzyme hydrolyses the gentianose as well as the glucoside. However, by extracting the root with alcohol, evaporating the extract to dryness, and extracting the residue with ethyl acetate (which only dissolves the gentiopicrin), it is possible to separate the glucoside from the accompanying carbohydrates and to estimate, in the manner described in the paper, the gentianose in the residue insoluble in the ethyl acetate and the gentiopicrin in the ethyl acetate solution.

The following observations have been made. At the beginning of June the root of the gentian contains a minimal amount (1·2%) of carbohydrates hydrolysable by invertase; from this month the amount increases until August (7·8%), and then remains approximately constant. The amount of gentiopicrin does not vary much throughout the year; it is about 2%, and shows a slight increase in June and July. Gentianose is always present to the extent of 3—5%, except during May and June, when the root contains gentiobiose; the amount of gentianose reaches its maximum in August and September. The amount of sucrose shows the greatest variations; it increases from about 1% in July to more than 4% in November, and is absent at the renewal of the growth in the spring. C. S.

Pæonol Produced by Decomposition of a Glucoside. G. PÉRON (*J. Pharm. Chim.*, 1911, [vii], 3, 238—241).—It is shown that pæonol, isolated by Martin and Jagi (Abstr., 1879, 206) from the roots of the tree peony (*Pæonia arborea*) occurs in this drug in the form of a glucoside, along with a specific enzyme, which decomposes the latter, furnishing pæonol and dextrose. The glucoside, which is also hydrolysed by hot dilute sulphuric acid, but not by emulsin, could not be isolated. The roots also contain sucrose. The specific enzyme also occurs in the roots of *Pæonia officinalis*. T. A. H.

Betaines of Plants. I. ERNST SCHULZE and U. PFENNINGER (*Zeitsch. physiol. Chem.*, 1911, 71, 174—185. Compare Schulze and Trier, Abstr., 1910, ii, 743).—Phosphatides from the latex of *Vicia sativa*, *Pisum sativum*, and *Phaseolus vulgaris* yield no base other than choline on hydrolysis; neither betaine, trigonelline, nor stachydrine could be identified. This is in agreement with previous experience with leguminous plants. Apparently the occurrence of betaine and trigonelline in the latex of such plants has no genetic relationship to the formation of the phosphatides.

The phosphatide of oats, *Avena sativa*, yields on hydrolysis a small proportion of betaine as well as choline. E. F. A.

Phosphates with Organic Linkings. P. A. BOORSMA (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 210—213).—Extraction of rice-bran with water or very dilute acetic acid yielded a liquid containing a considerable proportion of phosphates, both inorganic and organic, which were precipitated by heating. On ignition of the dry precipitate, 72·6% of ash containing only phosphates remained. Analysis of the ash gave the following results: P_2O_5, 59·7%; Fe_2O_3, 5·37%; CaO, 1·95%; MgO, 28·5%; K_2O, 3·7%.

Analyses of copper, silver, and lead derivatives indicated that the organic phosphate mixture contained at least two organic compounds. Attempts to isolate them were unsuccessful. A. J. W.

The Constituents of Scopolia japonica. MATAJIRO WATANABE (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VIII B, 134—135).—The leaves of *Scopolia japonica* contain about 0·18% of alkaloids, about 90% of which is hyoscyamine, together with 5% of scopolamine and a small quantity of atropine. C. H. D.

Symptoms shown by Plants under the Influence of Different Toxic Compounds. OSWALD SCHREINER (*Proc. Amer. Soc. Biol. Chem.*, 1910, xiii—xiv; *J. Biol. Chem.*, 9).—Organic substances cause changes in certain definite plant characteristics, and if occurring in the soil, may produce certain diseases in plants. From the numerous instances given, the following may be mentioned: coumarin causes distortion of the leaves; vanillin inhibits root growth; benzoquinone causes tall, slender growths. The coumarin effect is overcome by phosphates, the vanillin effect by nitrates, and the benzoquinone effect by potassium salts. W. D. H.

Influence of Nutrition on the Variability in the Composition of Sugar Beet in the First Year of Growth. KARL ANDRLÍK and JOSEF URBAN (*Zeitsch. Zuckerind. Böhm*, 1911, **35**, 369—378).—Sand culture experiments with sugar beet manured with definite amounts of potassium and sodium nitrates and superphosphate. The seed employed was from one root, the object being to ascertain the variations due to different manures in excess.

The variations in the different constituents were as follows: sugar, 4·8; N, 0·119; K_2O, 0·219; Na_2O, 0·075, and P_2O_5, 0·079%.

In the production of 100 parts of sugar the following amounts of nutritive substances were utilised: N, 2·75—6·64; K_2O, 3·79—8·64; Na_2O, 1·09—6·49, and P_2O_5, 0·87—1·46 parts. N. H. J. M.

Presence of Optically Active Non-sugars in the Beet Influencing the Polarisation Results. FRIEDRICH STROHMER and OTTOKAR FALLADA (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. V, 47—55).—In certain seasons the amount of sugar in the beet as determined by the hot water digestion method is larger than that determined by Clerget's method. This is due to the solution of dextrorotatory pectin substances present in excess of the quantity which the normal addition of lead acetate is able to precipitate.

The amount of dextrorotatory pectin dissolved increases with the temperature of extraction, and the cold water digestion method is therefore to be preferred. Alcoholic extraction gives trustworthy results for scientific work. E. F. A.

A Combination of Glycuronic Acid from the Sugar Beet.

K. Smolenski (*Zeitsch. physiol. Chem.*, 1911, **71**, 266—269).—A substance was separated out from sugar residues which is regarded as a glycuronide of Andrlík and Votoček's beetroot-resin acid (Abstr., 1898, i, 157). It has the formula $C_{28}H_{44}O_8$, and on hydrolysis splits into beetroot-resin acid ($C_{22}H_{36}O_2$) and glycuronic acid ($C_6H_{10}O_7$). The interest of the substance is that it is the first time glycuronic acid has been obtained directly from the vegetable world. W. D. H.

Nitrogen Nutrition of Leguminosæ.

Georg Ritter (*Centr. Bakt. Par.*, 1911, ii, **29**, 650—668).—Pot experiments are described in which blue lupins were grown in an exhausted heavy loam, without manure, with mineral manures, and with mineral manures in conjunction with ammonium salts or sodium nitrate. Some series were inoculated with soils on which lupins or other leguminous plants had grown.

The results show that, in absence of nodule organisms, blue lupins develop normally when supplied with sodium nitrate or with ammonium sulphate. Ammonium salts, which are directly assimilated, seem to produce more growth than the same amount of nitrogen as nitrates.

The plants which were inoculated and received no combined nitrogen beyond the small amount in the soil produced fairly large amounts of growth. Both the growth and the amount of nitrogen in the produce were less than when combined nitrogen was supplied. Application of nitrogenous manure during the early period of the growth of inoculated plants produced good results by preventing any injury during the period of hunger.

No nodules were produced in the soil unless inoculated with lupin or serradella soil. Clover, lucerne, pea, and bean soils had no effect. Serradella soil gave even better results than lupin soil.

Blue lupins can be grown on heavy soil containing calcium carbonate. N. H. J. M.

Removal of the Constituents of Peas by Water and Aqueous Solutions.

Edmond Poppe (*Bull. Soc. chim. Belg.*, 1911, **25**, 136—145).—Comparative measurements of the soluble substances removed from peas (*Pisum sativum*) by water and aqueous solutions of sodium chloride and sucrose have been made at 20°, 50°, and 100°. The analytical data obtained have reference to nitrogenous compounds estimated by Kjeldahl's method, to phosphates, chlorides, and to carbohydrates, which were estimated by means of Fehling's solution after hydrolysis by hydrochloric acid. In general, the extraction of soluble substances increases with rise of temperature, and in the case of water the quantities removed are greater than for the aqueous solutions under comparable conditions. H. M. D.

Mode of Action of Sulphur in Combating Oidium. RÉNE MARCILLE (*Compt. rend.*, 1911, **152**, 780—783. Compare Foreman, this vol., ii, 222).—The beneficial effect of finely divided sulphur for destroying cryptogams in viticulture is attributed to the small amount of sulphuric acid in the preparations usually employed. Samples examined contained 0·22—0·625% of sulphur trioxide. W. O. W.

Occurrence of Tyrosine Crystals in Roquefort Cheese. ARTHUR W. DOX (*J. Amer. Chem. Soc.*, 1911, **33**, 423—425).—In the course of the examination of several specimens of Roquefort cheese, small, white specks were observed in the cracks and crevices. These were carefully picked out and were identified as crystals of tyrosine. It is well known that cheese often contains tyrosine, but this substance has not previously been found to occur in it in the form of crystals. E. G.

Biochemical Circulation of the Phosphate Ion in Soils. JULIUS STOKLASA (*Centr. Bakt. Par.*, 1911, ii, **29**, 385—519).—In calcareous soils most of the soluble phosphoric acid applied as superphosphate is rendered insoluble in seven or eight weeks. In fertile soils most of the phosphoric acid is present in organic forms ; meadow and peat soils were found to contain 0 0018—0·0034% of phosphorus as phosphatides.

Assuming that soil organisms produce in twenty-four hours 15 mg. of carbon dioxide in 1 kilogram of soil to a depth of 40 cm. (five times as much may be produced in garden soil), the amount of carbon dioxide per hectare would be 75 kilos. per day. In addition to carbon dioxide there is a constant production of a variety of organic acids from the breaking down of carbohydrates, which not only act on phosphates, etc., but subsequently serve as food for micro-organisms.

As regards the decomposition of organic phosphorus compounds, nucleic acid is only attacked in presence of a sufficient amount of suitable carbon compounds, whilst some micro-organisms require nitrogen as well.

The intensity of absorption of phosphoric acid by bacteria depends to a great extent on the number of bacteria present ; in soil which was not inoculated, 66% of the total phosphoric acid was absorbed, whilst in the same soil inoculated the absorption was 98%. Inoculation of the soil with *Bacillus mycoides* increased the yield of barley by rendering the nutritive substances of the soil more readily available.

The energy of nitrogen assimilation in soils, and of the production of ammonia, furnish indications of the relative amounts of readily assimilable phosphoric acid present in different soils. N. H. J. M.

Production of Acids and Alkalis in the Soil. ALFRED D. HALL and NORMAN H. J. MILLER (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VII., 17—18).—Application of ammonium salts to soils deficient in calcium carbonate results in the production of free acid, owing to the withdrawal of the ammonia by lower and higher vegetation. This has occurred on some of the experimental grass plots at Rothamsted, the soil of which, when extracted with water, yields solutions containing small amounts of free mineral acid and much larger amounts of humic acid. Nitrification is almost suspended, and the plants take up most of their nitrogen in the form of ammonia (compare Hutchinson and Miller, Abstr., 1909, ii, 923).

Application of nitrates tends to produce an alkaline reaction, since the plants require more nitrogen than sodium (compare Hall and Miller, Abstr., 1906, ii, 119). Free sodium carbonate can be extracted from some of the Rothamsted plots which have received sodium nitrate continuously. An injurious effect on the soil is produced by the deflocculating action on the clay. Similar results may be produced when potassium sulphate and sodium chloride, etc., are applied to soils containing calcium carbonate. The injurious effect of potassium salts is evident on several of the Rothamsted plots. N. H. J. M.

Injurious Bacterial Activity in Soils. RUDOLF EMMERICH, W. GRAF ZU LEININGEN and OSKAR LOEW (*Centr. Bakt. Par.*, 1911, ii, **29**, 668—683).—Addition of 0·5% starch to a loam soil containing 0·6% of calcium carbonate and manured with ammonium chloride retarded the growth of flax; the roots were brown and mostly dead. As this result could not be due to the production of acidity, or to reducing processes (no nitrate or sulphate being applied), the injurious action is attributed to suffocation of the roots by the withdrawal of oxygen by overcrowded bacteria.

As regards injury by organisms producing hydrogen sulphide, it was found that a 0·42% solution of the gas, when diluted fifty times, is still injurious to twigs of *Tradescantia*. The examination of different soils showed that organisms which produce hydrogen sulphide from sulphates occur frequently.

The most important acid-producing microbes seem to be the different kinds of butyric acid bacillus, which occur very generally, and in subsoils as well as at the surface. The organisms were found at a depth of 85 cm. in a loam soil and frequently on plants.

The more favourable effect of rotted farmyard manure as compared with fresh manure is due to the production in the latter of formic, acetic, and butyric acids, indole, scatole, and hydrogen sulphide, whilst in old manure these substances have been mostly oxidised. Very injurious effects have been observed in tobacco plantations after the application of cotton cake.

The methods employed for examining soils for the different injurious organisms are described. N. H. J. M.

Changes Induced by the Addition of Carbohydrates to Soils. HENRY B. HUTCHINSON and FRANCIS S. MARR (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VII., 37—40).—Application of starch at the rate of 1 ton per acre to a part of the continuously unmanured barley plot at Rothamsted and to the plot receiving complete mineral manure resulted in an average reduction of 17·45% in the yield, whilst the subsequent application of the same amount of sucrose reduced the average yield, the next year, by 31·2%. The examination of the soil showed a striking increase in the number of bacteria and moulds where carbohydrates had been applied, the bacterial content of the untreated and the treated soil being 6·4 and 14·9 millions per gram respectively.

In order to throw some light on the rate of oxidation of carbohydrates in the soil, 2% of starch, mannitol, and dextrose respectively were added to soil (200 grams) in cylinders through which air was passed for fifteen minutes every day, and the carbon dioxide estimated. The series included soil without carbohydrate, and two additional lots with dextrose to which sodium nitrate and ammonium sulphate respectively, were added. The amount of carbon dioxide produced in thirty days, calculated as percentages of carbohydrate, were as follows : starch, 9·6 ; mannitol, 30·5 ; dextrose, 42·0 ; dextrose + $(NH_4)_2SO_4$, 53·1, and dextrose + $NaNO_3$, 55·5%. The bacterial contents of the soils were: 10·40, 5·52, 11·72, 17·01, and 10·59 millions per gram. The bacterial content of the untreated soil was 5·48 millions per gram, or about the same as soil + mannitol.

N. H. J. M.

Two Compounds Isolated from Peat Soils. CHARLES S. ROBINSON (*J. Amer. Chem. Soc.*, 1911, **33**, 564—568).

—Suzuki (Abstr., 1907, ii, 127) has obtained several amino-acids, including leucine, from a natural humic acid, and Schreiner and Shorey (this vol., ii, 65, 147) have isolated various nitrogen compounds from soils.

Leucine and *iso*leucine have now been isolated from certain peat soils.

E. G.

Sulphur Requirements of Farm Crops in Relation to the Soil and Air Supply. EDWIN B. HART and W. H. PETERSON (*J. Amer. Chem. Soc.*, 1911, **33**, 549—564).

—The amount of sulphur in various feeding materials has been estimated by the peroxide method (Osborne, Abstr., 1902, i, 251), and it is shown that such products contain a much higher total of sulphur trioxide than is found in the ash, a large proportion being lost by ignition. A table is given of the quantities of sulphur trioxide removed from the land per acre by average crops. Estimations have also been made of the sulphur trioxide in several soils, some of which had been manured, whilst others had not been manured.

The results show that considerable quantities of sulphur are removed from the soil by common crops. Although the loss is partly compensated by the supply of sulphur from the atmosphere, the latter is probably counterbalanced by the losses the land sustains by drainage. Soils which had been cropped for fifty to sixty years, and had received little or no manure, were found to have lost an average of 40% of the sulphur trioxide originally present, as determined by comparison with virgin soils, but in cases in which farm manure had been regularly and liberally applied, the sulphur content of the soil had been maintained or even increased.

It is evident, therefore, that it is necessary to supply sulphur to the soil in order to replace that removed by the crops and drainage. Suitable sources of the element are farm manure, commercial superphosphate, ammonium sulphate, potassium sulphate, and calcium sulphate.

E. G.

Influence of Calcium Carbonate and Ammonium Sulphate on the Assimilation of Phosphoric Acid from Different Sources. Dmitri Prianischnikoff (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VII, 87).—Addition of calcium carbonate, in conjunction with sodium or calcium nitrate, to sand cultures gives rise to a considerable depression in the yield when bone meal, crude phosphates, and pure tricalcium phosphates are employed. With aluminium and iron phosphates the depression is less marked, whilst with basic slag, acid phosphate, and dicalcium phosphate no effect is produced.

Ammonium sulphate renders even crude phosphates available, but at the same time acts injuriously on the plants, owing to the liberation of acid. The injurious action may be overcome by adding small amounts of calcium carbonate; larger amounts of carbonate render crude phosphates completely useless for gramineous plants.

The best results are obtained when sodium nitrate and ammonium sulphate are employed together. N. H. J. M.

Amounts of Chlorine and Sulphuric Acid in Rain-Water. J. Wituynj (*J. exper. Landw.*, 1911, **12**, 20—30 [in Russian], 30—32 [German abstract]. Compare Kinch, Trans., 1900, **77**, 1271).—The amounts of chlorine and sulphuric acid in rain-water were estimated in monthly samples, collected in eight different places, from April, 1909, to March, 1910. The average amounts per million of rain-water, and the total amounts for the year in lb. per acre were as follows:

	Rainfall		Per million		Per acre (lb.)	
	days.	inches.	Cl.	SO_3.	Cl.	SO_3.
1. St. Petersburg	225	25·41	3·56	12·21	20·53	70·37
2. Ochta	209	26·34	2·36	11·87	14·10	70·88
3. Pawlowsk	229	20·53	1·57	3·52	7·43	16·38
4. Sapolje	—	19·13	3·01	2·22	13·05	9·65
5. Smolensk	225	25·98	3·06	1·00	18·13	5·91
6. Mariupol	93	13·35	3·77	16·26	11·40	49·27
7. Tula	141	18·76	1·83	1·92	7·78	8·19
8. Borowoje, Samara	124	21·30	1·95	1·06	9·42	5·13

In the St. Petersburg Government (Nos. 1—4) the highest amounts of chlorine occur in spring and autumn, when sea winds predominate.

The results obtained at St. Petersburg, Ochta, and Mariupol indicate that the sulphuric acid is chiefly derived from the combustion of coal and wood. N. H. J. M.

Analytical Chemistry.

Simple Arrangement for Reading Ordinary Burettes. Jaroslav Milbauer (*Chem. Zeit.*, 1911, 35, 419).—The author imitates the ordinary Schellbach burette by marking a vertical line, 2 mm. broad, on a visiting card, and then cutting the latter so that it will slide over the burette. The reading can then be taken exactly as in the Schellbach burette. T. S. P.

Washbottle for Continuous Hot Water Supply. G. E. Boltz (*J. Amer. Chem. Soc.*, 1911, 33, 514—515).—A washbottle is described which provides a convenient method of washing precipitates in analytical work. It consists of a heavy, five-litre boiling flask, fitted with a rubber stopper with three holes. Through one of the holes passes a glass tube connected with the washing jet, and through another a tube leading from the flask to a large supply-bottle. In order to allow steam to escape from the flask and to prevent the latter from becoming filled, owing to condensation caused by the cold water from the supply-bottle, a special valve is provided. This consists of a tube which passes through the third hole in the rubber stopper, and towards the upper end has a constriction fitted with a ground-glass plug. The upper end of the tube is partly closed to prevent the escape of the plug. In the lower part of the tube is inserted a float, consisting of a glass bulb with a long stem. As the water from the supply-bottle enters the flask and raises the level of the water in the latter, the float rises until its stem raises the plug and thus allows air to enter. In order to obviate the bursting of the flask by the sudden condensation of the steam, a safety mercury-valve is recommended, which can be easily made by means of a bent glass tube, one end passing through the rubber stopper, and the other, which has a bulb 6″ from the end, dipping into a vessel of mercury.

E. G.

Calculation of Gas Analyses. Rud. Jeller (*Zeitsch. anal.*, 1911, 50, 250—263).—A paper containing useful formulæ for the calculation of analyses of mixtures of gases by the combustion process.

L. de K.

Exact Electrolytic Method for Estimating Metals. W. L. Perdue and George A. Hulett (*J. Physical Chem.*, 1911, 15, 147—154).—Electrolysis is carried out in an amalgamated platinum crucible containing a mercury cathode which dissolves the metal deposited on it. The anode is a spiral of platinum wire suspended near the surface of the electrolyte, which is covered with an inverted funnel. The current is passed until the liquid evolves gas freely, the consequent spraying washing down the funnel and the walls of the crucible. The cathode is washed by displacing the electrolyte with conductivity water, without breaking circuit, until the current falls to zero. Oxidation of the cathode is thereby prevented. The previous amalgamation of the platinum crucible enables the mercury to wet it, so that the electrolyte does not get behind the mercury and the latter can be washed without agitation. The crucible and amalgam are dried in a vacuum desiccator containing a dish of mercury to maintain the vapour pressure.

The method, it is claimed, avoids the error due to the inclusion of electrolyte and gases in solid metal cathodes, as in the case of the silver voltameter. It is well adapted to metals like cadmium which are easily soluble in mercury, but with metals, such as copper and zinc, which form solid amalgams, it is necessary to agitate the mercury by rotating the cathode so that the amalgams do not collect on the surface.

R. J. C.

New Apparatus for the Electro-Analytical Estimation of Metals. A Glass-Frame Anode for Use with Silver and Nickel Cathodes. HENRY J. S. SAND and WILLIAM M. SMALLEY (*Trans. Faraday Soc.*, 1911, 6, 205—211. Compare Abstr., 1910, ii, 66).—An apparatus for electrolytic estimations has been so designed as to require a minimum quantity of platinum. The anode consists of platinum gauze, attached to a central glass frame by fusion, and capable of rotation; the cathodes are of silver or nickel gauze on a frame of sheet metal, slipping over the outer guide-tube of the anode. Silver cathodes are found suitable for estimations of copper, stripping being effected by a 10% solution of sulphuric acid to which hydrogen peroxide has been added. Nickel cathodes serve for estimations of zinc.

Copper is deposited in about five minutes, using a current of 10 amperes, afterwards reduced to 5 amperes. Zinc, in acetic acid solution, requires twenty-five minutes, and the results are slightly high; in citric acid solution the tendency to be high is less, but the time required is greater. Copper and zinc are easily estimated in succession in the same solution. C. H. D.

Halogenimetry. JUAN A. SANCHEZ (*7th Intern. Congr. Appl. Chem.*, London, 1909, Sect. I., 144—145).—Fifty c.c. of a solution containing chlorides, bromides, and iodides, the quantity of iodide present being equivalent to not more than 0·3 gram of potassium iodide, are heated with 10 c.c. of 20% sodium nitrate and 5 c.c. of 1 : 4-sulphuric acid until all iodine is expelled. The difference between the estimations of total halogen before and after boiling gives the iodine. The solution, containing only chlorides and bromides, is distilled with 5 c.c. of 1 : 4-sulphuric acid and 5 grams of manganese dioxide. Bromine only is expelled, and is absorbed in potassium iodide solution and titrated. When chlorides are present in large excess, some chlorine passes over. The mixed vapours are absorbed in a solution of an alkali sulphite, the excess of sulphite decomposed by heating with sulphuric acid, and bromine estimated as above.

C. H. D.

Estimation of Halogens in Organic Compounds. W. O. WALKER and J. A. MACRAE (*J. Amer. Chem. Soc.*, 1911, 33, 598—599).—Stephanoff (Abstr., 1907, ii, 50) has described a method for estimating halogens in organic compounds which depends on the reducing action of nascent hydrogen formed by the action of sodium on ethyl alcohol. A study of Bacon's modification (Abstr., 1909, ii, 179) of this method has shown that it is not of general applicability, and cannot be used with substances which are difficult to reduce.

Maryott (this vol., ii, 66) has come to the same conclusion with regard to Stephanoff's original method, but has found that good results can be obtained by using potassium instead of sodium. E. G.

Estimation of Chlorine in Presence of Hydrochloric Acid. C. E. Bolser and J. W. E. Glattfield (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. I., 87—88).—The solution containing chlorine and hydrochloric acid is introduced into a Geissler bulb, connected with a second bulb containing potassium iodide solution. A current of air is then drawn through the bulbs until nearly all the chlorine has been driven over. The contents of the second bulb are then titrated with thiosulphate. The contents of the first bulb are transferred to a beaker containing some potassium iodide solution, the small quantity of liberated iodine titrated, and the acid is then titrated with *N*/2-sodium hydroxide and phenolphthalein. The solutions used are standardised by using known quantities in the same apparatus, the quantity of liquid used being always the same. The limit of accuracy is about 0·4%. C. H. D.

Estimation of Chlorides in Bromides. Otto Herting (*Pharm. Zeit.*, 1911, **56**, 253—254).—The method proposed is based on the fact that bromine is expelled from bromides by heating with acetic acid and lead peroxide, whilst chlorides which may be present are unaffected; this reaction is prescribed in the U.S. Pharmacopœia as a test for chlorides in zinc bromide. For the estimation of chloride in potassium or sodium bromide, 3 grams of the salt, about 6 grams of lead peroxide, and 50 c.c. of 50% acetic acid are heated together in a flask until bromine vapours cease to be evolved and the mixture has been concentrated to a syrupy consistence. After cooling, the residue is dissolved in water, the solution is filtered, and the filter and insoluble portion are washed. The filtrate is then treated with 20 c.c. of concentrated nitric acid, 15 c.c. of *N*/10-silver nitrate solution and 5 c.c. of ferric nitrate solution are added, and the excess of silver is titrated with *N*/10-thiocyanate solution. W. P. S.

Estimation of Small Quantities of Iodides, alone or in Presence of Other Substances. R. Bernier and G. Péron (*J. Pharm. Chim.*, 1911, [vii], **3**, 242—248).—The process employed is a combination and improvement of those due to Baubigny and Rivals (Abstr., 1904, ii, 81) and Longi and Bonavia (Abstr., 1898, ii, 570, 637).

The material taken for analysis should contain 0·01 to 0·03 gram of iodine as iodide. It should be dissolved in 50 c c. of water, made slightly alkaline with sodium hydroxide, and a few crystals of potassium permanganate added and the solution boiled for a few minutes, more permanganate being added until a faint permanent coloration is maintained. The slight excess of permanganate is destroyed by adding alcohol. The solution is then diluted to 110 c.c. when cold, and 100 c.c. of filtrate collected. To this, 10 c.c. of acetic acid and 5 c.c. of potassium iodide solution (10%) are added, and the liberated iodine titrated with *N*/10-sodium thiosulphate. For smaller quantities of iodine than those prescribed, *N*/100-sodium thiosulphate may be used, mucilage of starch being added towards the end of the reaction. The process is applicable in presence of fluorides, chlorides, bromides, or chlorates, but bromates must first be reduced by sodium hydrogen sulphite. Sulphides and other sulphur compounds, and also arsenites and antimonites, do not interfere with the accuracy of the process. Cyanides must be eliminated by boiling the solution with acetic acid, and ammonium salts by boiling with alkalis, since both these compounds give rise to nitrous acid in presence of permanganate.

T. A. H.

Formation of Hypoiodites and their Action on Sodium Thiosulphate. A Source of Error in Certain Iodine Titrations. J. P. BATEY (*Analyst,* 1911, **36**, 132—137).—Antimonious salts may, as is well known, be titrated with standard iodine in the presence of sodium hydrogen carbonate. The author, having added an excess of iodine and then titrated back with standard sodium thiosulphate, obtained results in excess of those obtained by the direct method.

It is found that unless the quantity of sodium hydrogen carbonate is reduced to a minimum, there takes place a formation of sodium hypoiodite, which has a powerful oxidising action on the thiosulphate (formation of sulphate), and so vitiates the results. Sodium hydrogen tartrate may be substituted with advantage for the acid carbonate.

L. DE K.

New Method for the Estimation of Fluorine. GUNNAR STARCK (*Zeitsch. anorg. Chem.*, 1911, **70**, 173—177).—No accurate method of estimating fluorine by precipitation is known, and the distillation methods are tedious. It is now found that lead chlorofluoride, $PbFCl$, is sufficiently insoluble, and is very readily filtered. The compound dissolves in water to the extent of 0·1241 millimols. in 100 c.c. at 18°, but is practically insoluble in dilute solutions of lead chloride. Hydrochloric or acetic acid increases the solubility.

About 50 c.c. of a solution containing 0·1 gram of sodium fluoride are rendered neutral to phenolphthalein, and 200 c.c. of a cold saturated solution of lead chloride are added. After remaining over night, the precipitate is collected on a Gooch crucible, washed with lead chloride solution, and then with water, and dried at 140—150°, or the precipitate may be dissolved and the chlorine estimated.

The method has been found to give accurate results with soluble fluorides, alone or mixed with other salts. C. H. D.

Estimation of Total Sulphur in Coals. THEODOR ST. WARUNIS (*Zeitsch. anal. Chem.*, 1911, **50**, 270—272).—One gram of the finely-powdered sample is placed in a porcelain crucible, and intimately mixed with 1 gram of dry sodium carbonate and 2 grams of copper oxide. The crucible is placed in a slanting position on a perforated asbestos board, and heated with a bunsen burner so as to let the lower part get red hot. The mass should be often stirred with a thick platinum wire; the coal will then be completely burnt in about two hours.

The mass, when cold, is treated with a little bromine water, and then dissolved in dilute hydrochloric acid containing bromine. After boiling off the excess of bromine and filtering off from any insoluble matter, the sulphuric acid is precipitated as usual with barium chloride.

L. DE K.

Kjeldahl's Process. VINCENT EDWARDS and DUDLEY CHADS (*Chem. News*, 1911, **103**, 138).—The addition of granulated tin instead of zinc to the contents of the distilling flask is recommended to obviate bumping and frothing. T. S. P.

Industrial Estimation of Nitrates and Nitric Esters. M. MARQUEYROL and D. FLORENTIN (*Bull. Soc. chim.*, 1911, [iv], **9**, 231—240).—Schlœsing's method for the estimation of nitrates has been compared with Lunge's nitrometer method and the sources of error in each determined, and it is shown that the two give concordant results if sulphuric acid of 94—95% strength is used in the nitrometer method.

The nitric oxide formed and measured in Schlœsing's method is impure, due to the inclusion of (1) air dissolved in the hydrochloric acid; (2) air and carbon dioxide from the water employed, unless the latter is distilled water which has been boiled recently. In the modified form of Schlœsing's method, devised for use with explosives, the nitric oxide is collected over potassium hydroxide solution with the aid of a current of carbon dioxide, and in this form is subject to the following errors: (1) inclusion of (*a*) gaseous impurities from the carbon dioxide, (*b*) air from the hydrochloric acid; (2) loss of nitric oxide, due to the action of potassium hydroxide. These errors compensate each other if the estimation does not occupy more than twenty to twenty-five minutes, and agitation not more than five minutes.

The results obtained with the nitrometer method vary with the strength of the sulphuric acid, the nitric oxide being partly absorbed by acid of 96—97% strength, and the error due to this cause is increased by excessive agitation. The best results are afforded by acid of 94% strength (compare Newfield and Marx, Abstr., 1906, ii, 628). T. A. H.

Magenta-S as a Permanent Standard for the Estimation of Nitrites in Water Analysis. JOSEPH H. KASTLE and ELIAS ELVOVE (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. VIII A, 289—294).—The coloration obtained with water containing nitrites by means of Griess's sulphanilic acid and α-naphthylamine reagent may be accurately matched by solutions of magenta-S. The standard solution is made by dissolving 0·2 gram of magenta-S in 50 c.c. of 2*N*-hydrochloric acid and diluting to 2000 c.c. with water. One hundred c.c. of this solution are diluted with 50 c.c. of 2*N*-hydrochloric acid and made up to 2000 c.c. This solution is found to be unchanged in colour after seven months. A number of test analyses are given. C. H. D.

The Estimation of Phosphoric Acid. GUNNER JÖRGENSEN (*Zeitsch. angew. Chem.*, 1911, **24**, 542—544).—A recapitulation of a previous paper on the same subject. The author upholds the accuracy of his molybdate process (compare also *Analyst*, 1909, **34**, 392). L. DE K.

Titrimetric Estimation of Phosphorus in Small Amounts. L. T. BOWSER (*Amer. Chem. J.*, 1911, **45**, 230—237).—The various methods employed hitherto for the estimation of small quantities of phosphorus are all colorimetric, with the exception of that described by Veitch (*U.S. Bur. Chem.*, *Bull.* **90**, 1904, 188), and are all open to some objection.

According to Veitch's method, the phosphomolybdate precipitate is titrated with potassium hydroxide solution of approximately *N*/6-strength. If, however, a much more dilute solution of potassium hydroxide is used, more accurate results can be obtained. The volume of solution when ready for precipitation should not be less than 20 c.c. It has been found that 0·5 gram of ammonium nitrate should be added, and for 1 mg. of P_2O_5 about 1·5 c.c. of the molybdate solution, or 1 c.c. for quantities of less than 0·8 mg. Precipitation should be effected at 55°, the mixture kept at this temperature for an hour, and afterwards left for two hours before filtering. The potassium hydroxide solution used for titrating should not be stronger than 0·02*N*. E. G.

Estimation of Phosphorus in Milk Ash. FRÉD. BORDAS and F. TOUPLAIN (*Compt. rend.*, 1911, **152**, 899—900. Compare Abstr., 1902, 587).—By comparison of the amount of phosphorus in the ash of milk with the sum of the amount present in the serum (mineral phosphorus) and the amount present in the curd (organic phosphorus) after coagulation with trichloroacetic acid, it is evident that practically no phosphorus is lost by volatilisation when the determination is made in the usual way on the total ash. W. O. W.

Detection of Arsenic, Phosphorus, and Antimony in the Medical Diagnosis of Poisoning from these Substances. FRANCESCO PEDRAZZINI (*Boll. Chim. Farm.*, 1911, **50**, 134).—The suspected substance is treated with zinc and sulphuric acid, and the evolved gas is passed into a very weak solution of silver nitrate. Any black precipitate which forms is collected, dissolved in a solution of tartaric acid, and tested for antimony with hydrochloric acid. A portion of the filtrate is tested for arsenic by observing whether a crystal of silver nitrate becomes yellow or black when it is placed in the gas evolved on treating it with zinc and sulphuric acid. Phosphorus is tested for in another portion of the filtrate by means of ammonium molybdate. R. V. S.

Estimation of Arsenic in Arsenical Greens. ALF. HEIDUSCHKA and A. REUSS (*Zeitsch. anal. Chem.*, 1911, **50**, 269).—About 0·5 gram of the sample is boiled with 5 grams of crystallised ferrous sulphate and 60 c.c. of hydrochloric acid (D 1·19) in a Kjeldahl distilling apparatus, and the vapours containing the arsenic are condensed in an Erlenmeyer flask placed in ice water to which is attached a Peligot tube; both of these contain aqueous potassium hydroxide, amounting together to about 40 grams of the solid reagent. When three-fourths of the acid has distilled over, the contents of both flask and tube are united, the liquid is neutralised with hydrochloric acid, and the arsenious acid titrated iodometrically in presence of sodium hydrogen carbonate and starch solution. L. DE K.

Direct Demonstration of Carbon Monoxide in the Tissues at a Time Long Subsequent to Death. Angelo De Dominicis (*Boll. Chim. Farm.*, 1911, 50, 6—8).—The bodies of dogs which had died by poisoning with coal-gas were examined after some months' exposure to light and air. Red colorations indicative of carboxyhæmoglobin could still be observed, especially at the articulations of the limbs, and the coloration was not destroyed by tannic acid. Control experiments with normal dogs did not yield such results.

R. V. S.

Spectro-photometric Method for the Estimation of Krypton. Charles Moureu and Adolphe Lepape (*Compt. rend.*, 1911, 152, 691—693).—The intensity of the very persistent line λ 5871·12 for krypton is observed and compared with the intensity of the line in mixtures of argon and krypton in known proportions. Small quantities of other rare gases do not influence the result.

The necessary mixture of argon and krypton is made by depriving crude argon of krypton by means of wood charcoal, and adding a definite amount of argon from air in which the proportion of krypton is constant. The mixture is passed over cocoanut charcoal at $-23°$, the absorbed fraction transferred to a Plucker tube, and its spectrum observed.

The estimation of about 0·000001 cu. mm. of krypton in 4 c.c. of gas may be effected by this method.

W. O. W.

Microchemical Test for Sodium. Wilhelm Lenz and Nikolaus Schoorl (*Chem. Weekblad*, 1911, 8, 266—268; *Zeitsch. anal. Chem.*, 1911, 50, 263—265. Compare Schoorl, Abstr., 1909, ii, 831).—When finely powdered ammonium uranyl acetate,

$$UO_2(C_2H_3O_2)_2,NH_4(C_2H_3O_2),3H_2O,$$

is brought into contact with the edge of a drop of solution of a sodium salt, pale yellow, sharply defined tetrahedra of the corresponding sodium double salt are rapidly formed at the line of contact. One part of sodium in 250,000 parts of solution can be detected by this test, but the presence of potassium hinders or prevents the formation of the tetrahedra.

A. J. W.

Estimation of Lithium. Ernst Murmann (*Zeitsch. anal. Chem.*, 1911, 50, 273).—The author has noticed that his "pyridine process" for the estimation of lithium in presence of potassium and sodium or barium (this vol., ii, 334) has already been published by Kahlenberg and Krauskopf (Abstr., 1908, ii, 777).

L. de K.

Separation of Strontium from Calcium. L. Moser and L. Machiedo (*Chem. Zeit.*, 1911, 35, 337—338).—Rawson's process (separation of the dry nitrates by means of strong nitric acid) is not accurate, as strontium nitrate is by no means insoluble in nitric acid. Most of the other processes on record are also untrustworthy. The only satisfactory method is that of Stromeyer, as improved by R. Fresenius, which is based on the solubility of anhydrous calcium nitrate in ether-alcohol mixture, whereas the strontium and barium nitrates are insoluble. Browning's proposal to use amyl alcohol instead offers no advantages. L. DE K.

Sulphite Method for Separating and Identifying Calcium and Strontium. J. I. D. HINDS (*J. Amer. Chem. Soc.*, 1911, **33**, 510—514; *Chem. News*, 1911, **103**, 157).—The separation of calcium and strontium can be effected by taking advantage of the difference in solubility of their sulphites, that of strontium being only slightly soluble (0 033 gram per litre), whilst that of calcium is soluble to the extent of 1·2 grams per litre. Comparative experiments with freshly prepared, concentrated sodium sulphite solution and calcium sulphate solution have shown that the sulphite ion in presence of a slight excess of acetic acid will give a precipitate in a 0·0001*N* solution of the strontium ion, whilst calcium sulphate requires a concentration of 0·005*N*. Calcium and strontium ions are about equally sensitive to the oxalate ion, and the precipitation limit is approximately the same as that of strontium sulphite. On adding sodium sulphite to a solution containing both calcium and strontium in presence of acetic acid, the strontium is precipitated, whilst the calcium remains in solution and can be precipitated with ammonium oxalate. In this way calcium and strontium can be easily and sharply separated.

A modified method for the qualitative analysis of the barium group is described which is both simple and trustworthy. E. G.

Separation of Calcium from Magnesium. ERNST MURMANN (*Monatsh.*, 1911, **32**, 105—115. Compare Abstr., 1910, ii, 897).—The following methods are recommended to replace the usual ammonium oxalate process for the separation of calcium from magnesium.

A solution is prepared from 0·0217 gram of calcium carbonate, 1 c.c. of concentrated aqueous magnesium chloride, 1 gram of aniline hydrochloride, a few drops of hydrochloric acid, and 70 c.c. of water. The solution is treated with 0·5 gram of aniline oxalate, heated, treated with an emulsion of aniline and water in slight excess (recognised by methyl-orange), and filtered after five minutes; 0·0118 gram of calcium oxide, corresponding with 0·0217 gram of calcium carbonate, is obtained. The separation can be effected in the cold under slightly modified conditions, using ammonium chloride instead of aniline hydrochloride, but the filtration must be postponed for twenty hours, and a little concentrated ammonium oxalate should be added fifteen minutes before filtering.

By using pyridine instead of aniline to neutralise the acid in the solution, equally good results are obtained, provided that the solution is just faintly acid, sufficiently dilute, and contains ammonium chloride; the solution may be filtered at once when hot, but the best results are obtained in the cold after twelve to twenty hours.

The preceding processes are prejudicially affected by the presence of potassium or sodium salts, and fail when less than 2% of calcium oxide is present, in which case the sulphate method (*loc. cit.*) must be employed.

If magnesium is not to be estimated in the same experiment, the best method for technical purposes is the following. The solution of the calcium and magnesium salts (50 c.c. of a solution containing 1·1204 gram of calcium oxide and 10 grams of crystallised magnesium chloride per litre) is treated with 3 c.c. of concentrated ammonium chloride and 3 drops of hydrochloric acid, precipitated hot with 5 c.c. of concentrated oxalic acid solution, treated with a slight excess of quinoline, and filtered hot after thirty minutes.

An advantage of these methods with aniline, pyridine, and quinoline is that the concentration of the magnesium salt may be very much greater than when the precipitation is effected in the presence of aqueous ammonia. C. S.

Separation and Estimation of Zinc. P. PIPEREAUT and ANTONY VILA (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. I., 141—143).—Zinc sulphide is precipitated in a very dense form, which is readily washed, by the addition of finely-powdered sulphur to its boiling alkaline solution. The precipitate is quite white, and the completion of precipitation is indicated by the appearance of a pink coloration.

In the analysis of zinc ores, heavy metals are first removed, and sufficient sodium hydroxide is added to retain all the zinc in solution. Insoluble matter is removed by filtration, and the zinc is then precipitated as above, distilled water is added, and the zinc sulphide is collected and washed, first with hot water, and then with boiling water containing ammonium sulphide; it is then ignited in a muffle and weighed as oxide. In the analysis of lithopone, the material is digested with bromine and then heated with nitric and hydrochloric acids, barium sulphate being then removed by filtration. C. H. D.

Assay of the Higher Lead Oxides and Some New Reactions of Lead Salts. A. CHWALA and H. COLLE (*Zeitsch. anal. Chem.*, 1911, **50**, 209—249).—A criticism of the various methods in use for the evaluation of lead peroxide and red lead, and a theoretical explanation of the processes.

The iodometric methods are very unsatisfactory, and some other methods are too tedious. The following process, a modification of Lux's method, may, however, be recommended.

To 1 or 2 grams of lead peroxide are added 100 c.c. of *N*-nitric acid and 25 c.c. of *N*-oxalic acid. The liquid is heated to boiling for about ten to fifteen minutes until the peroxide is reduced. When cooled down to about 80—70°, the excess of oxalic acid is titrated with *N*/5-permanganate; it is advisable to add the bulk of the permanganate at once, and then the last drops slowly. The presence of iron does not interfere, but manganese practically should be absent.

L. DE K.

The Estimation of Copper by means of Hypophosphorous Acid. JOSEF HANUŠ and ARN SOUKUP (*Zeitsch. anorg. Chem.*, 1911, **70**, 282—293).—The method of estimation of copper due to Mawroff and Muthmann (Abstr., 1896, ii, 338) is subject to certain errors, the precipitation of the copper being incomplete, whilst the oxidation of the copper may in some cases compensate this. The incomplete precipitation is due to the acidity of the solution, and if the acid liberated is progressively neutralised, the copper is precipitated almost quantitatively. The method is not suitable for the separation of copper from other metals. C. H. D.

Rapid Analysis of Babbitt Metal. PERCY H. WALKER and H. A. WHITMAN (*7th Intern. Congr. Appl. Chem*, 1909, Sect. I., 107—113).—It is desirable to estimate each metal in a separate portion of the alloy. Copper is estimated by dissolving 1 gram of the alloy in 20 c.c. of hydrochloric acid and 5 c.c. of water, adding nitric acid until dissolved. After evaporating until pasty, a solution of 10 grams of tartaric acid and 13 grams of sodium hydroxide is added. When all is dissolved, 25 c.c. of water are added, the whole boiled, and reduced with 25 c.c. of 0·2% invert sugar. The precipitated cuprous oxide is dissolved in nitric acid, and the copper estimated volumetrically. Cuprous oxide is not completely precipitated, and the results are uniformly low to the extent of 6% of the copper present.

Lead is estimated by dissolving as before, evaporating to dryness, adding 5 c.c. of hydrochloric acid, followed by 150 c.c. of 95% alcohol, and collecting the precipitated lead chloride after two hours. After drying at 105° for an hour, the precipitate is weighed, 0·0085 gram being added to its weight.

Antimony is estimated by Low's permanganate method (Abstr., 1907, ii, 304), but using rather less hydrochloric acid. Tin is estimated by heating so much of the alloy as to contain less than 0·2 gram of tin with concentrated sulphuric acid, adding hydrochloric acid, and reducing with steel turnings in a stream of carbon dioxide, finally titrating with iodine. C. H. D.

The Detection of Mercury in Explosives. G. W. PATTERSON (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. III B, 72—75).—Explosives which are completely soluble in alcohol, ether, or acetone, are dissolved, acidified with sulphuric or hydrochloric acid, and electrolysed. If the explosive is only partly soluble, 2 grams are extracted, and the residue, dried at a low temperature, is evaporated with nitric acid until the organic matter is destroyed. It is then dissolved in water and a little hydrochloric acid, and both this and the organic solution are electrolysed.

Electrolysis is carried out in a covered dish, the electrodes being platinum wires 0·02 inch in diameter, immersed to a depth of 0·5 inch. A current of 2 amperes and 10 volts is used, and is continued overnight. The cathode is then dried, and sealed into a prepared tube, which is then exhausted and examined spectroscopically. A platinum wire must not be used twice. The tube is gently heated during the spectroscopic examination. This method will detect 0·000001 gram of mercury. The cathodes may also be heated with iodine and the mercuric iodide used for quantitative estimation. C. H. D.

The Colloidal Substances in the Soil and their Estimation. D. J. HISSINK (*Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, 60—73).—Van Bemmelen's method for the determination of the nature and proportion of the weathered constituents of soils is discussed, and the results obtained by this are compared with those obtained by the settling and colorimetric methods. H. M. D.

Micro-chemical Reaction for Aluminium with Cæsium Chloride. NICOLAAS SCHOORL (*Zeitsch. anal. Chem.*, 1911, **50**, 266—267; *Chem. Weekblad*, 1911, **8**, 268—269).—The author (Abstr., 1909, ii, 521) has recommended cæsium chloride as a delicate microchemical reagent for aluminium. It appears that the pure chloride as now sold does not act properly, but if the solution is previously inoculated with cæsium-alum, the results are quite satisfactory. L. DE K.

Rapid Estimation of Nickel and Cobalt by means of the Gauze Cathode and Stationary Anode. RAYMOND C. BENNER and WILLIAM H. ROSS (*J. Amer. Chem. Soc.*, 1911, **33**, 493—504).—Benner (Abstr., 1910, ii, 999) has shown that copper, silver, cadmium, and bismuth can be satisfactorily estimated by an electrolytic method in which a gauze electrode is employed.

Experiments are now described which show that nickel and cobalt can be rapidly and accurately estimated by means of the platinum gauze cathode and stationary anode. Several electrolytes were used, most of which gave good results. The rate of precipitation is almost the same for all the electrolytes which can be used in ammoniacal solution, and is but little affected by the quantity of ammonia added. Precipitation takes place rather more slowly in acid solutions, and the rate decreases slightly as the amount of acid is increased. The rate of precipitation of nickel and cobalt on the gauze electrode is rather slower than that at which they are precipitated by the same current when the electrolyte is agitated mechanically, but is quite rapid enough for ordinary purposes. E. G.

The Detection of Chromium in Steel. VLADIMIR STANĚK (*Chem. Zeit.*, 1911, **35**, 308).—On account of the difficulty of treating steel with a fusion mixture, it is preferable to dissolve in 20% sulphuric acid, boil with ammonium persulphate, and shake with hydrogen peroxide and ether, chromium being detected by a blue coloration. C. H. D.

Volumetric Estimation of Uranium. FRED IBBOTSON and S. G. CLARKE (*Chem. News*, 1911, **103**, 146—147).—The uranyl sulphate solution containing 2 to 4 vol. % of sulphuric acid is poured into a flask containing 50 grams of finely-divided, amalgamated zinc, and the whole is heated until a dark brown colour is developed. The flask is then cooled rapidly and the solution filtered through a small pulp-filter, which is washed with cold water After aspirating air until the brown tint has completely disappeared and the liquid has a clear green colour, the uranium is titrated with *N*/20-permanganate.

Should ferric iron be present, its amount may be ascertained in a separate portion of the liquid by reduction with sulphur dioxide and subsequent titration with permanganate. L. DE K.

Sensitiveness of the Colorimetric Estimation of Titanium. ROGER C. WELLS (*J. Amer. Chem. Soc.*, 1911, 33, 504—507).—The coloration produced by the addition of hydrogen peroxide to titanium solutions serves, not only for the estimation of small quantities of titanium, but also for that of small amounts of fluorine (Steiger, Abstr., 1908, ii, 426).

An investigation of this test has shown that the accuracy of the colorimetric estimation of titanium is practically constant for concentrations ranging from 1·5 mg. to 20 mg. per 100 c.c., but decreases considerably with solutions containing less than 1·5 mg. The change in concentration required to produce an appreciable difference in intensity between two solutions of suitable concentrations is about 6·5%, which does not differ much from the results obtained by Horn and Blake (Abstr., 1906, ii, 253, 703) with chromium and copper solutions. If certain precautions are taken, estimations of titanium can be made by the colorimetric method with an accuracy of about 2%.
E. G.

Quantitative Gold Analysis with Ether. FRANZ MYLIUS (*Zeitsch. anorg. Chem.*, 1911, 70, 203—231).—The method of dry assaying is subject to several errors when applied to alloys of gold, whilst an exact method of separation in the wet way is unknown, although pure gold solutions are readily precipitated, the separation of metallic gold being quantitative, but greatly hindered by the presence of silver or copper.

Gold chloride is soluble in ether, and is extracted by ether from solutions containing hydrochloric acid, the removal of gold being complete after three extractions, whilst when hydrochloric acid is absent the extraction is only slow. Anhydrous cupric chloride is also soluble in ether, whilst the hydrated salt is almost insoluble. If a solution of gold and copper chlorides is evaporated to dryness, and water is added, the gold is not extracted by ether. By evaporating an aqueous solution on the water-bath and recrystallising, large, rhombic tablets of a double *salt*, $CuAu_2Cl_8,6H_2O$, are obtained. This salt is not hygroscopic, and melts at 142° without appreciable decomposition. It may also be obtained by neutralising a solution of the acid, $HAuCl_4$, with copper carbonate. This and similar salts do not give up gold to ether until after the acid has been set free by hydrochloric acid. Other chlorides extracted from acid solution by ether are those of iron, antimony, tin, and arsenic, whilst from neutral solution mercuric chloride is more completely extracted than gold chloride.

For the ordinary analysis of alloys, the solution, containing 5—10% of metal and 5—10% of hydrogen chloride, is extracted four or five times with ether, the mixed extracts are distilled, and the gold is precipitated by sulphurous acid. The separation from all other metals by this method is complete. When great accuracy is required, the small quantity of gold remaining in solution after extraction with ether is recovered by concentrating the aqueous layer, converting into sulphates, precipitating by sulphurous acid, dissolving the impure precipitate, and subjecting it to the ether process.

In the analysis of gold coins, nitric and hydrochloric acids are used for solution. The silver chloride is collected, and reduced to silver by hydrogen in a Rose's crucible. It is necessary to test its solubility in nitric acid, and to allow for any gold or iridium found in the residue. The gold is extracted from the solution by the ether method, special apparatus being used to avoid loss of ether. The aqueous layer yields a little silver chloride, and, after removing this, lead is estimated as sulphate. Copper is precipitated as sulphide, and may contain platinum metals. If arsenic, antimony, bismuth, tellurium, and tin are to be estimated, the solution remaining after the gold has been extracted is evaporated to dryness, and the residue heated in a quartz flask, when the volatile chlorides distil, and are completely driven over by a stream of hydrogen. Traces of copper pass into the distillate. Iron, nickel, and cobalt are estimated in the usual way. The platinum metals are mostly precipitated by sulphurous acid, but a part remains in solution, and is recovered by precipitating the copper as sulphide, roasting it to oxide, and extracting with formic acid, which leaves the platinum metals undissolved.

Complete analyses of a number of typical gold coins, conducted in this manner, are given. The brittleness of certain coins is attributed to the presence of minute quantities of lead, and not of iridium, as has been suspected. C. H. D.

Method for the Accurate Determination of Ash in the Analysis of Vegetable and Animal Materials. ÉMILE FLEURENT and LUCIEN LÉVI (*Compt. rend.*, 1911, **152**, 715—718).—The usual method of estimating ash, [even when Schlœsing's modification is employed, has the disadvantage of giving low results through loss of phosphorus. This loss may vary from 7·31% of the total phosphorus content in the case of haricots to 49% in certain varieties of barley, and is due, not only to reduction of phosphates, but also to the volatilisation of organic phosphorus compounds. The following method gives good results. The material is freed from fat, and then carbonised at as low a temperature as possible in a platinum crucible. The mass is triturated, replaced in the crucible, and treated with a solution or milk of lime, containing 0·04—0·15 gram of CaO for every 10 grams of material, according to the proportion of phosphorus. The mixture is evaporated to dryness, calcined by Schloesing's method, and the weight of lime added deducted from the final weight.

W. O. W.

Direct Estimation of Caoutchouc as Tetrabromide. F. WILLY HINRICHSEN and ERICH KINDSCHER (*Chem. Zeit.*, 1911, **35**, 329—330) —The results of experiments carried out by the authors show that loss of bromine occurs when caoutchouc tetrabromide is oxidised by means of nitric acid; this loss takes place even in the presence of silver nitrate, and, if the quantity of caoutchouc is calculated from the amount of bromine found, the result will be too low. The bromine present in the compound may, however, be estimated correctly by fusion with a mixture of potassium and sodium carbonates, or by combustion in oxygen. For the estimation of caoutchouc in vulcanised rubber articles, it is recommended that the bromination should be made after previous extraction with acetone, and that the caoutchouc tetrabromide be then dissolved in chloroform, re-precipitated by the addition of benzene, and weighed; instead of weighing the product, the bromine may be estimated in it as described, and the caoutchouc calculated from the result obtained. W. P. S.

Detection of Fusel Oil in Brandy. EDUARD HERZOG (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 280—282).—A test for amyl alcohol described recently by Holländer (which depends on the production of a green coloration when a mixture, prepared by boiling together a quantity of the brandy to be tested, glacial acetic acid, and phenylhydrazine, is allowed to flow over the surface of concentrated hydrochloric acid) is shown by the author not to be a test for this alcohol. The reaction is due to the presence of furfuraldehyde, and it is not given by either pure amyl alcohol or amyl acetate. Colorations similar to those yielded by furfuraldehyde are also given benzaldehyde, fennel oil, and cinnamon oil. In the case of furfuraldehyde, the test is less sensitive than other well-known reactions for this substance.
W. P. S.

Estimation of the Ash and Sugar in Syrups by the Determination of the Electrical Conductivity. HUGH MAIN (*7th Intern. Congr. Appl. Chem.*, 1909, Sect V., 66—68).—Five grams of sugar are dissolved in 100 c.c. of distilled water and the resistances of the solutions measured at 20° by Kohlrausch's method, using an alternating current between platinum electrodes. The constant (resistance × % of ash) is determined by a short series of experiments, and used for other samples of similar sugars. Samples of molasses are diluted to 33% B, and 2 grams made up to 100 c.c. E. F. A.

New Microscopic Test for Free Acid. J. L. KANTOR and WILLIAM J. GIES (*Proc. Amer. Soc. Biol. Chem.*, 1910, xxvi; *J. Biol. Chem.*, **9**).—Very dilute solutions of organic acids (for instance, acetic and lactic) cause prompt swelling of collagen (white connective tissue) fibres. Proportions of mineral acids which do not respond to the Töpfer and Günzberg tests do not produce this immediate effect.
W. D. H.

Estimation of Formic Acid. HARTWIG FRANZEN and F. EGGER (*J. pr. Chem.*, 1911, [ii], **83**, 323—325).—In Franzen and Greve's method of estimating formic acid (Abstr., 1909, ii, 1057), the hydrochloric acid liberated during the reaction retards its completion, and must therefore be neutralised by the repeated addition of sodium hydroxide. By working in the presence of sodium acetate, however, the concentration of the hydrogen ions is reduced enormously, and the estimation is performed smoothly as follows: the formate (not more than 0·5 gram) is dissolved in about 1 litre of water and treated with 50 c.c. of the reagent (200 grams of mercuric chloride, 300 grams of sodium acetate, and 80 grams of sodium chloride per litre; the solution must be kept for two days, and then decanted from a slight precipitate before use); the mixture is heated on the water-bath for three to three and a-half hours, the mercurous chloride being then collected and treated as described previously. C. S.

The Analysis of Tartrates. OSCAR TOBLER and R. CARAMELLI (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. I., 27—29. Compare Goldenberg, Geromont & Co., Abstr., 1898, ii, 465, 545; 1908, ii, 237).—The following method is proposed: Either 3 or 6 grams of the material are digested with 9 c.c. of hydrochloric acid, D 1·1, agitating for ten minutes. The liquid is then diluted to 100 c.c. and filtered. Fifty c.c. of the filtrate are added to 18 c.c. of a 20% solution of potassium carbonate and boiled for ten to fifteen minutes, and the calcium carbonate is collected and washed with cold water. The filtrate and washings are evaporated to 15 c.c., and 3·5 c.c. of acetic acid are added. After stirring for five minutes, 100 c.c. of 95% alcohol are added, and the precipitate is collected, washed with alcohol, dissolved in 200 c.c. of boiling water, and titrated. A correction is made for the volume of solid in the flask used for dilution. C. H. D.

Measuring Flask for Estimating the Iodine Number. M. DOMINIKIEWICZ (*Zeitsch. anal. Chem.*, 1911, **50**, 267—268).—The apparatus is intended for the determination of the iodine number of fats by Hübl's process, and to prevent any loss of iodine by volatilisation. It is simply a litre flask, the somewhat wide neck of which is enlarged at the top in funnel shape. After inserting the stopper, the funnel is filled with 10% potassium iodide solution, thus creating an effective seal. L. DE K.

The Sensitiveness of Certain Reactions for Blood and their Use in the Analysis of Urine. W. WEITBRECHT (*Chem. Zentr.*, 1910, ii, 1169; from *Schweiz. Woch. Chem. Pharm.*, 1910, **48**, 489).—As the result of experiments with solutions of pure hæmoglobin in water and urine, the author states that, in the case of aqueous solutions of hæmoglobin, the sensitiveness of various tests is in the following order: The phenolphthalein test of Lejeune, the guaiacum test with sodium peroxide (Abstr., 1910, ii, 664), the benzidine test, the guaiacum test with alcohol, and the original guaiacum test. For the detection of blood in urine, the guaiacum test in the presence of sodium peroxide is the most sensitive, then follows the phenolphthalein test, whilst the benzidine test is useless. W. P. S.

Physical Analysis of Peptones. New Form of Apparatus for Cryoscopic Determinations. L. LEMATTE (*Chem. Zentr.*, 1910, ii, 1094; from *Bull. Sci. Pharmacol.*, 1910, **17**, 328—337. Compare Abstr., 1909, i, 344).—The apparatus consists of a thin-walled test-tube, which is surrounded by a copper jacket; the outside of this jacket is covered with a layer of cotton-wool, and the apparatus is enclosed in a wide glass tube, the top of which is attached to the upper part of the copper tube by means of a metal plate. The narrow space between the test-tube and the copper tube is filled with alcohol, and a thermometer and a stirrer are suspended in the interior of the test-tube. The solution to be examined is introduced into the test-tube in sufficient quantity to cover the bulb of the thermometer. The cooling of the solution is brought about by allowing ether to flow from a tapped funnel on to the cotton-wool, and aspirating a current of dry air through the space between the cotton-wool and the outer glass vessel; the inlet for the dry air is situated at the bottom of the outer vessel, and a side-tube, connected with a pump, serves as the outlet.

W. P. S.

Histochemical Detection of Peroxydases. RICHARD FISCHEL (*Wiener. Klin. Woch.*, 1910, No. 44. Reprint 6 pp.).—A description is given by the author of the employment of benzidinesulphonic acid and hydrogen peroxide, which is specially adapted for staining the granula of leucocytes.

S. B. S.

"Salvarsan" in Medico-Legal Investigations. G. OTTO GAEBEL (*Arch. Pharm.*, 1911, **249**, 49—56).—The behaviour of "salvarsan" with the usual reagents for arsenic has been investigated with a view to the discovery of a method of distinguishing between the drug and "inorganic arsenic" in medico-legal cases.

Muscle from a patient who had died three weeks after the injection of "salvarsan," still gave reactions for arsenic.

Arsenic can be recovered from "salvarsan" by decomposing the latter with hydrochloric acid and potassium chlorate. The drug gives the Reinsch, Marsh, Gutzeit, and biological tests for arsenic.

The following tests serve to distinguish "salvarsan" from inorganic forms of arsenic. With Bettendorf's reagent, it gives an amorphous, yellow precipitate, which dissolves on warming and reappears on cooling. Hydrogen sulphide gives no precipitate even after a solution of the drug has been boiled with hydrochloric acid.

The organic part of the "salvarsan" molecule gives certain reactions, which may afford confirmatory evidence of the presence of the drug, thus: the corresponding diazo-derivative gives a characteristic red to violet precipitate with α-naphthylamine, which may be isolated and examined for arsenic by the Reinsch or Gutzeit test. "Atoxyl" behaves similarly, giving a red azo-dye, but the two may be distinguished by the fact that diazotised "salvarsan" gives no colour with β-naphthylamine, whilst "atoxyl" gives a vermilion-red azo-colouring matter with the β-amine. Minced horseflesh sprayed with "salvarsan" solution and kept for fourteen days was extracted with alcohol, slightly acidified with hydrochloric acid, and the residue so obtained tested. It gave positive results with the Reinsch, Gutzeit, and α-naphthylamine tests, but negative results with Bettendorf's reagent and with hydrogen sulphide.

So far it has proved impossible to obtain good results by applying to "salvarsan" ordinary toxicological methods for the estimation of arsenic, the latter being obtained only to the extent of from 29·0 to 29·5% out of the 34% actually present in the drug. T. A. H.

General and Physical Chemistry.

Relation between the Optical Constants and the Potential of Metals. Vsevolod Fréedericksz (*Physikal. Zeitsch.*, 1911, **12**, 346—347).—The author's measurements of the optical constants of various metals are not in agreement with the relationship which is supposed by Bernoulli (*ibid.*, 1910, **11**, 1173) to exist between the optical constants and the position of the metals in the electrochemical series. H. M. D.

Anomalous Dispersion of Light in Gases. W. H. Julius and B. J. van der Plaats (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13** 1088—1093).—The question whether there is a necessary correlation between selective absorption and the rapid variation of the refractive index for waves differing little in length from the absorbed waves has been examined. Photographic records of the absorption spectra and of the interference fringes have been obtained for nitrogen peroxide, bromine and iodine vapour. From a minute comparison of these, the authors draw the conclusion that the thousands of lines which occur in the spectra of these gases produce anomalous dispersion of the waves in the immediate neighbourhood of the absorption lines. H. M. D.

Line Spectrum of Air Given by the Self-induction Spark. Gustave A. Hemsalech (*Compt. rend.*, 1911, **152**, 1007—1009).—The introduction of self-induction into the spark circuit is followed by the progressive disappearance of the line spectrum due to non-ionised air as the induction is increased. Simultaneously another series composed of nebular lines appears, and ultimately reaches a maximum intensity. This secondary spectrum has its principal lines in the red, and is produced by the oscillations following the initial discharge through a layer of air ionised by the spark. It is particularly brilliant when copper or silver electrodes are employed, with high capacity and relatively low self-induction (0·044 Henry units). A list of the chief lines of the secondary spectrum is given, with their relative intensities. With the exception of the red line for hydrogen, none of them are identical with lines of the primary series. W. O. W.

The Spectra of Argon. Willy Stahl (*Zeitsch. wiss. Photochem.*, 1911, **9**, 302—312).—Wave-length measurements of the lines in the "blue" and "white" spectra of argon between $\lambda = 3454$ and $\lambda = 4300$ have been made by means of a Rowland concave grating of 6·5 metres curvature and containing 20,000 lines to the inch. The maximum difference between the wave-lengths of lines in the two spectra amounts to 0·03 Ångström units, and the author draws the conclusion that the relative displacement which Eder and Valenta claim to have established by their observations has no real existence.

In reference to the "blue" and "red" spectra of argon, the authors observations also indicate that there is no essential difference except in the relative intensities of the lines. These variations in the relative intensities are determined by variations in the gas pressures and in the nature of the electrical discharge.

H. M. D.

The Minute Structure of the Spectral Lines of Mercury. M. Glagoleff (*Chem. Zentr.*, 1911, i, 538; from *J. Russ. Phys. Chem. Soc.*, 1910, **42**, 450—461).—The author has investigated the duplication of the green mercury line, and comes to the conclusion that the phenomenon is not due to the Doppler effect, but must be considered as an "autoinversion" of the line. F. B.

Influence of the Solvent on the Rotatory Power of Optically Active Substances. Bernhard Landau (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1911, **11**, 31—35).—The author has determined the rotation and rotation dispersion at five different concentrations of solutions of *l*-methyl malate in various solvents. The solvents were chosen from the following classes of compounds: Hydrocarbons, alcohols, ketones, aldehydes, acids, esters, and halogen, sulphur and nitrogen derivatives of the same. The solvents were so chosen that the influence of substitution of one group by another, or of an increase in the number of substituted halogen atoms could be determined. Phosphorus and arsenic trichlorides were also used as solvents in some experiments. In a few cases determinations were also made with *d*-ethyl tartrate as the solute.

Organic halogen derivatives have the tendency to reverse the rotation of the active ester; exceptions are formed by chloral, bromal, and acetyl chloride. Solvents containing a nitro- or hydroxyl group behave similarly to the halogen derivatives, whereas those containing the free amino-group, or nitrogen in the nucleus, increase the lævorotation of the ester. Substitution of the hydrogen in the hydroxyl or amino-group by an alkyl group diminishes the effect which these groups exert on the rotation.

The inorganic solvents exert quite abnormal effects. Thus both the malate and the tartrate give lævorotatory solutions in phosphorus trichloride.

Anomalies occur in the dispersion curves whenever the solvent shows a tendency to reverse the sign of rotation of the solute.

The experimental details are to be published later. T. S. P.

Rotation Dispersion. III. Colourless Compounds. Leo Tschugaeff (*Zeitsch. physikal. Chem.*, 1911, **76**, 469—483).—It has been shown by Walden (Abstr., 1905, ii, 130) that the mean value of the dispersion coefficient $[\alpha]_F/[\alpha]_C$ for optically active compounds is about 1·95. The author has obtained values of this coefficient for a number of colourless hydrocarbons, alcohols, and ketones, and finds that whereas the numbers for the first two classes of compounds approximate to those found by Walden, many ketones give much higher values for the coefficient in question. The deviations may in some cases be accounted for on the assumption that the compounds in question are not pure, but are mixtures of isomerides, tautomerides, etc., and another possible explanation is that it is connected with the presence of an absorption maximum in the ultra-violet region very near to the visible region. The latter explanation receives support from the fact that camphor, α-bromocamphor, and benzylidenecamphor, which have absorption bands in the ultra-violet, have abnormally high dispersion coefficients, whereas borneol, *iso*borneol, and camphoroxime, which have no absorption bands, have normal dispersion coefficients.

The stereoisomeric *d*-menthone and *l*-menthone differ considerably in the magnitude of their optical dispersion, and as they rotate the plane of polarised light in opposite directions, mixtures of the two in different proportions should show great differences in the magnitude of the dispersion coefficient. This conclusion has been confirmed by direct observation. On these observations a method of determining the components of an optically active mixture can be based, as has already been shown in a somewhat different way by Darmois (compare Abstr., 1908, ii, 747). G. S.

Theory of Geometrical and Stereo-Isomerism. Edward C. C. Baly (*Zeitsch. Elektrochem.*, 1911, **17**, 211—217).—It is assumed that almost every group of atoms possesses more or less residual or unsaturated affinity. This gives rise to a field of force in the ether surrounding the group. If two such groups are attached to a carbon atom the two fields of force will tend to unite, and since the lines of force have direction, according as they run to or from the group of atoms, this union of the fields of force may occur in two ways. Hence two forms of the substance should exist. It is supposed that light is able to disunite the fields of force, and so cause one form of union to pass into the other, which gives rise to an absorption band in the spectrum of such substances. In the case of an asymmetric carbon atom there are two skew arrangements of the lines of force which give rise to the right- and left-handed rotation of the plane of polarisation. An unsaturated solvent affects the field of force of the molecule, and so changes the rotation. Cis- and trans-isomerism is explained on similar lines. T. E.

Mechanism of Photosynthetic Transformation of Energy. M. Tsvett (*Zeitsch. physikal. Chem.*, 1911, **76**, 413—419).—The author's theory as to the photosynthetic transformation of energy is based on the modern view that fluorescent substances are such as undergo under the influence of light a reversible change into a tautomeric or dissociated form. This change is associated with the taking up of energy which is given out as luminescence when the reversible change occurs. It is suggested that chlorophyllin and other active chlorophyll components act in this way, and that the luminescence rays are absorbed by carbon dioxide. On this view, the function of chlorophyllin is to change polychromatic light energy into monochromatic red light of high tension. This theory accounts for the observation of Brown and Escombe (Abstr., 1905, ii, 849) that carbon dioxide is assimilated almost as rapidly in intermittent as in continuous light; the assimilation proceeds during the time of non-illumination at the cost of the energy stored up during illumination. G. S.

Decomposition of Water by Ultra-violet Light. A. TIAN (*Compt. rend.*, 1911, **152**, 1012—1014. Compare Thiele, Abstr., 1908, ii, 79; Kernbaum, Abstr., 1909, ii, 717).—The effect of ultra-violet light on water has been followed by exposing it to the light from a quartz-mercury lamp whilst undergoing distillation in a vacuum. Portions of the gases were withdrawn at intervals and analysed. Oxygen and hydrogen were liberated in gradually diminishing quantities; the proportion of the former was very small at first, but increased until it reached 92% of the amount in detonating gas. These results are explained by the formation of hydrogen and hydrogen peroxide, followed by decomposition of the latter with liberation of oxygen. The total amount of oxygen diminishes on prolonged exposure, owing to the combination of hydrogen with oxygen and to its interaction with the hydrogen peroxide. W. O. W.

Photochemical Studies. I. Oxidation of Iodoform by Oxygen. III. JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1911, **76**, 743—752).—The effect of a number of compounds (mainly organic) on the rate of oxidation of iodoform by oxygen in benzene solution (compare this vol., ii, 4) under the influence of monochromatic blue light ($\lambda = 436$ $\mu\mu$) has been investigated. Triphenylmethane and chloroform accelerate the after-reaction (*loc. cit.*), crystal-red retards it. Anethole and sodium nitrite destroy the after-reaction, and anethole also greatly retards the action of light. The remaining substances, including potassium dichromate, nitrogen peroxide, and aminoazobenzene have no influence on the rate of reaction.

The character of the catalysis is the same in alcohol as in benzene. Cyanine, when moistened with a drop of alcohol, is soluble in water and in benzene. G. S.

The Cleavage of Lactic and Pyruvic Acids. HANS EULER (*Zeitsch. physiol. Chem.*, 1911, **71**, 311—314).—Free lactic and other oxy-acids are decomposed by ultra-violet light, with the evolution of carbon dioxide, and this action is similar to that produced by certain micro-organisms, by means of photo-catalases. In the present research it is shown that the quantity of carbon dioxide developed per unit of time is about six times greater in the case of pyruvic acid than in the case of lactic acid; acetaldehyde is also formed. Alanine yields carbon dioxide also under the influence of ultra-violet light, but the evolution of the gas is very slow. W. D. H.

Bleaching and Polymerisation. HANS STOBBE [and ERICH EBERT] (*Ber.*, 1911, **44**, 960—963).—The polymerisation of ethylene derivatives consists in the union of two molecules and the loss of the double bond; it is accompanied by a diminution of the intensity of the colour. Such polymerisation is as a rule accelerated or actually brought about by the action of light. This bleaching has been studied by the optical analysis in the ultra-violet of a number of compounds.

Cinnamic acid shows strong selective absorption; α-truxillic acid, the polymeride, is transparent at the same concentration. Cinnamylidenemalonic acid has a very broad selective absorption band reaching into the visible part of the spectrum. The polymeride, diphenyl*cyclo*butanebismethylenemalonic acid, is colourless, and only shows a small band in the extreme ultra-violet. Cinnamylideneacetophenone and the colourless polymeride, $(C_{17}H_{14}O)_2$, show a similar behaviour.

E. F. A.

A New Apparatus for Radioactive Measurements. JULIUS VON WESZELSZKY (*Chem. Zentr.*, 1910, ii, 1729—1730; from *Ion*, **2**, 388—396).—The apparatus consists of a combination of Elster and Geitel's apparatus with that of Engler and Sieveking, the measuring instrument consisting of a single leaf, aluminium electroscope.

F. B.

Who First Suggested that the Radioactive Elements are Elements undergoing Decomposition at the Ordinary Temperature? GEOFFREY MARTIN (*Chem. News*, 1911, **103**, 169).—The author maintains that his statement, "the radioactive elements appear to be actually decomposing at the ordinary temperature" (*Chem. News*, 1902, **85**, 205), is the first that appeared on the subject.

E. J. R.

The Scattering of α- and β-Particles by Matter and the Structure of the Atom. ERNEST RUTHERFORD (*Phil. Mag.*, 1911, [vi], **21**, 669—688).—A new hypothesis is developed which ascribes the scattering of α- and β-particles in passage through matter primarily to single large deflexions, due to a single encounter of the particle with the atom, rather than to a multitude of small deflexions produced in successive encounters. The experiments of Geiger (Abstr., 1910, ii, 472) have shown that 1 in 20,000 α-particles are turned through 90° in passing through gold foil 0·00004 cm. thick, and this cannot be ascribed to multiple deflexion. On this theory the angle of deviation when the direction of initial motion of the particle passes the centre of the atom at different distances is calculated, and also the probability of single deflexion through any angle, and the alteration of velocity after the encounter. The latter for an α-particle deflected through 90° by an atom of gold is only 2%, and for an atom of aluminium is 14%. On the other hand, interesting changes of velocity and distribution of the α-particles are anticipated when the encounters occur with helium or hydrogen atoms. The theory leads to the view that the atom possesses a concentrated central charge, rather than to the view of an atom consisting of a sphere of uniform electrification, in which point charges of opposite sign are distributed, as suggested by J. J. Thomson. For the same magnitude of charge, the average deflexion due to the central charge is three times greater on the former than on the latter view, the magnitude of the central concentrated charge being about 100 *e* for the atom of gold. The experiments of Geiger, and of Geiger and Marsden on the scattering of α-particles are in agreement with the theory, and indicate that the magnitude of the central charge is proportional to the atomic weight for elements between gold and aluminium. The experiments of Crowther on the scattering of β-rays are re-considered from the new standpoint, and lead to conclusions similar to those derived from the study of the α-rays. The value found for the central charge on the gold atom is about what would be expected if it consisted of 49 atoms of helium each carrying a charge of 2 *e*.

This theory of a "Saturnian" atom is independent of the sign of the central charge, but it should be possible to examine the sign because the effect of radiation in reducing the velocity of a β-particle should be far more marked if the central charge is positive, than if it is negative. If the central charge is positive the initial velocity of expulsion of the α-particle may be accounted for without supposing the α-particle to be initially moving at this velocity within the atom.

F. S.

The Ratio between Uranium and Radium in Minerals. II. (Miss) RUTH PIRRET and FREDERICK SODDY (*Phil. Mag.*, 1911, [vi], 21, 652—658. Compare Abstr., 1910, ii, 922).—Details are given of the estimation of uranium and radium in a number of different specimens of pitchblende, thorianite, and autunite. A standard solution of radium provided by Rutherford was employed to calibrate the electroscope. The ratio of radium to uranium in Joachimsthal pitchblende was found to be $3{\cdot}15 \times 10^{-7}$. The thorianite previously investigated contained about 6% more radium than would correspond with this ratio, but a number of new specimens obtained in large quantities directly from the importers contained almost the normal amount of radium, the mean for four specimens being about 3% below the pitchblende ratio. The first result is ascribed to probable contamination of the specimen before purchase. The ratio for various specimens of Portuguese autunite varied from 74 to 24% of the pitchblende ratio.

F. S.

Specific Chemical Actions of the Canal Rays of Different Elements. HERMANN VON DECHEND and W. HAMMER (*Zeitsch. Elektrochem.*, 1911, 17, 235—238).—Canal rays are produced in a tube containing hydrogen sulphide under relatively high pressure. They are projected through a capillary into a tube which is constantly evacuated; in this they are submitted to the action of an electrical and of a magnetic field, the lines of force in the two fields being parallel. The result is that all rays with the same ratio of electrical charge to mass are deflected in such a way that their intersection with a plate at right angles to their original direction is a parabola. As many parabolas are observed as there are groups of rays with the same value of e/m. Using a silvered glass plate, a black neutral spot (produced by undeviated rays) and three blackened negative and one positive parabola were observed. By breathing on the plate a widely deviated parabola due to hydrogen became visible. The atomic weights of the charged atoms producing the parabolas, calculated from the observed deviations, are 6, 12, and 60, and the rays probably consist of C'', C', and S_2'. The nature of the chemical action is not known. It is pointed out that the enormous velocity of the canal rays corresponds with an extremely high temperature, and that chemical actions unknown at ordinarily high temperatures may occur.

T. E.

Ionisation of Gases by Light Emitted from Geissler Tubes. The Existence of Selective Effects in the Ionisation. H. G. Cannegieter (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1114—1119).—In the expectation that the ionisation produced in a gas by rays emitted from the same gas will be greater than that obtained when the gas is acted on by rays emitted by another gas, the author has made measurements of the ionisation of gases under the influence of light from Geissler tubes. The apparatus consisted of a discharge tube, an absorption chamber, and an ionisation chamber. Observations were made with hydrogen, oxygen, nitrogen, carbon monoxide, and air, but in no case were selective effects exhibited. The data obtained at different pressures show that, when the pressure is high, the ionisation is always greatest in hydrogen, and diminishes in the series—carbon monoxide, nitrogen, air, oxygen.

H. M. D.

Ionisation of Saline Vapours Produced by a Corpuscular Radiation. Georges Moreau (*Compt rend.*, 1911, **152**, 1171—1173).—Ionisation in a flame charged with the vapour of a salt, such as potassium iodide, is very considerably increased when the cathode is covered with a layer of calcium oxide maintained at incandescence by the flame. The current due to the vapour is proportional to the square root of the concentration of salt when this is small, but reaches a limit, K, at high concentrations. K varies with the nature of the salt, except when calcium oxide is present, when it is practically constant. It is supposed that the corpuscular radiation from the incandescent substance ionises the salt molecules by the shock of impact. The number of positive or negative ions produced per second, Q, is given by the equation $Q = pN(1 - e^{-\omega x})$, where N is the number of active corpuscles traversing the distance x, and p the number of molecules ionised by each corpuscle, ω being proportional to the molecular concentration of the vapour.

At the limit, the current I calculated from the equation $I = K(1 - e^{-\omega x})$ is found to agree with the experimental numbers.

W. O. W.

Ionisation Produced by Phosphorus. A. Blanc (*Compt. rend.* 1911, **152**, 1170—1171).—The effect of an electrical field on the oxidation of phosphorus has been studied by coating one electrode with a layer of vaselin mixed with a solution of phosphorus in carbon disulphide. Oxidation and the production of ions is increased by the electrical field to an extent which increases with the strength of the field. The curve showing the intensity of ionisation as a function of the field shows a concavity towards the axis representing the intensity, indicating that the latter increases more rapidly than if it obeyed Ohm's law. When the phosphorescent layer has aged sufficiently and oxidation has become feeble, the curve corresponds with one of complete saturation. W. O. W.

Chemical Actions and Ionisation by Splashing. III. Léon Bloch (*Ann. Chim. Phys.*, 1911, [viii], **23**, 28—144. Compare Abstr., 1909, ii, 781; 1910, ii, 381, 480; this vol., ii, 357).—This paper consists chiefly of a more detailed account of the experiments on which the previously published conclusions were based; it also contains a full bibliography of the subject.

Fresh instances of chemical action in the dry way have been examined in the oxidation of zinc and aluminium amalgams, the formation of sulphur and arsenious chlorides, and the action of hydrogen chloride on zinc. In these cases the actions are not essentially accompanied by ionisation, since the electrical effects due to the production of ions may be sufficiently accounted for by the subsidiary phenomena of incandescence, convection currents, etc.

The ions produced when a gas is bubbled through a liquid are heterogeneous and of varying degrees of mobility. The mean mobility in a number of cases has been measured, and is found to depend principally on the nature of the liquid. Thus for water it is of the order of 0·2 cm., whilst with sulphuric acid it is 0·0002 cm., mixtures of the two giving ions of intermediate mobility. Gases prepared in the wet way also contain neutral particles capable, however, of assuming an electrostatic charge. The only difference between such gases and those prepared externally and bubbled through a liquid is that depending on differences in the size of the bubbles. Generally speaking, the smaller the bubbles the more intense the electrical effects. W. O. W.

The Positive Potential of Aluminium as a Function of the Wave-length of the Incident Light. J. R. Wright (*Physikal. Zeitsch.*, 1911, **12**, 338—343).—Measurements have been made of the velocity with which electrons are emitted by an aluminium plate when acted on by ultra-violet light in a highly exhausted tube. The method consisted in determining the maximum positive potential acquired by the plate. Although the first observation gave a value of 0·25 volt, it was found that this increased to an apparently limiting value of 14·1 volts when exposure to the ultra-violet radiation was continued for a very long time.

The maximum positive potential acquired by the plate is dependent on the wave-length of the incident radiation, and exhibits a sharp maximum for ultra-violet light of wave-length $\lambda = 2166$. In experiments in which the spark discharge between zinc, cadmium, and iron electrodes was used as the source of the incident light, identical values were obtained for the maximum potential and for the wave-length of the most active rays. H. M. D.

Rays of Positive Electricity. SIR JOSEPH J. THOMSON (*Phil. Mag.*, 1910, [vi], 20, 752—767; 1911, [vi], 21, 225—249).—The investigation of the positive rays is facilitated by the use of large discharge-tubes which permit of working at very low pressures without the potential difference increasing to such an extent as to give rise to sparking. At these low pressures, effects of the positive rays are observed which are absent or inconspicuous at higher pressures.

The positive rays were allowed to fall on a willemite screen after passing through superposed magnetic and electric fields. The patterns which are produced on the phosphorescent screen at the lowest pressures are described, and from the form of these, conclusions are drawn relative to the nature of the positive rays. The rays may be divided into three groups: (1) rays which are not affected by electric or magnetic fields; (2) secondary positive rays, produced by the undeflected rays; these are characterised by a constant velocity of about 2×10^8 cm. per second, and a constant value of $e/m = 10^4$, which is independent of the potential difference between the electrodes; (3) rays characteristic of the gases in the tube which produce bright spots on the screen. Each of these spots is connected with a thin parabolic band of luminosity, the bands forming a kind of spectrum characteristic of the gases in the tube. The velocity of these rays depends on the potential difference between the electrodes, and the value of e/m is inversely proportional to the atomic weight of the gas from which they are derived. Measurements of the parabolic curves give values of e/m corresponding with the atoms of hydrogen, helium, carbon, oxygen, and mercury, and also with the molecule of hydrogen.

The retrograde rays which travel from the cathode in the same direction as the cathode rays belong to groups (1) and (2). In addition to the positively charged rays there are negatively charged rays of type (2) and in some cases of type (3).

In the second paper, a more convenient and accurate method of registering the effects produced by positive rays is described, in which the phosphorescent willemite screen is replaced by a photographic plate which is placed in the discharge tube in the path of the rays. The plate is much more sensitive than the screen, and an exposure of three minutes is sufficient to give distinct records. Two kinds of curves are exhibited by the photographs. One type consists of short parabolic arcs of varying length, the positions of the heads of these arcs indicating that the minimum electrostatic deflexion experienced by the particles which give rise to them is the same whatever the nature of the particles may be. The second type consists of curves which pass through the point on the plate which is struck by the undeflected rays.

From measurements of the curves, values of m/e have been deduced, and these are expressed in terms of the electric atomic weight, which is the ratio of m/e for any ray to the value of m/e for the atom of hydrogen.

The electric atomic weights of both primary and secondary rays are recorded which have been obtained in the examination of tubes containing hydrogen, oxygen, carbon monoxide, methane, cyanogen, helium, hydrogen chloride, and mercury vapour. Such values vary from 1·4, which is attributed to H_3 with two units of charge, to 800, which corresponds with Hg_4 with one unit of charge. Other electric atomic weight values involve the assumption of He_3 with one positive charge, of a nitrogen atom with two positive charges, of C_3, O_3, and O_6 with one positive charge. H. M. D.

Dielectric Cohesion of the Rare Monatomic Gases. EDMOND BOUTY (*Ann. Chim. Phys.*, 1911, [viii], 23, 5—28. Compare Abstr., 1904, ii, 309, 604; 1910, ii, 178, 571, 680).—A résumé of previously published observations. W. O. W.

Dielectric Constants of Some Liquid Hydrides. R. C. PALMER and HERMAN SCHLUNDT (*J. Physical Chem.*, 1911, 15, 381—386. Compare Abstr., 1910, ii, 12).—The dielectric constants of liquid ammonia, liquid phosphine, liquid antimony hydride, and solid ammonia were determined by Drude's method at temperatures from −90° upwards.

Ammonia has its maximum dielectric constant, 25·4 at its melting point, −77°. Solid ammonia at −90° has dielectric constant only 4·01. The constant of liquid ammonia decreases from −77° by 0·4% per degree rise in temperature, and at +24·5° has the value 14·9.

Liquid phosphine and antimony hydride have much lower capacities, phosphine giving the value 2·55 at −60° and antimony hydride 2·93 at −80°. The electrical conductivity of these liquids is very small.

The analogy of the series ammonia–phosphine–antimony hydride to an homologous series of organic acids is seen in the particularly large difference in dielectric constant between the first and second members of each. R. J. C.

Dielectric Constants of Organic Compounds in Relation to their Composition and Structure. I, II, III, and IV. DIMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 73—130, 225—318, 454—496. Compare Abstr., 1910, ii, 94).—The author describes in detail the apparatus and procedure adopted to measure to within ±0·5% by Drude's method (Abstr., 1897, ii, 438; 1902, ii, 439) the dielectric constants of 154 organic compounds belonging to the following classes: (1) hydrocarbons; (2) halogen derivatives of hydrocarbons; (3) nitro-hydrocarbons; (4) alcohols and phenols and their halogen derivatives; (5) aliphatic and aromatic ethers; (6) esters; (7) amines; (8) acids and anhydrides; (9) aldehydes and ketones, their halogen derivatives and oximes; (10) heterocyclic compounds; (11) solutions of hydrogen peroxide and formaldehyde; (12) carbon disulphide.

From the results thus obtained and those given by other investigators, a large number of conclusions have been drawn, the principal ones being as follows.

As a rule, the dielectric constant of a compound is a pronouncedly constitutive property, and no formula can be given by means of which it is possible to calculate the constant for a compound from those of its components. In homologous series, the constant diminishes continuously with increase of the molecular weight. The principal cause of the large differences between the dielectric constants of different classes of organic compounds lies in the presence of multivalent elements, especially nitrogen. The effect produced on the dielectric constant by the entry of any one radicle into a compound usually varies with the nature of the latter, and is influenced in high degree by constitutive factors, being sometimes increased and sometimes even neutralised by the presence of other radicles in the molecule. Sulphur generally exerts a greater influence than oxygen on the dielectric constant, SH having a greater effect than OH. Change from a saturated to an unsaturated compound is accompanied by increase of the dielectric constant, the magnitude of this effect increasing with that of the constant itself. The dielectric constant is increased by cyclic combination of carbon, especially by ring-closure by means of oxygen; it increases also with the symmetry of the compound. Isomeric compounds possess different dielectric constants, the influence of isomerism increasing with the magnitude of the constant.

T. H. P.

Electrical Conductivity of the Chloroacetic Acids in Aqueous Solution.

EFISIO MAMELI (*Gazzetta*, 1911, 41, i, 294—319).—The author has measured the conductivity at 25° and D_4^{25} of aqueous solutions of mono-, di-, and tri-chloroacetic acids of all possible concentrations. The principal conclusions indicated by the numerical data and the curves expressing them are as follows:

The specific conductivity increases rapidly as the concentration of the acid is increased from 0 to 15—20%, and subsequently rises less rapidly to the maximum value (χ_{25}), which is given in ohm.$^{-1}$ cm.$^{-1}$ in the following table, together with the concentration in % by weight (*c*) and in mols. per litre (*m*):

	χ_{25}.	*c*.	*m*.
Monochloroacetic acid	168·4	19·7	2·2
Dichloroacetic acid	896·0	21·6	1·8
Trichloroacetic acid	2500·0	27·8	2·0

Beyond the maximum value, the conductivity decreases rapidly until the concentration reaches 75—80%, and more slowly after that, so that the curve becomes asymptotic to the concentration axis. None of these curves resembles any geometrical curve which can be represented by equations. The ascending portion, from zero to maximum conductivity, approximates closely to the arc of an ellipse and is represented very nearly by the equation: $x^2/a^2 + y^2/b^2 = 1$, *a* being the maximum value of the specific conductivity, and *b* the corresponding concentration. Comparison of the curves with those for hydrochloric, nitric, formic, acetic, propionic, and butyric acids exhibits the same general characters in all, but with hydrochloric and nitric acids the curves rise more rapidly than with the three chloroacetic acids, and have their maxima of conductivity at greater molecular concentrations (5·7—5·8) than with any of the organic acids examined, excepting formic acid (7·0). Further, with the two mineral acids and with formic acid, the descending limbs of the curves do not show the final asymptotic portion.

For the three chloroacetic acids, the values of the maximum specific conductivity stand in the same relations as the mean values of the affinity constants. But, if the values for hydrochloric acid be taken as 100, the maximum specific conductivities for the three chloroacetic acids must be multiplied by 2·33 to make them correspond with the mean affinity constants, thus:

	Affinity constants.	Maximum spec. conductivities.	Maximum spec. conductivities × 2·33.
Hydrochloric acid	100·00	100·00	—
Nitric acid	97·2	102·00	—
Chloroacetic acid...............	68·63	29·62	69·01
Dichloroacetic acid	25·13	10·62	24·74
Trichloroacetic acid	4·68	2·00	4·66

Similar results are obtained with acetic, propionic, and butyric acids, the factor in this series not differing greatly from 2·33. This behaviour indicates a sharp distinction between completely ionisable inorganic acids and carboxylic acids, between which, however, formic acid occupies an intermediate position. T. H. P.

Electrochemistry of Proteins. VI. The Conductivities of Solutions of the Caseinogenates of Potassium and of the Alkaline Earths in Mixtures of Water and Alcohol. T. Brailsford Robertson (*J. Physical Chem.*, 1911, **15**, 387—413. Compare this vol., i, 407).—The conductivity of potassium caseinogenate dissolved in alcohol-water mixtures is related to the conductivity in aqueous solution by the equation: $x_{H_2O}/x_{Alc.} = A^y$, where A is a constant, and y is the percentage of alcohol by volume. This rule holds with basic and neutral potassium caseinogenates up to 60% alcohol, and also with strontium caseinogenate up to 20% alcohol. It bears a striking resemblance to the Arrhenius-Euler formula: $\eta_{Alc.}/\eta_{H_2O} = B^y$, where η is the viscosity.

Within the limits of alcohol concentration for which the above rule holds, the solutions obey Ostwald's dilution law. When the alcohol is increased beyond 60%, potassium caseinogenate solution becomes opaque, and the conductivity suffers a marked diminution at 75%, although actual precipitation does not take place up to 98·6% alcohol. The electrochemical equivalent of the caseinogen also increases considerably with addition of alcohol beyond 60%, and the solutions no longer obey Ostwald's law.

The effect of alcohol on the alkaline earth caseinogenates is more marked, both as regards the conductivity and the precipitating power. Strontium caseinogenate is less susceptible to alcohol than the calcium and barium salts which are precipitated by 50% alcohol.

The effect of alcohol up to 60% on basic potassium caseinogenate is held to be almost entirely due to the effect of the increased viscosity on the ionic mobilities.

The ionic mobilities at infinite dilution tend to be inversely proportional to the viscosities of the solvents.

At 75% the effect of the alcohol is attributed mainly to polymerisation and a profound decrease in the degree of dissociation of the caseinogenate. The solution in 75% alcohol partakes of the nature of a suspension capable of electric endosmose. Precipitation of protein salts by alcohol is preceded by a diminution of the dissociation, so that the salts are precipitated rather than the uncombined proteins.

R. J. C.

Effect of Sucrose on the Accuracy of the Copper Voltameter. L. DEDE (*Zeitsch. Elektrochem.*, 1911, **17**, 238—239).—Using a solution of 10 grams of copper sulphate and 15 grams of sucrose in 100 c.c. of water, the copper voltameter gives correct results with current densities as low as 9×10^{-5} ampere per sq. cm. of cathode surface.

T. E.

Employment of Silver Fluoride Solutions in the Silver Coulometer. KURT EISENREICH [and, in part, FRITZ FOERSTER] (*Zeitsch. physikal. Chem.*, 1911, **76**, 643—712).—At a soluble silver anode, the equilibrium $Ag^{\cdot} + Ag \rightleftarrows Ag_2^{\cdot}$ is established, as can be shown by the reducing effect of the anode solutions on potassium permanganate (compare Jellinek, Abstr., 1910, ii, 279). If the anode liquid obtains access to the cathode, the value of the electrochemical equivalent obtained for silver is for this reason higher than the true value. Accurate values are obtained if by any means, such as the use of a porous diaphragm or a siphon, the anode and cathode solutions are prevented from mixing, and the error is very slight for low values of the $Ag_2^{\cdot}$ ion concentration in the anode compartment, and when a large quantity of solution is used in the cathode compartment. The error in question is increased by increasing the concentration in the anode department and by raising the temperature. If the precautions just indicated are taken, fairly accurate results are obtained with solutions of any silver salt. The results obtained with silver fluoride, however, agree with those obtained with silver nitrate only when the current density is small; the deviation is ascribed to the formation of a small quantity of hydrofluosilicic acid by the action of hydrofluoric acid on the diaphragm. Silver is deposited from neutral solutions of silver silicofluoride as a thick, smooth coating, but the equivalent is slightly too high. When very concentrated solutions of silver nitrate ($8N$) are used, the anode becomes coated with salt and is no longer attacked; under analogous conditions the anode in silver fluoride solution becomes coated with silver subfluoride, Ag_2F.

Under the influence of light, silver fluoride solutions are decomposed with formation of silver subfluoride and silver peroxide. In the experiments very concentrated solutions of silver fluoride were exposed to the light of a mercury quartz lamp.

The paper contains a detailed account of earlier experiments on the silver coulometer.

G. S.

Passivity. FR. FLADE (*Zeitsch. physikal. Chem.*, 1911, **76**, 513—559).—The behaviour of electrodes of iron, cobalt, and nickel in the passive condition has been examined under very varying conditions. When such a passive electrode is connected in circuit, the current, which at the first instant of measuring is fairly high, falls fairly rapidly, and finally attains a minimum value. The behaviour is not reproducible; the time taken to reach the minimum current, the magnitude of the minimum current, and other factors differ considerably under conditions apparently similar. If the polarisation potential of a passive electrode in the stationary state is altered by altering the resistance in the circuit, nickel and chromium show normal behaviour, inasmuch as the current increases with diminished resistance and consequent increase of polarisation potential. In the case of iron, however, the current is, within fairly wide limits, independent of the potential. With rise of temperature, the potential of a stationary passive electrode diminishes; the current increases. The temperature-coefficient varies in different experiments.

The change of electrodes immersed in dilute sulphuric acid from the passive to the active modification when the circuit is broken proceeds as follows. In the case of iron, the potential falls rapidly at first, and then the fall becomes slower with considerable variations of potential. In the case of nickel, the rate of fall in potential is much more regular. In the case of iron there is a definite potential, largely independent of the experimental conditions, at which the iron suddenly becomes active. The potential is independent of the presence of ferrous and ferric ions, but depends on the acid concentration.

As an explanation of the passive state, the formation of layers of oxide of varying composition appears most plausible. The sudden return to an active state in the case of an iron electrode might be connected with the presence of an iron-oxygen alloy. G. S.

Influence of Pressure and Temperature on the Electrolytic Conductivity of Solutions. Silvio Lussana (*Zeitsch. physikal. Chem.*, 1911, **76**, 420).—A claim for priority (compare *Nuovo Cim.*, 1897, [4], **5**, 357, 441; Schmidt, this vol., ii, 12). G. S.

Theory of the Chemical Action of the Electric Discharge in Electrolytic Gas. P. J. Kirkby (*Proc. Roy. Soc.*, 1911, *A*, **85**, 151—174. Compare Abstr., 1905, ii, 236; 1907, ii, 221).—Further measurements of the amount of water formed in the positive column in the passage of an electric discharge through electrolytic gas at low pressure have been made in parallel experiments with positive columns of different lengths. At a given pressure, the amount of water formed by the passage of unit quantity of electricity through one centimetre of the positive column is independent of the current, and appears to depend only on the field of force. If the strength of the field is y, the number of water molecules formed at pressure p during the passage of the atomic charge is represented approximately by $7{\cdot}9pe^{-42{\cdot}7p/y}$. The formation of the water is a result of collisions between negative corpuscles and oxygen molecules, whereby oxygen atoms are produced, each of which enters into combination with a molecule of hydrogen.

The energy required for the dissociation of an oxygen molecule is shown to be less than $6{\cdot}1 \times 10^{-12}$ erg., and is probably about $5{\cdot}3 \times 10^{-12}$ erg. The energy of formation of a molecule of water is about $6{\cdot}4 \times 10^{-12}$ erg. It is further shown that actual dissociation of oxygen molecules takes place in only 50% of the total collisions between molecules and electrons which are moving with sufficient velocity to effect such dissociation.

H. M. D.

The Boiling of Electrolytes on the Passage of an [Electric] Current. ROMAN CEGIELSKIJ (*Ber. Deut. physikal. Ges.*, 1911, **13**, 227—248).—The temperature changes which occur when an electric current is passed through a boiling aqueous solution of an electrolyte, heated by a constant flame, have been submitted to investigation. These changes depend on the intensity of the current and on the nature of the electrolyte. In the case of electrolytes which yield hydrogen and oxygen or other gases on electrolysis, the passage of a direct current is accompanied by a fall of temperature, the magnitude of which increases at first as the strength of the current increases. For larger current intensities the temperature of the solution rises, and in many cases exceeds considerably the boiling point of the solution. On the other hand, electrolytes which do not yield gaseous products do not exhibit the initial lowering of temperature.

Similar differences between the two classes of electrolytes are also exhibited in the changes of temperature which take place when the flame is removed whilst a direct current is passed through the solutions.

H. M. D.

Formation of Hydrogen Peroxide, Nitric Acid, and Ammonia in the Arc Discharge, using Water as One Electrode. ALEX. MAKOWETZKY (*Zeitsch. Elektrochem.*, 1911, **17**, 217—235).—The essential part of the apparatus used was a H-tube containing very weak sulphuric acid. One limb contained the platinum electrode, through which the current passed into the acid; the gas evolved at it was collected separately. Above the surface of the acid in the other limb, which was closed so that the gaseous products could be collected, the second electrode was placed. The arc was formed between this second electrode and the surface of the dilute acid. The second electrode was sometimes a water-cooled platinum tube, sometimes a Nernst glower, which was allowed to become hot. The voltage required is a minimum with from 1/20 to 1/10 ampere. The fall of potential along the arc is about 500 volts per cm., and the arc consumes about 350 volts more when the cathode is cold than when it is hot.

When the arc is formed in an atmosphere of nitrogen using the liquid surface as anode and a hot cathode, the only products are hydrogen and a little ammonia. When the current is reversed, oxygen, hydrogen, hydrogen peroxide, ammonia, and nitric acid are found. The hydrogen peroxide is formed at the surface of the liquid in the very large cathode fall of potential. The gas at the surface of the liquid is almost entirely steam, which is probably decomposed into hydrogen peroxide and hydrogen; as much as 9 millimols. of the former per 1000 coulombs were found. The yields of ammonia and nitric acid are greatest with about 0·04 ampere (about 2 millimols. per 1000 coulombs) and they appear to be formed throughout the length of the arc.

T. E.

Magnetic Properties of Fluorine. Paul Pascal (*Compt. rend.*, 1911, **152**, 1010—1012. Compare this vol., ii, 91, 183, 251, 252).—The value $\chi = -65{\cdot}5 \times 10^{-7}$ has been calculated for the atomic susceptibility of fluorine from determinations of the molecular susceptibility of fluorobenzene and *p*-fluorophenetole. The element is therefore diamagnetic, and has a specific susceptibility of $-3{\cdot}447 \times 10^{-7}$, which is somewhat lower than the number calculated from the law previously enunciated connecting susceptibility with atomic weight.

The aliquot portion, $-0{\cdot}2468 \times 10^{-7}$, occurring in the specific susceptibilities of chlorine, bromine, and iodine, is common also to that of fluorine. The additive character of the constant is not lost when three fluorine atoms are united with the same carbon atom, as in tri-ω-fluorotoluene or its *m*-nitro-derivative, whereas it shows a marked diamagnetic deficit when another halogen is present, as in the compound $CPhF_2Cl$. This is found to correspond with the disappearance of a number of aliquot parts, attributable to the saturation of supplementary valencies.

In compounds such as butyryl or benzoyl fluorides, the oxygen is diamagnetic, as in the corresponding acids. Fluorine in these substances, therefore, behaves as oxygen, unlike chlorine, which does not influence doubly-linked oxygen in this way. W. O. W.

Use of the Magnetic Field in Determining Constitution. IX. Paul Pascal (*Bull. Soc. chim.*, 1911, [iv], **9**, 336—339. Compare this vol., ii, 251, 252).—The magnetic susceptibility of nitrogen in organic compounds is not always a purely additive property, but in compounds in which it is united with oxygen it behaves as carbon linked in the same way. Thus in hydroxylamines, the oxygen has an atomic susceptibility equal to that of the carbon in a primary alcohol, whilst in oximes the nitrogen resembles the carbon of a tertiary alcohol in increasing the diamagnetism of the neighbouring oxygen. The nitroso-group resembles the carbonyl group in its magnetic properties, but the oxygen shows an atomic susceptibility -36×10^{-7}. In aromatic nitro-derivatives the nitro-group has a molecular susceptibility -96×10^{-7}, whilst in aliphatic compounds the value is $-92{\cdot}15 \times 10^{-7}$. Experimental values for the susceptibilities of a number of hydroxylamines, oximes, nitroso- and nitro-derivatives show good agreement with the calulated numbers. W. O. W.

Physico-chemical Methods of Measurement. I. Transparent Thermostat for a Wide Range of Temperature. M. H. Palomaa (*Chem. Zentr.*, 1910, ii, 1848; from *Ann. Finn. Akad. Wiss.*, 1910, **A2**, No. 6).—A description of a thermostat in which the temperature is maintained constant by the circulation of the vapour of a suitable liquid, boiling either under ordinary or diminished pressure. A sketch of the apparatus is given. F. B.

Theory of Specific Heats and the Application of the Doctrine of Definite Increments of Energy to Physical Chemical Questions. Walther Nernst (*Zeitsch. Elektrochem.*, 1911, **17**, 265—275).—The kinetic theory regards the molecules of a gas as rigid systems of material points. The mean kinetic energy of a molecule at the absolute temperature T is made up of the energy of rectilinear motion and of that of rotation. The first is the same for all gases, and is $\frac{1}{2}RT$ for each of the three directions of motion in space. A single atom has no energy of rotation; a molecule containing two atoms can rotate in two planes, and a molecule with three or more atoms can rotate in three planes at right angles to each other; for each degree of freedom the energy of the molecule is $\frac{1}{2}RT$. The molecular heats of the three classes of gases should, therefore, be $\frac{3}{2}R$, $\frac{5}{2}R$, and $\frac{6}{2}R$ (2·98, 4·96, and 5·95) respectively, and these values should be independent of the temperature. This is not in accordance with experience; the molecular heats of all gases (except those with one atom) increase with the temperature, and the values for the halogens and all polyatomic gases are much larger than the above values.

The energy of an atom of a solid substance consists of the kinetic energy of vibration about a position of equilibrium and of potential energy due to the distance of the atom from this position, the two parts being equal. Assuming that the kinetic energy of an atom of a solid is the same as that of a gas in the temperature equilibrium with it, it follows that the total energy of a solid atom should be $3RT$, and the atomic heat $3R = 5·955$. This should hold most accurately at low temperatures, where the amplitude of the atomic vibrations is small, but recent measurements show that the deviations from Dulong and Petit's law increase at low temperatures. According to Maxwell's views, the kinetic energies of the atoms of a solid are distributed about the mean value, all values from 0 to infinity being represented. The new hypothesis, introduced by Planck (*Vorlesungen uber theoretische physik*, 1910) to explain the phenomena of radiation, and extended by Einstein (*Ann. Physik*, 1907, [iv], 22, 185) to specific heats, is that energy can only be taken up by an atom vibrating about a position of equilibrium in definite, *per saltum*, increments (*Energiequanten*) which are directly proportional to the frequency of vibration of the atom. A solid must, therefore, contain a group of atoms with no kinetic energy, another group with the energy e, and other groups with the energies $2e$, $3e$, etc., and there will be no atoms possessing intermediate quantities of energy. Since the molecules of gases move in straight lines (circles of infinite radius), their frequency of vibration is infinitely small, and they can, therefore, receive infinitely small increments of energy, as is assumed by the kinetic theory. The total energy of an atom of a solid on the new hypothesis is $3R\beta\nu/(e^{\beta\nu/T}-1)$ instead of $3RT$, and the atomic heat is $3R\{e^{\beta\nu/T}(\beta\nu/T)^2/(e^{\beta\nu/T}-1)\}$ instead of $3R$; ν is the frequency of vibration of the atom, and β a constant.

Setting out from the idea that a substance melts when the amplitude of vibration of the atoms is equal to the distance between them, Lindemann (*Physikal. Zeitsch.*, 1910, 11, 609; also Abstr., 1910, ii, 580) has shown that the frequency, ν, is proportional to $\sqrt{T_s/mV^{2/3}}$, where T_s is the melting point, m the atomic weight, and V the atomic volume at the melting point. It is thus possible to predict the deviations from the law of Dulong and Petit. Substances with large atomic weights and low melting points, and therefore low frequencies, must obey the law even at comparatively low temperatures; lead and mercury are good examples of this. On the other hand, carbon with its small atomic weight and very high melting point is the classical exception to the law.

The increase in the specific heat of a gas with the temperature may be explained by supposing that the atoms in a molecule can vibrate along the line joining them. The energy of this vibration is subject to the hypothesis of definite increments. In very stable molecules the frequency of the vibration will be very great, and the energy due to it small, whilst the opposite may be expected in less stable molecules, such as chlorine or bromine.

The specific heat of a liquid is probably the same as that of the corresponding solid at low temperatures, and becomes equal to that of the gas near the critical temperature, so that the theory cannot be developed until the specific heats of solids and gases are understood.

A further consequence of the hypothesis is that near the absolute zero a rise of temperature does not increase the energy of a solid substance, hence the temperature-coefficients of both the total and free energies are zero, which is the author's well known thermodynamic theorem.

The application of the hypothesis to radiation is considered. It is suggested in conclusion that the ordinary laws of mechanics do not necessarily apply to the velocities of the atomic vibrations, which are much larger than any of which we have experience.

The following table contains the most recent determinations of the frequencies of certain atoms, calculated from specific heat determinations and from the melting points.

	ν from sp. heat.	$2{\cdot}12 \times 10^{12}\sqrt{\frac{T_s}{mV^{\frac{2}{3}}}}$.
Lead	$1{\cdot}44 \times 10^{12}$	$1{\cdot}4 \times 10^{12}$
Silver	$3{\cdot}3 \times 10^{12}$	$3{\cdot}3 \times 10^{12}$
Zinc	$3{\cdot}6 \times 10^{12}$	$3{\cdot}3 \times 10^{12}$
Copper	$4{\cdot}93 \times 10^{12}$	$5{\cdot}1 \times 10^{12}$
Aluminium	$5{\cdot}96 \times 10^{12}$	$5{\cdot}8 \times 10^{12}$
Iodine	$1{\cdot}5 \times 10^{12}$	$1{\cdot}4 \times 10^{12}$

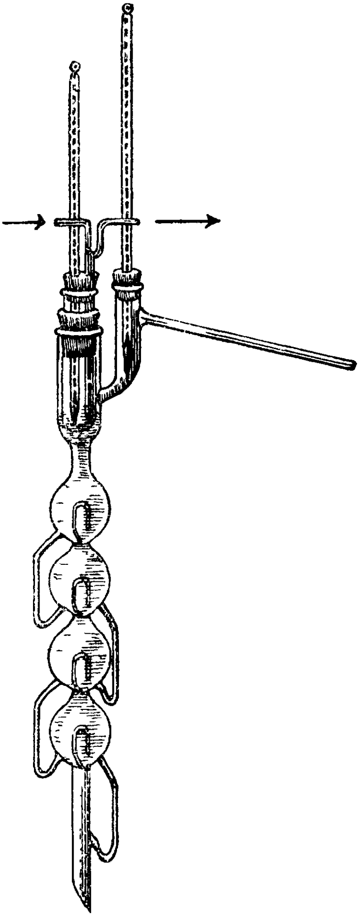
T. E.

Specific Heat at Low Temperatures. V. WALTHER NERNST and F. A. LINDEMANN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 494—501. Compare Abstr., 1910, ii, 263).—For all substances which have been investigated, the decrease in the atomic heat with falling temperature is less rapid than that required by Einstein's formula. A modified formula is proposed, in which the atomic heat is represented as the sum of two terms, one of which corresponds with the potential energy and the other with the kinetic energy of the vibrating atoms. It is shown that the measured specific heats of copper, aluminium, silver, and lead at temperatures between about 25° and 90° (absolute), and of diamond between 30° and 1170° (absolute) are in good agreement with the values calculated from the modified Einstein formula.

This atomic heat formula is shown to be consistent with Planck's radiation equation and with the results which have been derived on the basis of this, if it is assumed that the elementary units of potential energy are half as large as the units which are postulated in Planck's theory. H. M. D.

Isotherms of Monatomic Substances and of their Binary Mixtures. IX. The Behaviour of Argon with Regard to the Law of Corresponding States. H. Kamerlingh Onnes and C. A. Crommelin (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1012—1021. Compare this vol., ii, 203).—In connexion with the deduction of a mean reduced equation of state, the authors have compared the isotherms of argon with those of *iso*pentane, ethyl ether, and carbon dioxide between the reduced temperatures 1·00 and 1·1323. The respective deviations from the provisionally adopted mean reduced equation are plotted in terms of certain special functions. From the experimental data for argon, certain factors have been evaluated, and from these it appears that the behaviour of argon is more closely in agreement with the requirements of van der Waals' theory than is that of any other gas which has been carefully examined. In reference to the relationship, indicated by Young, between the inclination of the rectilinear diameter and the value of the critical volume, it appears that argon is either an exception to Young's rule or that its diameter is somewhat curved. H. M. D.

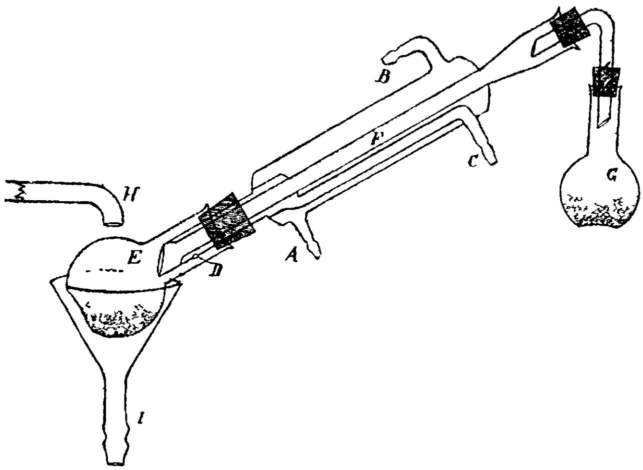
A Fractionating Column. E. Baum (*Chem. Zeit.*, 1911, **35**, 497).—The column is shown in the annexed diagram. The dephlegmator at the top is generally filled with paraffin oil, and, by means of a current of water, maintained at a temperature 10° below that of the liquid distilling over. It is claimed to work better than any other column, especially in the fractionation of mixtures containing substances of low-boiling point, such as ethyl chloride. T. S. P.



Vapour-pressure Curves and Heat of Evaporation of Some Volatile Metals of High Boiling Point. HAROLD C. GREENWOOD (*Zeitsch. physikal. Chem*, 1911, **76**, 484—490).—In a previous paper (Abstr., 1909, ii, 720) data have been given for the variation of the boiling points of a number of metals with the pressure, and in the present paper, from the known thermodynamic formulæ connecting these data with heats of vaporisation, approximate values of the latter have been obtained. The final values for the molar heats of vaporisation of the metals in question are as follows: copper, 70,600 cal; tin, 73,900 cal.; silver, 55,800 cal.; lead, 45,500 cal.; bismuth, 42,700 cal.; zinc, 28,500 cal. G. S.

Fall of Temperature in High-boiling Vapours at Low Pressures. CHRISTIAN J. HANSEN (*Zeitsch. physikal. Chem.*, 1911, **76**, 753—756).—Polemical (compare Abstr, 1910, ii, 827; von Rechenberg, this vol., ii, 95). G. S.

New Condenser for Vacuum Distillations. H. GODECKER and R. ROSE (*Chem. Zeit.*, 1911, **35**, 463).—The arrangement of the condenser is best understood from the diagram. The advantages claimed for it are that the vapours cannot easily be sucked into the pump, and that it can be directly connected to the pump without it being necessary to insert a safety trap. T. S. P.



Reciprocal Action of Associated Liquids. ANTONY G. DOROSCHEWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 46—66. Compare Doroschewsky and Roschdestvensky, Abstr., 1910, ii, 931).—Favre (*Jahrsber.*, 1864, 66) found that the mixing of alcohols is accompanied by absorption of heat, the magnitude of which is greater the more the molecular weights of the alcohols mixed differ one from the other.

The author has determined the D_4^{15} of mixtures, in various proportions, of the following alcohols: (1) methyl and ethyl; (2) methyl and propyl; (3) methyl and *iso*butyl; (4) ethyl and propyl; (5) ethyl and *iso*butyl. The results show that when alcohols are mixed expansion occurs in amount increasing with the difference between the molecular weights of the alcohols. With methyl + ethyl, and ethyl + propyl alcohols, expansion probably takes place, although it is very small in extent.

These results are well explained by assuming that the mixing of alcohols is accompanied by an association process of the type $mA \longrightarrow (A)_m$, such a process proceeding with absorption of heat and expansion. Different mixtures differ only in the degree of such association.

Similar relations are found with the refractivities of mixtures of alcohols and also with vapour pressures. The index of refraction of such a mixture is either equal to, or less than, the calculated value.

T. H. P.

The "Floating" Method of Determining the Density of Homogeneous Solid Substances. J. L. ANDREAE (*Zeitsch. physikal. Chem.*, 1911, **76**, 491—496).—The method of determining the density of a crystal by causing it to float in a mixture of methylene iodide and benzene can be greatly improved in accuracy by placing a small homogeneous crystal of the substance along with a mixture of approximately the same density in a graduated dilatometer, which is placed in a thermostat, the temperature being then altered until the crystal floats. From the weight and known volume of the dilatometer the density of the liquid can be very accurately determined. With most salts, data were obtained at two temperatures some distance apart in order that the expansion coefficients, E.C., might be obtained. The results for the densities and expansion coefficients $\times 10^6$ are as follows: $AlK(SO_4)_2,12H_2O$: $D^{16·3}$ 1·7532; E.C. 38. $CuSO_4,5H_2O$: $D_{17·0}$ 2·2855; E.C. 96. $MnSO_4,5H_2O$: $D^{14·5}$ 2·1006; $MgSO_4,7H_2O$: $D^{17·5}$ 1·6784; E.C. 106. $FeSO_4,7H_2O$: $D^{14·8}$ 1·8987; E.C. 72. $ZnSO_4,7H_2O$: $D^{16·2}$ 1·9661. K_2SO_4: $D^{16·4}$ 2·6627; E.C. 110. K_2CrO_4: $D^{18·0}$ 2·7319; E.C. 101.

G. S.

The Turbulence Viscosity of Different Liquids. TH. VON KÁRMÁN (*Physikal. Zeitsch.*, 1911, **12**, 283—284).—The conclusions of E. and M. Bose (this vol., ii, 257) relating to the turbulence viscosities of liquids in a condition of "hydraulic flow" are criticised, and it is shown that there is no ground for the assumption that the relative viscosities in the conditions of steady and "hydraulic" flow are different. From the general hydrodynamic equation a formula is deduced in which the turbulence viscosity is expressed in terms of the Poiseuille constant and of the density, and it is found that the observed turbulence viscosity data are in satisfactory agreement with the requirements of this formula.

H. M. D.

Cohesion Pressure. V. ISIDOR TRAUBE (*Pflüger's Archiv*, 1911, **140**, 109—134. Compare Abstr., 1908, ii, 565; 1909, ii, 216, 325, 647; 1910, ii, 590).—The advantages of the author's theory of cohesion pressure over the osmotic pressure theory of van't Hoff are further emphasised and illustrated by application to a number of phenomena with a biochemical bearing, such as the action of poisons on bacteria, blood, etc., the distribution of a substance between two phases, including the permeability of membranes, and the activity of muscles. The osmotic theory of Overton is adversely criticised. The experimental data on which these views are based, in so far as they are due to the author himself, have already been published. G. S.

Adsorption. I. Chemical Hysteresis of Starches. Adam W. Rakowski (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 170—186).—The term chemical hysteresis was applied by van Bemmelen (Die Absorption, Dresden, 1910) to a phenomenon observed with certain inorganic colloidal substances in the "gel" condition, the curve connecting vapour pressure and amount of water present varying according as the gel is taking up or losing water. The author has studied this phenomenon in the case of the following starches: maize, St. Vincent arrowroot, and potato.

The curves obtained with maize starch are more regular in form than those given by van Bemmelen, the middle, horizontal portions being missing. The magnitude of the hysteresis is considerably less than with inorganic colloids, and does not amount to more than 2—3%. The curves, which are both irreversible, coincide only at the points corresponding with zero and the maximum vapour pressure. The curves for St. Vincent arrowroot starch are perfectly analogous to those of maize starch, but those for potato starch are more complex.

Solutions of water in sulphuric acid are analogous to those of water in starch in the following directions: (1) The temperature-coefficient of the vapour pressure of the water is approximately the same in the two cases. (2) In both instances, the intensity with which the first 15—16% of water (at 19°) combines differs from that with which the remainder of the water combines. T. H. P.

Adsorption. II. Chemical Hysteresis. Adam W. Rakowski (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 186—201. Compare preceding abstract).—According to van Bemmelen's theory (Die Absorption, Dresden, 1910), a colloid in the gel condition contains neither ions nor hydrates, but the system is a complex one, since coagulation is a process of decomposition of the colloid into two solutions, one more (a_2) and the other (a_1) less concentrated.

Examination of the curves obtained for gelatinised starches (preceding abstract) shows that they are complex curves made up of two sine curves, the general expression being:

$$y - a = b \sin(\sigma - \beta) + c \sin n(\sigma - \beta_1),$$

where y is the vapour pressure of the water present in the gel; a, b, and c are constants; σ is the content of water in the starch expressed as a fraction of π, so that the maximum water, x_m, is taken as 180°. The magnitudes of β and β_1 do not differ greatly from 90°. In the case of the starches the hysteresis is small, the values of a and c being about 8·2 and 0·7 respectively (at 19°); a and c are temperature-coefficients, and are independent of the nature of the substance and of the direction of the curve.

Preliminary investigation shows that, at low temperatures (0°), where the influence of ions and of hydrates is small, the vapour pressures of solutions of potassium and sodium hydroxides and of lithium chloride are expressed satisfactorily by the equation: $y - a = a \sin (\sigma - 90)$. T. H. P.

Adsorption. III. ADAM W. RAKOWSKI (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 362—374).—The author extends the considerations previously developed (see preceding abstracts) to aqueous solutions of potassium and sodium hydroxides; lithium, calcium, and magnesium chlorides; phosphoric acid, and calcium iodide, in order to exhibit the analogy between gels and ordinary solutions. Divergences from the simple sine curve for the vapour pressure are explained by the influence of ions and of hydrates present in the solutions.

T. H. P.

Decolorising Action of Various Forms of Charcoal. EDMUND KNECHT (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV B, 17—18).—When the nitrogen in an animal charcoal is diminished, the affinity of the latter for acid colours like crystal-scarlet is diminished. Continuing his work on the subject, the author now finds that by decreasing the percentage of nitrogen, the affinity of the charcoal for a basic colour like methylene-blue is not materially altered. If, however, purified animal charcoal is heated with aluminium powder or zinc dust, and then treated successively with hydrochloric and hydrofluoric acids, its affinity for methylene-blue is greatly diminished, as also is its affinity for crystal-scarlet, but to a greater extent. The author supports the view that animal charcoal owes its decolorising action to the presence of organic compounds which are stable at a red heat. From a discussion of the decolorising action of other forms of charcoal, it is shown that the more nearly the substance approaches pure carbon in composition, the less is its decolorising power. The absorption of iodine from solution in potassium iodide by animal charcoal also depends on the amount of fixed nitrogen contained in the charcoal. The absorption of dyes cannot therefore be adduced as evidence that dyeing is a mechanical process. R. V. S.

Function of the Walls in Capillary Phenomena. SAMUEL L. BIGELOW and F. W. HUNTER (*J. Physical Chem.*, 1911, **15**, 367—380). —The capillary rise of water, benzene, and aqueous salt solutions in tubes of various substances was measured by a method originally applied by Oersted.

The capillary tube consisted of a hole about 0·6 mm. in diameter drilled in a plate of the material in question. When such a plate is laid on the smooth top of a glass tube the height at which the liquid breaks away from the aperture is the same as the capillary rise would be in a tube of like diameter. The plates were not cemented to the smooth top of the glass tube, since as long as the crack between the plate and the tube is narrower than the hole the break will always occur at the hole. The usual correction for meniscus must be applied.

The apparent surface tension of water at 20° with a glass plate was 7·35, a value in close agreement with that given by Volkmann, 7·40. The metals give distinctly higher values, and beeswax and paraffin considerably lower ones.

The real surface tension being constant, it is assumed that the angle of contact differs with various surfaces, and in particular the angle of contact with glass is not zero, as ordinarily supposed (compare Quincke, *Ann. Phys. Chem.*, 1897, [iii], **62**, 507). Thus the capillary ascension of liquids is primarily a measure of the adhesion between the liquid and solid surfaces, unless this be greater than the surface tension. The adhesion values of water are with zinc 15·15, copper 15·11, nickel 15·00, aluminium 14·78, silver, 14·75, platinum 14·72, glass 14·69 (= 2 × 7·35), celluloid 14·12, beeswax 13·02, and paraffin 9·69. The order of the metals is roughly the electrochemical series. With benzene the metals and glass fall into a similar series.

Experiments with crystalline capillaries, using the corresponding saturated solutions, have led to no trustworthy results. R. J. C.

Experiments on Diffusion [of Dissolved Substances]. II. and III. OSCARRE SCARPA (*Gazzetta*, 1911, **41**, i, 113—121, 122—126).—II. The author has made further experiments on the diffusion of hydrochloric acid and sodium chloride (compare Abstr., 1910, ii, 1044) with the object of ascertaining the cause of the divergences between the true values of the coefficients of diffusion and those obtained by applying the theory of diffusion to Vanzetti's results (Abstr., 1908, ii, 20, 88 ; 1909, ii, 978), taking account of the condition of false equilibrium in which the silver haloid may exist before forming the septum in the tube. The results show that these divergences may be attributed to the colloidal state initially assumed by the silver haloid.

III. Further experiments with solutions of hydrochloric acid and of sodium and potassium chlorides with a specially designed apparatus show that, when the capillary tubes in which the septum of silver haloid is formed are washed out with potassium cyanide solution and then with water, so as to remove all traces of the precipitate previously formed, the results are generally similar to those obtained by Vanzetti. But when water alone is used for washing the tubes, so that traces of precipitate remain, the results are usually in good agreement with the theoretical ones. Vanzetti's method is hence regarded as inapplicable to the quantitative study of diffusion, since the results may depend on phenomena of false equilibrium, the existence of which it is not possible to recognise with certainty.

T. H. P.

Dynamics of Osmotic Cells. I. Preliminary Communication. ANDREAS VON ANTROPOFF (*Zeitsch. physikal. Chem.*, 1911, **76**, 721—731).—It has been shown, more particularly by Kahlenberg (Abstr., 1906, ii, 337), that the direct measurement of osmotic pressure leads in some cases to results which are apparently incompatible with van't Hoff's theory. The author ascribes this to the imperfection of the semipermeable membranes used, and develops a theory of osmosis for membranes which are not entirely impermeable for the solute. The velocity with which the pressure rises is given by $dp/dt = \sigma(P - p_t) - \sigma'P$, and the equation $p_m = P(\sigma - \sigma')/\sigma$ holds for the dynamical equilibrium, where P is the driving force of osmosis (the osmotic pressure in van't Hoff's sense), p_m is the observed osmotic pressure, σ is the permeability of the membrane for the solvent, and σ' the permeability for the solute. It is only when the permeability coefficient, $(\sigma - \sigma')/\sigma$, becomes unity that $P = p_m$. In this way the apparent incompatibility of the experimental results with van't Hoff's theory is accounted for, since the permeability coefficient varies between 0·3 and 0·7 for membranes hitherto regarded as practically semipermeable. It is hoped that on the basis of the theory it may be possible to determine osmotic pressures with the help of measurements with permeable membranes. G. S.

Relation of Osmotic Pressure to Temperature. III. Regulation of Temperature. HARMON N. MORSE, WILLIAM W. HOLLAND, and E. G. ZIES (*Amer. Chem. J.*, 1911, **45**, 383—396).—In earlier work on the determination of osmotic pressures near 0° (Abstr., 1907, ii, 440), the temperature was not maintained at exactly 0°, but varied between 0·15° and 0 30°. An arrangement has now been devised, and is fully described, by means of which the cells can be kept just as accurately and constantly at 0° as they can be at higher temperatures.

Three types of baths are also described for temperatures above 0°, which are constructed on the principle previously defined (Abstr., 1909, ii, 299). These are (1) for general occasional use; (2) those in which the membranes are deposited and the solutions are maintained at constant temperature, and which are always "at temperature" while work is in progress; and (3) the baths in which osmotic pressure is measured which are also always "at temperature."

The paper is illustrated with numerous diagrams. E. G.

Relation of Osmotic Pressure to Temperature. IV. The Membranes. HARMON N. MORSE, WILLIAM W. HOLLAND, and C. N. MYERS (*Amer. Chem. J.*, 1911, **45**, 517—556. Compare this vol., ii, 191, 375).—A full account is given of the method of preparing the membrane of an osmotic cell, and of the various difficulties encountered and the precautions to be observed. In the earlier part of the work, the copper ferrocyanide membranes were deposited within the cell wall (Morse and Horn, Abstr., 1901, ii, 543), but, as there are several objections to this plan, they are now deposited on the inner surface of the cell. Considerable trouble has been caused by the infection of the membranes with *Penicillium* and probably with other organisms, but it has been found that if the cells are left in a saturated solution of thymol until required for use, they remain in an excellent condition (compare Morse, Frazer, and Hopkins, Abstr., 1906, ii, 600). E. G.

New Method of Determining the Solubility of Gases. E. MOLES (*Anal. Fis. Quim.*, 1911, **9**, 79—82. Compare Drucker and Moles, this vol., ii, 23).—By reading in a capillary tube graduated in mm. (1 mm. = 0·00337 c.c. ± 0·3 per cent.), but small quantities of solvent were needed and about one-third of the gas introduced was absorbed.

The values for the solubility of hydrogen and nitrogen in water at 25° were 0·01962 and 0·01561 respectively, in close agreement with the data of other workers. With the apparatus it has been possible to measure solubilities in 95 to 100% glycerol, the smallest value observed being 0·0024. G. D. L.

The Ionic Solubility Product. James Kendall (*Proc. Roy. Soc.*, 1911, *A*, **85**, 200—219).—With the object of testing the constancy of the ionic solubility product, measurements have been made of the solubility of slightly soluble acids in aqueous solutions containing a second acid. In different series the acids were chosen so as to give combinations of two weak acids, of a weak and a strong acid, and of two strong acids. Salicylic, *o*-nitrobenzoic, hippuric, formic, acetic, malonic, hydrochloric and picric acids, and 2 : 4 : 6-trinitro-*m*-cresol were used in the experiments, which were carried out at 25°.

The data obtained indicate that the solubility of one acid in aqueous solutions of another may be regarded as consisting of two parts, one of which (*a*) increases or decreases regularly according as the acid is more or less soluble in the solvent acid than in water, whilst the other (*b*) decreases more or less rapidly according to the ionic strength of the solvent acid. The divergences of the experimental solubility values from those required by the theory of the constant ionic solubility product can be accounted for in all cases by the solvent effect (*a*). According to whether the substances are chemically similar (for example, salicylic and *o*-nitrobenzoic acid) or dissimilar (for example, salicylic and hydrochloric acid), the divergences are positive or negative.

On account of the solvent effect of the second substance, the calculation of the degree of dissociation of one substance from its solubility in pure water and in a known solution of a second substance with a common ion may lead to very erroneous results. H. M. D.

Influence of Impurities on the Lower Limits of Crystallisation. Maurice Padoa and L. Mervini (*Gazzetta*, 1911, **41**, i, 198—203).—The authors have investigated the effect of addition of varying proportions of (1) benzophenone, amyl alcohol, aniline, apiole, or α-naphthylamine on the lower limit of crystallisation of triphenylmethane; (2) benzophenone, bromonitrobenzene, apiole, or amyl alcohol on that of diacetylcotoin, and (3) benzophenone or bromonitrobenzene on that of salypirine. The results obtained lead to the following conclusions:

The addition of a foreign substance always produces a depression of the lower limit of crystallisation, and, in the majority of cases, this limit remains constant over a large range of concentration of the added substance, although in some cases the lower limit is depressed progressively as this concentration increases. It cannot be asserted that the displacement of the lower limit of crystallisation depends on the nature of the added substance, as this may produce different effects in different solvents. The phenomenon probably depends largely on the internal friction of the glassy mass obtained on supercooling. T. H. P.

The Analogy between Swelling (Imbibition) and Mixing. I. J. R. Katz (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 958—975).—The close connexion which exists between the phenomena of imbibition and of mixing is discussed in detail, and experimental measurements of the heat of imbibition and of mixing are recorded in support of the view that the processes are essentially the same. The dependence of the heat (W) liberated when i grams of water are taken up by one gram of the dry substance can be represented by an equation of the form $W = Ai/(B+i)$ in the case of cellulose, artificial starch granules, woody fibres, sulphuric acid, and glycerol. The dependence of the pressure of aqueous vapour on the degree of imbibition has also been determined for a large number of different substances, including casein, cellulose, gelatin, gum arabic, serum-albumin, tricalcium phosphate, and artificially aged silicic acid, and in all cases the form of the hygrometric line (which is obtained when the ratio of the vapour pressure to the maximum pressure is plotted as a function of the degree of imbibition) is the same.

The volume concentrations and the relationships between volume contraction and heat of imbibition are also found to be the same for swelling amorphous substances as for liquids when water is taken up. The similarities thus brought to light lead the author to the conclusion that amorphous swelling substances only differ from liquids in the high viscosity which causes them to assume apparently the solid state. H. M. D.

The Analogy between Swelling (Imbibition) and Mixing. II. Swelling (Imbibing) Crystals and Mixed Crystals. J. R. Katz (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 975—981. Compare preceding abstract).—The dependence of the vapour pressure on the degree of imbibition has been determined for three crystalline albuminous substances—carboxyhæmoglobin, a globulin from seeds of *Cucurbita Pepo*, and Bence Jones's albumose—and also for crystalline amylodextrin. For each of these swelling crystals the hygrometric line is continuous, and of the same form as that found for imbibing amorphous substances. The swelling is supposed to be due to the formation of a solid solution of water in the imbibing substance. To test this hypothesis the hygrometric line has been determined in the case of four substances which are known to form solid solutions with water.

The curves plotted from the data for quercitrin, thorium oxalate, the zeolite, calcium chabasite, and basic zirconium oxalate are of the same form as those found for the swelling crystals. This points to a close connexion between swelling crystals on the one hand, and mixed crystals on the other. H. M. D.

Equilibrium in the System Composed of Zinc Nitrate, Ammonia, and Water. N. Stasevitsch (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 354—362).—Investigation of the compositions of the liquid and solid formed by the interaction of zinc nitrate and ammonia in water under various conditions of concentration shows that the deposit is probably in the region of increasing precipitate, and certainly in the region of diminishing precipitate, not a basic salt of definite composition. It is also not a simple mixture of zinc hydroxide and nitrate, and, owing to the dependence of its composition on the amount of ammonia present, must be regarded as a product of combination of the second class. The equation usually employed to express the action of ammonia on zinc nitrate is applicable only to the region of increasing precipitate. The view that the dissolution of zinc nitrate in excess of ammonia is due to the formation of a complex requires confirmation. T. H. P.

The Ternary Systems Silver Chloride, Bromide and Iodide, and Lead Chloride, Bromide and Iodide. Fritz Matthes (*Jahrb. Min. Beil. Band*, 1911, 31, 342—385).—The products obtained on solidification of fused ternary mixtures of the halogen salts of silver and lead have been investigated by means of cooling curves and by microscopic examination of the crystallised solids.

In the case of the silver salts, there is no compound formed which contains all three components, such as the iodobromite described by von Lasaulx (Abstr., 1879, 365). The various fused mixtures give rise, however, to two series of mixed crystals, one of which contains very little silver iodide, and the other a considerable proportion of this component.

Fused ternary mixtures of the lead salts, on the other hand, do not yield ternary mixed crystals; the only solid phases consist of binary mixed crystals containing lead chloride and bromide and of pure lead iodide. H. M. D.

Quantitative Relations in the Distribution of a Substance between Two Phases: Adsorption. Rudolf Krulla (*Zeitsch. physikal. Chem.*, 1911, **76**, 497—508).—A mathematical paper. A method, which cannot easily be given in abstract, is described by means of which the variation with temperature of the distribution of a substance between the liquid and gas phases is represented by a hyperbola which approximates closely to a straight line. The method is applied to ammonia, sulphur dioxide, carbon dioxide, and nitrous oxide, and it is shown that the "straight lines" representing the behaviour of these systems coincide. Conversely, from a knowledge of these and certain other data, the properties of such a system can be calculated. The method is also applied to systems of two partly miscible liquids. G. S.

A New Method for the Analysis of Some Binary Compounds, Based on the Law of Mass Action. Iwan Ostromisslensky (*Ber.*, 1911, **44**, 1189—1190. Compare this vol., ii, 195).—Mainly a reply to Ruff's claim of priority (this vol., ii, 264). F. B.

Application of the Phase Rule to Stereoisomeric Compounds and the Recognition of Racemic Compounds. T. VAN DER LINDEN (*Ber.*, 1911, **44**, 963—965).—Polemical (compare Ladenburg, this vol., ii, 265). It is contended that the question of the identification of liquid racemates is not yet settled, the solubility method used by Ladenburg being inadmissible. It is doubtful whether liquid racemates exist. The phase rule fully explains all the observed facts in the case of liquid stereoisomerides. E. F. A.

Recognition of Racemic Compounds. HUGO R. KRUYT (*Ber.*, 1911, **44**, 995—999).—Polemical. The results of Ladenburg (this vol., ii, 265), which he interpreted as proof of the existence of liquid racemates, are considered in reality to justify the directly opposite conclusion. Roozeboom's contention (Abstr., 1899, ii, 73) that the phase rule applies to stereoisomerides is upheld. E. F. A.

Hydrolysis of Acid Amides. E. EMMET REID (*Amer. Chem. J.*, 1911, **45**, 327—343).—Acree and Nirdlinger (Abstr., 1907, ii, 857) found that on the hydrolysis of acetamide by hydrochloric acid, the molecular reaction velocity varied with the concentration both of the acid and the amide in such a way as to indicate that the reaction involves the formation of a complex ion by the union of the hydrogen ion of the acid with the amide.

A study has now been made of the hydrolysis of benzamide and acetamide with barium hydroxide at 25°. In the case of benzamide, the velocity of the reaction decreases as the concentration of the amide increases, whilst in that of acetamide the velocity remains constant until comparatively high concentrations are reached, and then decreases as the concentration is further increased. The velocity of hydrolysis of acetamide is reduced slightly by the presence of barium chloride, and to a much greater extent by that of barium acetate. The velocity of hydrolysis of benzamide diminishes regularly as the dilution of the barium hydroxide is increased. The change is much smaller in the case of acetamide, but is in the same direction.

From the result obtained on hydrolysing a 0·04*N*-solution of benzamide with 0·1*N*-barium hydroxide at 100° (Abstr., 1901, i, 30), and that now found for the same concentrations at 25°, the temperature-coefficient is found to be 1·963 for each 10°.

E. G.

Esterification. IV. Interdependence of Limits as Exemplified in the Transformation of Esters. E. EMMET REID (*Amer. Chem. J.*, 1911, **45**, 479—516).—It is shown from theoretical considerations that when ethyl alcohol is heated with a methyl ester, or methyl alcohol with an ethyl ester, the equilibrium point can be calculated from measurements made with the acid and each of the two alcohols in turn. The same should be true of other alcohols and esters, as well as of mercaptans and their esters, provided that other influences do not interfere. Similarly, if one acid reacts with the ester of another acid, equilibrium should occur at a point which can be calculated from the esterification limits of each acid with the alcohol.

The partition of an acid between two alcohols has been studied by the aid of the reciprocal transformations of ethyl and methyl benzoates. These esters are particularly suitable for the purpose, since they are almost insoluble in water and can therefore be easily washed with but little loss. The densities of the esters differ so widely from one another as to furnish a method for ascertaining the composition of a mixture of the two. The results obtained agree closely with those calculated on the assumption that the partition of the benzoyl group between the methoxyl and ethoxyl groups takes place in accordance with the partition factors derived from determinations of the esterification limits of the acid with each alcohol.

The partition of an alcohol between two acids has been investigated by means of ethyl benzoate and *p*-bromobenzoate, which also have very different densities, and can therefore be estimated by the density method. The results obtained agreed only approximately with those calculated, but this was partly due to an error introduced by insufficient heating. They show clearly, however, that when either benzoic or *p*-bromobenzoic acid is heated with the ester of the other acid a partial replacement occurs, the alcohol being divided between the two acids approximately in proportion to their concentrations. An experiment was also made with benzyl acetate and benzoate.

When ethyl benzoate and benzyl acetate are heated in a sealed tube at 210—216°, double decomposition takes place.

The partition of an acid between an alcohol and a mercaptan has been investigated in the transformation of ethyl benzoate into ethyl thiolbenzoate by mercaptan, and of the thiolbenzoate into the benzoate by alcohol.

In studying the partition of an acid between two alcohols, some experiments were made in which hydrochloric acid and sodium alkyloxides were used as catalysts, but in the one case the equilibrium is disturbed by the unequally rapid action of the hydrochloric acid on the two alcohols to form alkyl chlorides, and in the other by the formation of dense precipitates. It was therefore necessary to carry out the work without a catalyst, and in order to hasten the reactions a temperature of 200—230° was employed. E. G.

Velocity of Saccharification of Starch. III, IV, and V. Henri van Laer (*Bull. Acad. Roy. Belg.*, 1911, 84—109, 305—320, 362—370).—In continuation of previous work (Abstr., 1910, ii, 839, and this vol., ii, 28) it is now shown that the hydrolysis of starch by diastase takes place in accordance with the logarithmic law for a unimolecular reaction, but this simple action may be modified by secondary actions to such an extent that the reaction appears not to take place in accordance with this law (compare Brown and Glendinning, Trans., 1902, 81, 388). These secondary actions may either increase or decrease the velocity of reaction. The most important of them are the rapidity with which the hydrolysis is effected, the heterogeneity of the starch mucilage, the weakening of the diastase by the action of heat, the presence of chemical agents, and the removal of certain constituents by coagulation in the course of the experiments. The results of experiments supporting these conclusions are tabulated in the original.

The fourth memoir is devoted to the consideration of the influence exerted by the concentration of the starch mucilage. It has been shown already (Abstr., 1910, ii, 839) that in the action of dilute acids on starch, the rate of hydrolysis is proportional to the concentration of starch so long as this is not above 5·5%. In the case of diastase the law also holds when the concentration of starch is below 4·5%; above this the rate of transformation increases slightly. This rule, however, only holds when throughout the same series of experiments the "diastatic change" is the same, that is, that the ratio between the concentration of starch and diastase remains the same. This implies that in the action of diastase on starch combination takes place between the ferment and the starch, and that it is this compound which is hydrolysed in the later stages of the reaction. This matter is dealt with experimentally in the fifth memoir, and it is shown that if starch is added to a solution of diastase and the mixture left for a time and then filtered, the diastatic power of the filtrate shows considerable reduction as compared with that of the original solution.

This falling off in diastatic power is not due to inhibitive action of the reducing substances produced. The interaction of diastase and starch probably results in the formation of an adsorption compound, similar to that produced when filter paper is dipped in a solution of Congo-red. T. A. H.

Application of the Kinetic Theory to the Study of Catalytic Phenomena. Jacques Duclaux (*Compt. rend.*, 1911, 152, 1176—1179).—A theoretical discussion. The author regards porous catalysts, such as platinum black, as aggregates of minute chambers, in some of which the pressure and temperature are considerably higher than the mean pressure and temperature of the system. The combination of gases, such as oxygen and hydrogen, takes place with increased rapidity in these regions. W. O. W.

The Influence of Foreign Substances on the Activity of Catalysts. Carl Paal [with A. Karl] (*Ber.*, 1911, 44, 1013—1018. Compare Ipatieff, this vol., i, 31).—The metals magnesium, aluminium, iron, nickel, cobalt, copper, zinc, silver, tin, and lead were coated with palladium by immersion in a slightly acid solution of palladous chloride, the products being washed with alcohol and ether, and dried in a vacuum. Their action as hydrogen carriers in the reduction of a liquid unsaturated ester was then investigated, using the apparatus previously described (Abstr., 1908, ii, 392). Only magnesium, nickel, and cobalt have no influence on the catalytic effect of the palladium; the other metals act as anti-catalysts.

Not only are most of the metals anti-catalysts, but also solvents, such as benzene and acetone. The action of benzene on the nickel-palladium powder is such that the activity of the powder cannot be regenerated by removing the benzene with ether. Ether and alcohol have no anti-catalytic effect. T. S. P.

Periodic System of the Elements. EMIL BAUR (*Zeitsch. physikal. Chem.*, 1911, **76**, 569—583. Compare Schmidt, this vol., ii, 198).—The atomic weights of the elements are plotted as abscissæ against the logarithms of the atomic volumes as ordinates; in calculating the latter, the maximum values of the densities of the elements are used. The following principal periods are distinguished: the first half-period from lithium to boron, the second from boron to aluminium, the third from aluminium to titanium, the fourth from selenium to zirconium, the fifth from tellurium to cerium, the sixth from the element with the atomic weight 210 to uranium. There are three subsidiary periods: (1) from vanadium to arsenic; (2) from niobium to antimony; (3) from tantalum to bismuth.

The figure shows a sharp distinction between principal and subsidiary periods. The curves of the former are steep, and are nearly parallel; the curves of the latter are flatter, and also nearly parallel. The lines joining corresponding elements in different periods are nearly parallel, but in some cases spread out in a fan-shaped manner, so that the directions are reciprocally controlled to some extent; this admits of interpolation and extrapolation with some degree of certainty. The atomic weights of some hitherto unknown elements are deduced in this way.

The paper contains a useful summary of the available data regarding the densities of the elements, especially at low temperatures. G. S.

Determinations of the Size of Molecules. JEAN PERRIN (*Compt. rend.*, 1911, **152**, 1165—1168. Compare Abstr., 1908, ii, 927; Millikan, this vol., ii, 175).—After criticising the values for *e*, the atomic charge, obtained by Millikan ($4·9 \times 10^{-10}$ *E.S.U.*), Ehrenhaft (from 1×10^{-10}), Rutherford ($4·65 \times 10^{-10}$), and Regener ($4·8 \times 10^{-10}$), the author gives $4·24 \times 10^{-10}$ as the value derived from a repetition of his earlier experiments, instead of the number $4·1 \times 10^{-10}$ previously given. In arriving at this result, corrections have been introduced which will be described in a further communication. Millikan's value is based on an application of Stokes' law, which is only valid in the case of solid, homogeneous spheres. In the liquid droplets actually used, a circulation of particles between the centre and periphery probably occurs during the rise and fall of the drop, owing to the viscosity of the liquid. This would necessitate a correction, for which Cunningham's formula is not entirely adequate.
W. O. W.

A Simple Laboratory Suction-pressure Pump. F. LIEBERT (*Chem. Weekblad*, 1911, **8**, 382—383).—A description of a pump for forcing a current of gas through apparatus in which the back pressure cannot be overcome by the aid of an ordinary gas-holder. The gas does not come into contact with lubricants. A. J. W.

The Direct Measurement of Alterations in Vapour Pressure, and the Vapour Pressure Method for Showing, as a Lecture Experiment, the Existence of Compounds. RUDOLF KRULLA (*Chem. Zeit.*, 1911, **35**, 471—472).—Fitted into a vessel immersed in a thermostat and containing the one liquid component is a bung through which pass an air-tight stirrer, the nose of a burette, and a tube connecting with a manometer and with the top of the burette, so as to form a closed circuit. The burette contains the second liquid component, known volumes of which are run into the vessel from time to time and manometric readings taken.

Curves showing the relation between vapour pressure and composition are given for the pairs of substances: carbon tetrachloride–aniline and aniline–phenol. In the latter case, the existence of the compound $C_6H_5{\cdot}OH,C_6H_5{\cdot}NH_2$ is well shown. T. S. P.

Experimental Illustration of the Law of Definite Proportions through Combination of the Halogens with Finely-divided Silver. JOSEPH H. KASTLE (*Amer. Chem. J.*, 1911, 45, 396—403).—As no adequate or suitable method has hitherto been described for experimentally illustrating the law of definite proportions, the author has studied the action of halogens on finely-divided silver.

By the action of cuprous chloride on an ammoniacal solution of silver chloride, a finely-divided precipitate of silver is produced, which when dried at 110—120° forms a grey powder containing a few glittering particles. This product combines energetically with the halogens, either moist or dry.

The experiments are carried out by placing a weighed quantity of the silver in a porcelain crucible, adding excess of bromine or iodine, and heating on the water-bath until the excess of the halogen has been removed. The crucible is then heated at 120—150° until the weight is constant. The silver halide is fused, and the crucible again weighed. The increase of weight gives the weight of the halogen with which the given amount of silver has combined. The experiment can be carried out completely in about an hour.

In the case of chlorine, the silver in the crucible is treated with chlorine water. The liquid is evaporated to dryness, and the crucible heated at 120° until of constant weight. The residue is treated repeatedly with chlorine water in the same way, until it ceases to gain weight. The silver chloride is then fused and the crucible again weighed.

From a number of such experiments in which a considerable excess of the halogen is always employed, it is evident to the student that, in every case, the silver unites with a definite quantity of halogen. This can be rendered even more convincing by preparing the silver halides from the metal in other ways, namely, by dissolving a known weight of silver in nitric acid, and (1) evaporating the solution with a halogen acid, or (2) by precipitating the halide as in ordinary gravimetric work. E. G.

Two Experiments on the Sulphuration of Metals. O. OHMANN (*Chem. Zentr.*, 1911, i, 458—459; from *Zeitsch. physikal.-chem. Unterr.*, 1910, 23, 345—349).—One experiment illustrates the formation of ferrous sulphide by introducing iron powder on the end of a magnet in sulphur vapour; iron is spontaneously inflammable in sulphur vapour, the ignition temperature lying below 448°.

The other demonstrates quantitatively the formation of cuprous sulphide by burning copper foil in sulphur vapour. F. B

Inorganic Chemistry.

The Electrolytic Preparation of Hyposulphites from Solutions of Hydrogen Sulphites. KARL JELLINEK (*Zeitsch. Elektrochem.*, 1911, 17, 245—261).—Previous observers (Abstr., 1904, ii, 556, 615) have found that sodium hydrogen sulphite is reduced electrolytically to sodium hyposulphite, and that the formation of this substance stops when the solution contains some 3 or 4% of it. Whether this is due to electrolytic reduction of the hyposulphite or to its decomposition independently of the current is not known. The author first shows that sodium hyposulphite, in solutions containing hydrogen sulphite, decomposes spontaneously into thiosulphate and sulphite, $2Na_2S_2O_4 = Na_2S_2O_3 + Na_2S_2O_5$; $Na_2S_2O_5 + H_2O = 2NaHSO_3$. In concentrated solutions the rate of decomposition is practically unaffected by the presence of platinum or lead, whilst in dilute solutions the greater part of the change takes place at the surface of a platinised platinum plate.

In a set of electrolyses of sodium hydrogen sulphite solutions it is then shown that the stationary condition, in which the concentration of the hyposulphite does not increase, is reached when the rate of formation of hyposulphite by the current is equal to its rate of spontaneous decomposition previously measured, from which it follows that hyposulphite is not reduced electrolytically, and that in order to obtain a high concentration in solution it is only necessary to increase the rate of formation by applying a large current to a small volume of solution. T. E.

A Chemically Active Modification of Nitrogen Produced by the Electric Discharge. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1911, 85 *A*, 219—229).—When pure nitrogen is subjected to the action of an electric discharge from a Leyden jar in an exhausted tube, it undergoes some change which causes it to glow for some time after the discharge has been discontinued. For the purpose of examining the properties of the modified nitrogen, a current of gas was drawn through the discharge tube into an observing vessel, the current being maintained by a mechanical pump. The glowing nitrogen has a characteristic band spectrum; in the visible region it shows a green, a yellow, and a red band of not very unequal intensity, although the yellow one is usually the brightest.

When the glowing nitrogen is passed through a long tube, which is heated moderately at one point, the glow is extinguished locally, but the gas recovers its luminosity on reaching the cooler parts of the tube. If the tube is strongly heated, the glow is permanently extinguished. On passing through a tube immersed in liquid air, the gas glows with increased brilliancy as it approaches the cooled portion of the tube, but the glow is completely and finally extinguished when the fully cooled portion of the tube is reached. These experiments show that the change which gives rise to the after-glow is accelerated by cooling and retarded by heating. When the gas is passed through an electric field so as to remove gaseous ions, the glow is unaffected.

The action of the modified nitrogen on various metals, non-metals, and compound substances has been examined. When the gas is drawn over a small pellet of ordinary phosphorus, a violent reaction occurs, accompanied by absorption of some of the gas and the formation of red phosphorus. This reaction has been used to determine the percentage of active nitrogen in the gas leaving the discharge tube. In one experiment, the phosphorus increased in weight by 15·5 mg. after the passage of 2540 c.c.; this corresponds with an absorption of 12·2 c.c. or 1/210th part of the total gas.

On contact with iodine, the normal yellow glow is replaced by a magnificent light blue flame, and a slight rise of temperature is observable at the point of contact. The blue flame gives a brilliant banded spectrum. Sulphur and arsenic when heated give faint blue and green flames respectively; selenium, antimony, and carbon are without action. Hydrogen merely acts as a diluent, but oxygen destroys the glow without any new luminosity effect.

The modified nitrogen combines with sodium and mercury at a gentle heat, forming with the latter an explosive compound; in each case the reaction is accompanied by the development of line spectra of the metal. Line spectra of cadmium, magnesium, potassium, zinc, and lead are also obtained under similar conditions.

Compound substances, when volatilised in a current of the gas, give rise to the corresponding band spectra, and in this way spectra of compounds which are unstable at the temperature of the Bunsen flame may be readily obtained. The modified nitrogen reacts with organic halogen compounds, setting free the halogen and combining with carbon to form cyanogen, of which a brilliant spectrum is obtained during the reaction. Cyanogen is also formed when the gas acts on acetylene. With nitric oxide, it yields nitrogen peroxide, the action being accompanied by the production of a green flame showing a continuous spectrum. It is suggested that this reaction may be represented as $2NO + N = NO_2 + N_2$.

Water and carbon dioxide have no action on the glowing nitrogen; ammonia destroys the glow, and the same effect is exerted by cupric oxide and manganese dioxide. H. M. D.

Flames Containing Ammonia and Nitric Oxide. Alfred Reis (*Zeitsch. physikal. Chem.*, 1911, 76, 560—568).—It is shown by experiments with the ammonia-oxygen flame in the Teclu-Smithells' flame separator that the yellow part of the flame is connected with the presence of undecomposed ammonia, and is not to be ascribed to the system nitrogen + oxygen, as has been suggested. The sharp boundary of the yellow region marks the passage of the gas into a region free from ammonia. This conclusion has been confirmed by the analysis of the gases removed from different portions of the flame by means of a cooled platinum capillary.

In the inner cone of the coal gas–oxygen–nitric oxide flame considerable amounts of ammonia and of cyanogen or cyanogen compounds are present when the coal gas is in excess. In this flame when separated, a second explosion cone has been observed in the gas between the two flames; under suitable conditions it can be caused to vibrate up and down in the cylinder. G. S.

The So-called Sulphammonium and the Spectroscopic Test for New Compounds. OTTO RUFF (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1911, **11**, 24—25).—The author has previously expressed the opinion that the reaction between nitrogen sulphide and hydrogen sulphide in liquid ammonia is a balanced one, according to the equation $N_4S_4 + 6H_2S \rightleftarrows 10S + 4NH_3$ (compare Abstr., 1905, ii, 699). This is now supported by measurements of the absorption of light of solutions of the same total concentration, which were made up either from liquid ammonia, nitrogen sulphide and hydrogen sulphide, or from liquid ammonia, hydrogen sulphide and sulphur. The same absorption curves were obtained in the two cases.

For other details see this vol., ii, 277. T. S. P.

Aqua Regia. EDUARD PŘIWOZNIK (*Oesterr. Zeitsch. Berg.-Huttenw.*, 1910, **58**, 549—550).—The results of numerous experiments show that the solution of gold in aqua regia takes place according to the equation: $Au + HNO_3 + 4HCl = 2H_2O + NO + HAuCl_4$, and these proportions are recommended as being most economical for employment.

F. M. G. M.

Compounds of Phosphorus and Sulphur. JULIUS MAI (*Ber.*, 1911, **44**, 1229—1233. Compare Abstr., 1903, ii, 363).—The author's experiments confirm Stock's results (Abstr., 1910, ii, 201, 499) that the existing sulphides of phosphorus, other than P_4S_3, are P_4S_7 and P_4S_{10}.

The heptasulphide, P_4S_7, is best prepared by heating to a temperature above the melting point, and in an atmosphere of carbon dioxide, a mixture of the purified trisulphide, P_4S_3, and sulphur in such proportions that the compound P_3S_6 would, if possible, be formed. The crude product is recrystallised from naphthalene, all impurities being finally removed by carbon disulphide, when yellow crystals of prismatic habit are obtained. The compound may also be obtained directly by dissolving the trisulphide and sulphur in naphthalene at 175—180°; the crystals separate immediately, whereas the more easily soluble pentasulphide, P_4S_{10}, generally crystallises only after cooling.

The pentasulphide may be obtained from sulphur, and either the trisulphide or heptasulphide, using naphthalene as a solvent, and then extracting with carbon disulphide.

In the preparation of the heptasulphide from the trisulphide and sulphur, naphthalene may be replaced by benzene when the mixture is heated in a sealed tube at 180°. Xylene and cumene can be used at the ordinary pressure and at their boiling-point temperatures when a small quantity of iodine is used as a catalyst. With cumene as solvent and excess of sulphur, the pentasulphide is one of the products.

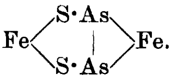
Endeavours to prepare a compound P_4S_5 and a hypersulphide met with no success. T. S. P.

The Adsorption of Arsenic by Ferric Hydroxide. GEORG LOCKEMANN (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1911, **11**, 25—28).—The quantity of ferric hydroxide necessary for the complete adsorption of arsenic present in a solution as arsenite or arsenate has been determined at 0°, 25°, and 80°, the ferric hydroxide being precipitated from the arsenic solution by means of ammonium hydroxide.

The results are in accordance with the formula $E = \beta A^p$, where E is the number of milligrams of ferric hydroxide in 100 c.c., A the number of milligrams of arsenic in 100 c.c., β a constant which varies with the temperature, and p has the value 0·57 for all temperatures. The value of A varied from 0·1 to 500, and the values of β were respectively 70, 90, and 130 for the above-mentioned temperatures. With rise in temperature, the adsorption decreases considerably. At all temperatures very small quantities of arsenic require relatively much more ferric hydroxide for complete adsorption than do larger quantities of arsenic.

In the above experiments twice the theoretical quantity of ammonium hydroxide necessary for the precipitation of the iron was added. If only the theoretical quantity is added, the adsorption of arsenic is considerably increased. T. S. P.

Experiments with Mispickel. A. BEUTELL (*Centr. Min.*, 1911, 316—320).—When mispickel is heated in a cathode vacuum the distillate is at first yellow, then brown, and finally black; after two hours the amount distilled was: free sulphur, 0·39%; arsenic sulphide, 1·58%; arsenic, 12·20%. A portion (1·00%) of the arsenic was amorphous, being soluble in carbon bisulphide. When heated for a longer period, a larger proportion, but not all, of the arsenic was expelled. If, however, the mineral be first roasted, the whole of the arsenic and sulphur can be distilled by heating in a cathode vacuum. From the experiments, it is concluded that the formula of mispickel is $Fe_2As_2S_2$, which is written in the form:



L. J. S.

Solubility of Orthoboric Acid, its Molecular Weight, and its Transformation into other Hydrates. RAFFAELO NASINI and F. AGENO (*Gazzetta*, 1911, **41**, i, 131—136).—The experimental results given in this paper have been published already (Abstr., 1909, ii, 999).

The curve of solubility of orthoboric acid in water proceeds regularly from 0° to 120°, no change of direction being exhibited at 107—108°, at which temperature transformation into metaboric acid occurs. The solubility does not correspond with any one equation, but is represented almost exactly by the three following expressions: between 0° and 70°, $S=2\cdot60+0\cdot072713t+0\cdot001649t^2$; between 70° and 100°, $S=5\cdot77+0\cdot2872(t-70)+0\cdot004667(t-70)^2$, and between 100° and 120°, $S=28\cdot6+0\cdot8942(t-100)+0\cdot0148(t-100)^2$, S being the number of grams of H_3BO_3 per 100 grams of solution.

The cryohydric point of aqueous boric acid is $-0\cdot76°$, the acid having the normal molecular weight even at this temperature (compare Kahlenberg and Schreiner, Abstr., 1897, ii, 30). Orthoboric acid also exhibits normal ebullioscopic behaviour at concentrations as high as 20—30%.

The existence of intermediate hydrates, such as $H_6B_4O_9$, has not been established. T. H. P.

Crystallographic Examination of Some Silicides, Carbides, and Borides obtained by Moissan and his Pupils. August de Schulten (*Compt. rend.*, 1911, **152**, 1107—1108).—The results of crystallographic measurements are given for silicides of iron, cobalt, manganese, and chromium, aluminium and glucinum carbides, and calcium, strontium and barium borides. W. O. W.

Temperature Measurements in an Experimental Carborundum Furnace. Horace W. Gillett (*J. Physical Chem.*, 1911, **15**, 213—305. Compare Lampen, Abstr., 1906, ii, 598; Tucker and Lampen, *ibid.*, 610).—A furnace of commercial pattern, but taking only 150 pounds of charge, has been investigated by the methods indicated by Turner and Lampen. The furnace, which was tapered in section to reduce dead space, was provided with water-cooled graphite electrodes 2″ × 4″ in section and a conducting core of granular graphite 2″ × 4″ × 16″. The formation of carborundum is supposed to take place in the following stages: (I) $SiO_2+2C=2CO+Si$; (II) $tSiO_2+uSi+vC=wCO+Si_xC_yO_z$; (III) $Si_xC_yO_z=xSiC+zCO$, or $Si_xC_yO_z+mC=xSiC+nCO$.

The charge consisted of sand (53·5%), coke (40%), sawdust (5%), and sodium chloride (1·5%). This is practically the mixture used at Niagara, and contains a 10% excess of carbon, as otherwise silicon vapour liberated in the cooler parts of the furnace attacks the core, coating its granules with non-conducting carborundum and stopping the current.

Observation tubes of carborundum were inserted in the furnace, these being preferred to graphite, since carborundum, unlike graphite, has a temperature gradient which approximates very closely to that of the charge. Temperatures were measured by sighting an optical pyrometer on the graphite plug closing the inner end of the observation tube, or, in the cooler parts of the furnace, by a thermocouple. The tubes were very porous, and, consequently, a current of air was slowly aspirated through in order to remove the fume (possibly $CaSiO_3$), which penetrated and obscured the radiation plug. Crystals of carborundum were slowly formed on the inside of the tube. The graphite plugs were found to be uniformly heated over their whole surface, but there was a drop of 20° between the back and front of the plug ($\frac{3}{8}''$).

It was decided, after direct comparison with a thermocouple, that the radiation from an unpolished graphite disc is ideal black body radiation within the limits of error of the Wanner or Morse pyrometers which use red light, or the Thwing pyrometer which measures total radiation, or the Lummer-Brodhun spectrophotometer. The pyrometers were calibrated against the spectrophotometer on the basis of Wien's law, and gave concordant indications of the furnace temperatures. The data obtained in the calibration indicate 14,200 as the value of the constant in Wien's law.

The temperature of formation of siloxicon is given as $1540° \pm 30°$; crystalline carborundum is formed at $1820° \pm 20°$, and decomposes yielding graphite at $2220° \pm 20°$. The temperatures 1540° and 1820° are considerably lower than those found by Tucker and Lampen, owing to the use by the latter of a graphite tube which has a lower temperature gradient than the contents of the furnace after it leaves the graphite zone. The decomposition point, 2220°, is the same as that found by Tucker and Lampen. The purest carborundum has a greenish-golden colour, the usual black colour being due to incipient decomposition into graphite, owing to the excessive temperature of the commercial furnace.

No evidence could be obtained of the formation of amorphous carborundum in the furnace, and it is suggested that the so-called amorphous carborundum which has been obtained is the product of the action of hydrofluoric acid on siloxicon. The highest temperature observed was 2675°, at the core. Most attempts to exceed 2400° failed, because of the progressive liberation of conducting graphite round the core. An efficient carborundum furnace must have a very flat temperature gradient between 1820° and 2200°. R. J. C.

A Simple Method for the Preparation of Inert Gases, Hydrogen and Nitrogen in the Pure State. GEORG GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1911, **13**, 271—277).—The method of purification of the inert gases is based on the rapidity which which alkali metal vapours enter into combination with other gases at elevated temperatures. The apparatus consists of a special form of discharge tube, in which molten potassium heated at about 200° forms the cathode. A mixture containing 10% of helium, 45% of air, and 45% of coal gas was found to exhibit no other lines than those of helium and potassium after the discharge had been passed through the tube for six minutes, the original pressure of the gas being 10 mm.

Impure hydrogen and nitrogen, as obtained from commercial bombs, can be rapidly freed from impurities by passing through the potassium discharge tube. H. M. D.

Liquid Helium. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1093—1113. Compare this vol., ii, 368).—Details are given respecting the arrangements of a liquid helium bath and of the use of a constant volume helium thermometer.

With the aid of this apparatus, measurements have been made of the vapour pressure and density of liquid helium at temperatures reaching down to 1·48° on the absolute scale. For the vapour pressure, the results obtained are :

Absolute temperature	1·48°	2·37°	3·23°	3·97°	4·29°
Pressure (mm. mercury)	3	51	197	565	760

The density of liquid helium at 4·29° (absolute) and 760 mm pressure is 0·122. With fall of temperature the density of the liquid appears to pass through a maximum, expansion taking place when the temperature is lowered from 2·37° to 1·48°.

The density of the saturated vapour at a pressure of 760 mm. is 85·5 times the normal density. The value of $K = RT_k/p_k v_k$, taking $T_k = 5·5°$ and $p_k = 2·75$, is found to be 2·68, which is almost exactly the theoretical value deduced from van der Waals' equation.

The theoretical interpretation of the occurrence of a maximum density in the case of such a simple substance as helium is considered in reference to the theories of atomic structure and to the question of the significance of the absolute zero of temperature in relation to molecular attraction.

The helium thermostat and thermometer have also been employed in the investigation of the electrical resistance of platinum at these very low temperatures. The resistance measurements indicate that a considerable diminution in the resistance occurs on descending from liquid hydrogen to liquid helium temperatures, but that when these temperatures (1·5° to 4·3° absolute) are reached, the resistance attains a constant value. By taking into account the effect of the slight impurities in the metal, the conclusion is drawn that the resistance of pure platinum is, within the limits of experimental error, already zero at helium temperatures. The bearing of this result on the theory of electric conduction is discussed. H. M. D.

Hydrates of Potassium Fluoride. ROBERT DE FORCRAND (*Compt. rend.*, 1911, **152**, 1073—1077).—A dihydrate of potassium fluoride is already known ; this is deposited from a solution of the salt above 20° when kept in a vacuum over phosphoric oxide. Below this temperature a new hydrate, containing $4H_2O$, separates in large crystals, m. p. 19·3°. This substance is not deliquescent, and remains unaltered in the air. The heat of dissolution is −6·160 Cal. at 15°, whilst the same value for the dihydrate is −2·140 Cal. Thermochemical considerations point to the possible existence of a hexahydrate which should be stable at about 0°. W. O. W.

Crystal-habit of Sodium Chloride in Relation to the Solvent. ALBERT RITZEL (*Zeitsch. Kryst. Min.*, 1911, **49**, 152—192). —A large series of determinations were made of the rate of solution of rock-salt on the cube face and on other artificially polished faces of definite crystallographic orientation, the solvent being a solution of sodium chloride of varying degrees of under-saturation, and in some experiments containing, in addition, carbamide, formamide, or potassium nitrate. The rate of solution in each case varies directly as the degree of under-saturation. In a pure sodium chloride solution the rate is slightly greater on an octahedron face than on a cube face, but with the addition of a little carbamide (5 grams per 100 c.c.) the rates on the two faces are the same; with more carbamide the rate of solution is greater on a cube face than on an octahedron face. This explains the well-known fact, first observed by Haüy, that sodium chloride crystallises as octahedron from a solution containing carbamide. Formamide produces the same result as carbamide, but potassium nitrate has no effect on the relative rates of solution on the different faces. L. J. S.

Preparation of Highly Oxygenated Salts in a Solid Condition. George François Jaubert (D.R.-P. 229572).—Salts containing a high percentage of available oxygen can be conveniently prepared in a solid form by the interaction of metallic peroxides and acids at a temperature of about 30° in the presence of an anhydrous liquid as diluent.

Sodium peroxide hydrochloride, $Na_2O_2,2HCl$, is obtained by passing dry hydrogen chloride into a suspension of sodium peroxide in carbon tetrachloride until the necessary gain of weight is obtained, collecting, and drying the product, which forms a colourless powder, readily soluble in water and containing about 10% available oxygen.

Sodium peroxide formate, $Na_2O_2,2CH_2O_2$, is obtained in a similar manner.

Sodium peroxide ethyl acetate, $Na_2O_2,Me\cdot CO_2Et$, is prepared from sodium peroxide and ethyl acetate in chloroform solution, whilst *sodium peroxide benzoate*, $Na_2O_2,2C_6H_5\cdot CO_2H$, is analogously obtained in carbon tetrachloride. F. M. G. M.

Reciprocal Solubility of Sodium Carbonate and Sodium Hydrogen Carbonate in Water. Désiré de Paepe (*Bull. Soc. chim. Belg.*, 1911, **25**, 173—177).—The results of the determinations of the reciprocal solubility of these two salts in water, at 25° and at atmospheric pressure, are in good agreement with those calculated from Ostwald's dissociation law, if it be assumed that both salts, under the conditions of this experiment, dissociate into two ions, one of which is common to each, for example, $NaCO_3,Na$ and $NaCO_3,H$. No evidence could be obtained of the formation of a compound of the two salts under these conditions. T. A. H.

An Insoluble Sodium Phosphate and Complex Compounds of Ammonium Citrate with Alkaline Earths. Antonio Quartaroli (*Chem. Zentr.*, 1911, i, 6—7; from *Staz. sperim. agrar. ital.*, 1910, **43**, 545—558).—The filtrate from the barium phosphate, produced by mixing solutions containing 1 mol. of phosphoric acid, one equivalent of barium, and two equivalents of sodium, deposits after some time a sparingly soluble *sodium barium phosphate*, $NaBaPO_4$. Lithium yields a similar compound, but not potassium. Analogous salts containing calcium could not be obtained.

The precipitate, produced by adding ammonia to a dilute solution of monobarium phosphate, redissolves on the addition of ammonium citrate. If ammonium aconitate or tricarballylate be used instead of ammonium citrate, solution does not take place. This behaviour is due to the formation of the compound

$$BaPO_4\cdot O\cdot C(CH_2\cdot CO_2NH_4)_2\cdot CO_2NH_4.$$

Since a corresponding calcium salt could not be obtained, the author draws the conclusion that in this case dissociation takes place according to the scheme RCa—PO_4, whilst the barium salt dissociates into R and $BaPO_4$. A similar explanation is given for the non-formation of double salts of calcium phosphate with the alkali metals. F. B.

Lithium Silicates. R. RIEKE and K. ENDELL (*Sprechsaal*, 1910, 43, 683—685).—The naturally-occurring lithium-containing minerals are lepidolite and eucryptite, whilst the orthosilicate, $2Li_2O,SiO_2$, m. p. 1215°, the metasilicate, Li_2O,SiO_2, m. p. 1180°, and an acid silicate, $Li_2O,5SiO_2$, have also been prepared. Pure lithium carbonate and sand (99·6% SiO_2) were mixed in the required proportions and heated in a platinum vessel. The products were analysed, and the eutectic, molecular composition, and crystallising points of the fusions demonstrated in tabular form and by curves. F. M. G. M.

Studies on Photohalides. III. WILLEM REINDERS (*Chem. Weekblad*, 1911, 8, 299—307. Compare this vol., ii, 39).—The sensitiveness of silver salts to light is increased by crystallisation from aqueous ammonia containing small amounts of gelatin. This effect is not due to reduction by the gelatin, but to its occlusion in the crystals of the silver salt. A solution of one part of gelatin in ten million causes an appreciable increase in sensitiveness to light. Solutions of strengths from 0·00001% to 1·0% have been examined. Gum-arabic, casein, and egg-albumin similarly increase the sensitiveness of silver chloride to light. Dextrin increases it slightly, but sucrose, dextrose, and agar-agar have no action. The presence of gelatin hinders the absorption of colloidal silver. A. J. W.

Constitution of the Photohalides. WILLEM REINDERS (*Chem. Weekblad*, 1911, 8, 316—321. Compare Trivelli, this vol., ii, 281).—Polemical. A reply to Trivelli's criticism of the author's absorption theory, and a criticism of Trivelli and Schaum's solarisation theory. A. J. W.

Action of (1) Potassium Hydroxide, (2) Sodium Hydroxide Solution on Calcium Carbonate. WILLIAM OECHSNER DE CONINCK (*Bull. Acad. Roy. Belg.*, 1911, 212, 216).—Calcium carbonate when boiled with a concentrated aqueous solution of potassium hydroxide is partly decomposed, and lime can be detected in the filtrate. A like change occurs with sodium hydroxide solution. T. A. H.

Inorganic Peroxides. I. Preparation of Cadmium and Zinc Peroxides. I. S. TELETOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 131—135).—By the addition of ammonia to a concentrated cadmium sulphate solution until the precipitate formed disappears, followed by the addition of a large excess of 30% hydrogen peroxide solution, the following two cadmium peroxides were obtained: (1) $5CdO_2,CdO,3H_2O$, and (2) $5CdO_2,3CdO,5H_2O$. The use of zinc sulphate in place of cadmium sulphate leads to the formation of the peroxides: (1) $10ZnO_2,4ZnO,5H_2O$, and (2) $8ZnO_2,4ZnO,7H_2O$. T. H. P.

Nature of the Metallic "Fog" in Fused Salts.

RICHARD LORENZ, GEORG VON HEVESY, and E. WOLFF (*Zeitsch. physikal. Chem.*, 1911, **76**, 732—742).—It has been shown by Lorenz (*Electrolyse geschmolzener Salze*, Halle, 1906) that when lead is heated to 600° in contact with fused lead chloride, the liquid, previously yellow, becomes reddish-brown, and finally almost black; on cooling, a fine black "fog," which looks like a finely divided metal, settles out. It is now shown that this fog is metallic lead, and a method for estimating the lead dissolved in fused lead chloride is described; it depends upon the decolorising of the liquid by the addition of known amounts of lead peroxide, which reacts with the lead according to the equation: $PbO_2 + Pb \longrightarrow 2PbO$. In this way it is shown that at 550° fused lead chloride dissolves $1\cdot54 \times 10^{-4}\%$ by weight of lead.

The solubility of lead in lead chloride is very small when sufficient potassium chloride is added to form a mixture of the composition $2PbCl_2,KCl$. As there is probably very little free lead chloride in such a mixture (Abstr., 1902, ii, 152), it is suggested that the dissolved lead forms a compound with the lead chloride according to the equation: $(Pb)_n,PbCl_2 \rightleftharpoons PbCl_2 + (Pb)_n$, where n is very probably unity. It is shown that the recent observations of Aten (Abstr., 1909, ii, 537) on the electrical conductivity of mixtures of metals and their salts lead to the same conclusion. G. S.

Double Salts of Lead Fluoride and the Other Halides of the Same Metal.

CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 253—257. Compare this vol., ii, 284).—The present communication deals with the thermal study of the systems $PbBr_2$–PbF_2 and PbI_2–PbF_2. The former system is analogous to that of $PbCl_2$–PbF_2 previously described. In the part of the diagram $PbBr_2$–$PbBr_2,PbF_2$ the eutectic lies at 349° (composition 7·5 mol. %). From the behaviour of mixtures containing 2·5 and 45 mol. % of fluoride, it appears probable that the bromide and the salt $PbBr_2,PbF_2$ crystallise pure from the fused mixtures. In the part of the diagram

$$PbBr_2,PbF_2\text{–}PbBr_2,4PbF_2$$

the mixture containing 75 mol. % of fluoride deposits pure eutectic. $PbBr_2,4PbF_2$ is a *compound* formed at 585°, and decomposing on fusion. The cooling curve at this concentration has only one resting point.

The curve of the system PbI_2–PbF_2 shows an eutectic point at 383° (composition 10 mol. % of fluoride). It then rises, pausing slightly at 432° (20 mol. %) to 573° (76·5 mol. %), where there is an evident pause; finally, it rises to the m. p. of pure fluoride. Indications were obtained of the existence of *compounds*, $PbI_2,4PbF_2$ and PbI_2,PbF_2, decomposing on fusion. R. V. S.

Investigations of Vapour Pressure. VII. The Vapour Pressure of Dried Calomel. ALEXANDER SMITH and ALAN W. C. MENZIES (*Zeitsch. physikal. Chem.*, 1911, **76**, 713—720).—Calomel was contained in one bulb of a sealed glass apparatus which comprised two further bulbs; one contained phosphoric oxide, and the other larger bulb was destined to determine the vapour density of calomel. The bulbs were in communication. The apparatus was placed in a thermostat, the temperature of which was kept constant at 115°; the phosphoric oxide bulb, however, was kept at 25° by circulating cold water round it. After five and a-half months, the phosphoric bulb was removed by sealing it off, and the remainder of the apparatus immersed in a constant temperature bath at 352°, and after fifteen minutes the larger bulb was sealed off and weighed. Only one experiment has, so far, been made, and it showed that under these conditions no calomel had passed into the large bulb; in other words, the vapour pressure of extremely dry calomel at 352° is zero. When the drying was less complete, the observed vapour pressure corresponded with that of a mixture of mercuric chloride and mercury. Baker (Trans., 1900, **77**, 646), on the other hand, with dry calomel, but presumably less thoroughly dried than that of the authors, obtained a density corresponding approximately with the formula Hg_2Cl_2, and observed no difference in the rate of vaporisation of dried and undried calomel. In order to clear up this discrepancy, the experiments are being continued. G. S.

Compounds of Dysprosium. GUSTAV JANTSCH and A. OHL (*Ber.*, 1911, **44**, 1274—1280. Compare Abstr., 1908, ii, 189).—*Dysprosium bromate*, $Dy(BrO_3)_3,9H_2O$, prepared from the sulphate by double decomposition with barium bromate, forms shining, slightly yellow, hexagonal needles, m. p. 78°. By prolonged heating at 110°, $6H_2O$ only are lost. *Dysprosium selenate*, $Dy_2(SeO_4)_3,8H_2O$, was obtained from a solution of the nitrate and selenic acid by precipitation with alcohol; it forms bright yellow needles, and is dehydrated completely at 200°. *Dysprosium phosphate*, $DyPO_4,5H_2O$, forms first as a gelatinous precipitate on mixing a solution of the nitrate with ammoniacal sodium phosphate solution; on keeping for three or four days it becomes crystalline, and then forms a white powder with a yellow tinge. It loses $5H_2O$ above 200°. *Dysprosium chromate*, $Dy_2(CrO_4)_3,10H_2O$, is obtained as a sparingly soluble precipitate from the interaction of solutions of the nitrate and potassium chromate. It is a greenish-yellow, finely crystalline powder; at 25°, 100 c.c. of the solution contain 1·0002 grams of the salt; at 150° it loses $3·5H_2O$; above 150° it decomposes.

Dysprosium carbonate, $Dy_2(CO_3)_3,4H_2O$, is formed as an insoluble powder when an aqueous suspension of the hydroxide is saturated with carbon dioxide. At 15° it loses $3H_2O$. When added to a concentrated solution of ammonium carbonate, it gradually changes into the white, crystalline, and sparingly soluble *dysprosium ammonium carbonate*, $NH_4Dy(CO_3)_3,H_2O$, which loses ammonia at 60°.

Dysprosium platinocyanide, $Dy_2[Pt(CN)_4]_3,21H_2O$, prepared from the sulphate and barium platinocyanide, forms bright, cinnabar-red, cubic crystals with a green surface sheen, which disappears when dehydration takes place, the crystals becoming yellow, and finally white. *Dysprosium formate*, $(H\cdot CO_2)_3Dy$, forms pale yellow crystals, as also does the *acetate*, $(C_2H_3O_2)_3Dy,4H_2O$; they are obtained from dysprosium hydroxide and the solutions of the respective acids. The acetate forms a basic salt when heated at 120°.

Dysprosium oxalate, $Dy_2(C_2O_4)_3,10H_2O$, is precipitated on the addition of a solution of the nitrate to a concentrated solution of oxalic acid. It forms microscopic prisms, insoluble in water, but soluble in normal sulphuric acid to the extent of 0·1893 gram of the anhydrous salt in 100 c.c. of solvent at 20°. *Dysprosium potassium oxalate*, $KDy(C_2O_4)_2,3H_2O$, is obtained as a sparingly soluble, white, crystalline powder from solutions of the nitrate and potassium oxalate; it is readily soluble in dilute acids. T. S. P.

Aluminium Alloys Containing Magnesium. ALFRED WILM (*Metallurgie*, 1911, 8, 225—227).—Alloys consisting of aluminium to which small quantities of magnesium have been added are hardened by quenching, but the process is quite different from the hardening of steel. If quenched from 500° in cold water, the metal is at first soft, but the hardness increases in the course of a few days. The initial hardness is independent of the quenching temperature, but the hardness attained after storage increases with the quenching temperature up to 470°, beyond which it is constant. Unlike steel, these alloys become more ductile by this treatment.

Experiments with an alloy containing 3·5% of copper and 0·5% of magnesium show that the hardened alloys can receive a greater amount of cold work than those which are not hardened. If slowly cooled from 500°, the initial hardness is greater than that of the newly quenched alloys, but little increase in hardness or strength occurs.

The addition of manganese increases the hardness, whilst that of nickel gives greater toughness. Aluminium alloyed with small quantities of manganese is not wetted by mercury. C. H. D.

Aluminium Bromide as Solvent. W. A. IZBEKOFF and WLADIMIR A. PLOTNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 18—37).—Aluminium bromide in the pure state has no conducting power, but it is a good solvent for inorganic salts and for certain organic compounds. The authors have determined the conductivities of solutions in aluminium bromide of various bromides, the following results being obtained.

Except in a few cases (stannic bromide, arsenic tribromide), solutions of salts in aluminium bromide are good conductors. The molecular conductivity of the solution of mercuric bromide diminishes with dilution, whilst with antimony tribromide it passes through a maximum. The conductivity observed in these cases is conditioned by the formation of complex compounds and complex ions. The solutions of antimony tribromide and of mercuric and cobalt bromides exhibit negative temperature-coefficients of conductivity.

T. H. P.

Kinetic Investigation of the Action of Hydrogen on Solutions of Potassium Permanganate (Auto-reduction). GERHARD JUST and YRJO KAUKO (*Zeitsch. physikal. Chem.*, 1911, **76**, 601—640).—It is shown by using neutral solutions of potassium permanganate of different concentrations and by varying the hydrogen concentration by mixing it with nitrogen in varying proportions, that the rate of reaction is proportional to the concentration of each of the reacting substances, and therefore that one molecule of hydrogen reacts primarily with one molecule of permanganate. It follows from these results that a quinquevalent, very unstable salt of manganese is formed as an intermediate product. The manganese dioxide formed in the course of the reaction has no effect on the rate. The speed of the reaction is approximately doubled by raising the temperature from 15° to 25°. The effect of altering the rate of stirring has been investigated.

A method whereby a solution can be kept practically saturated with a gas, even when the latter is being rapidly used up, is described.

G. S.

The Stable System Iron–Carbon. RUDOLF RUER and NIKOLAUS ILJIN (*Metallurgie*, 1911, **8**, 97—101).—The solubility of elementary carbon in solid iron has been studied by experiments on a Swedish iron containing 3·75% C, 0·21% Mn, 0·05% Si, 0·006% S, and 0·01% P. This was re-melted with carbon in a magnesia crucible, raising the carbon content to 4 or 4·5%. This was rendered grey by re-melting and slow cooling in a vacuum, after which the structure was found to consist of ferrite and graphite, with only small quantities of pearlite. Small specimens were then heated to definite temperatures for six hours each, and then quenched. Further heating at the same temperatures had little effect on the quantity of carbon dissolved.

The solubility curve thus obtained is parallel with that of cementite, the maximum being reached at 1120° with 1·25% C (compare Charpy, Abstr., 1908, ii, 110). Equilibrium is not reached in the other direction, owing to the slowness with which graphite (temper-carbon) separates above 800°. The velocity of separation of graphite below 800°, however, depends on the time during which the alloy has been heated at the higher temperature, at which centres of crystallisation are probably formed. In order to hinder the formation of temper-carbon as far as possible, it is necessary to quench at 800°.

C. H. D.

The Influence of Nitrogen in the Case-Hardening of Steel. J. KIRNER (*Metallurgie*, 1911, **8**, 72—77).—Experiments have been made with two hardening mixtures containing nitrogen. Both mixtures carburise iron readily between 600° and 850°, the action then becoming irregular or stationary, and only increasing again above 950°. Hardening material containing alkali carbonate, but free from nitrogen, increases regularly in activity with the temperature. The outer layers of iron, when nitrogenous materials are used, take up nitrogen to a maximum of 0·6% between 600° and 850°; at higher temperatures the proportion of nitrogen diminishes rapidly, becoming a

mere trace at 1000°. Sections of the layers containing nitrogen show a constituent for which the name "flavite" is proposed, coloured yellow by picric acid. This constituent is assumed to be a solid solution containing nitrogen. It disappears when the steel is quenched.
C. H. D.

The Etching of Steels. Austenite and Martensite. F. ROBIN and P. GARTNER (*Rev. de Métallurgie*, 1911, **8**, 224—240).—Steels containing austenite and martensite may be etched by immersing in an alcoholic solution of picric acid, transferring to water, and finally drying in a current of air. Coloured films are thus produced, and indicate the structure if sufficiently thin to remain adherent. Steel containing 1% of manganese and 1·6% of carbon yields pure austenite when rapidly quenched from 1400°. Steel containing much less carbon yields pseudomorphs, retaining the form of the austenite crystals, but having a martensitic structure. The forms assumed by martensite have been studied in detail. C. H. D.

The Internal Structure of Pearlitic Steel. M. OKNOFF (*Metallurgie*, 1911, **8**, 138—139).—The method of cutting serial sections, employed in histology to determine the arrangement of a structure in space, has been applied to steel, successive small thicknesses being removed by grinding, and a marked area examined after each operation. Photographs of successive layers have thus been taken of steels containing 0·1%, 0·7%, and 1·7% of carbon. It is shown that the eutectoid pearlite forms a continuous mass in each case, the "cell-walls" of ferrite or cementite appearing as distinct structures embedded in the ground-mass. C. H. D.

The Synthesis of Meteoric Iron. CARL BENEDICKS (*Rev. de Métallurgie*, 1911, **8**, 85—107).—Alloys having the structure of a meteoric iron may be obtained artificially by preparing an alloy of iron with 12% of nickel by the aluminothermic process, and cooling very slowly below 350°. Plessite is readily formed in this way, and the structure of octahedral irons is closely reproduced. An alloy containing 6% of nickel yields an artificial cubic iron. Oxidised specimens have a structure closely resembling the Widmanstätten figures, the components being oxidised. The conclusion is drawn that the structure of meteoric irons is a stable one (compare Fraenkel and Tammann, Abstr., 1909, ii, 157; Guertler, Abstr., 1910, ii, 833).
C. H. D.

Action of Heat on Ochres. A. BOUCHONNET (*Bull. Soc. chim.*, 1911, [iv], **9**, 345—351).—Analyses of six ochres are given; the amount of ferric oxide varies from 20·67—72·72%, and of water 9·04—19·79%. The colour of ochres gradually deepens on heating at 100° to 250°, and between 230° and 260°, at a definite temperature differing with the ochre, changes sharply from yellow to red. Above this transition temperature the colour deepens until 700—800°, and at about 900° the material undergoes marked contraction. At 1000—1100° it usually changes suddenly to black, owing to conversion of ferric oxide into the magnetic oxide. One variety (from Vaucluse) became magnetic whilst still yellow, pointing to the existence of an allotropic form of ferric oxide. The duration of heating only influences the colour below 700° and above 1000°. The rate of cooling has no influence on the shade. The general conclusion is that the colour changes are due, in part, to diminution in the size of the grains and not solely to dehydration. In this respect ochres resemble ferric oxide studied by Woehler and Condrea (Abstr., 1908, ii, 287). W. O. W.

Regularity of Composition of Eutectic Alloys. K. LOSEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 375—392).—Among the various exceptions to the regularity in the composition of eutectics indicated by the work of Gorboff (Abstr., 1910, ii, 111) there occur a number of cases in which alloys seem to contain eutectics differing but slightly from one or other of the pure metals. In such cases, it is, however, almost impossible to determine the composition of the eutectics by means of thermal analysis. In these instances, the eutectic composition may be determined by a study of the microstructure, and the author applies this method of investigation to alloys of (1) cobalt and antimony, and (2) nickel and antimony. The results obtained, which are given in the form of micro-photographs, and in case (1) also as an equilibrium curve, show that it is highly improbable that, for these alloys, eutectics exist approximating to pure antimony.

The alloys of nickel and antimony exhibit one noteworthy peculiarity. When they contain between 57% and 92·5% by weight of nickel, they show on solidification a second temperature-halt, owing to the formation of crystals of the compound Ni_4Sb from two kinds of solid saturated mixtures. T. H. P.

Molecular Weight of Uranous Oxide. WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1911, **152**, 1179. Compare this vol., ii, 403).—Uranic hydroxide was reduced in a current of hydrogen at dull redness. The mean of five determinations gave 270·66 as the molecular weight of uranous oxide. W. O. W.

Mineralogical Chemistry.

The Melting Points of Minerals. ARTHUR L. DAY and ROBERT B. SOSMAN (*Amer. J. Sci.*, 1911, [iv], 31, 341—349).—Various high temperature determinations made during the last five years in the Geophysical Laboratory of Washington, and already published, have been re-calculated on the basis of the newly-determined scale with the nitrogen thermometer (Day and Sosman, Abstr., 1910, ii, 261). A selection of these are :

Inversion Points.

α-Quartz $\rightleftarrows$ β-quartz		575°
Quartz to cristobalite	above	800
Wollastonite $\rightleftarrows$ pseudo-wollastonite	about	1190
α-$MgSiO_3$ $\rightleftarrows$ clinoenstatite	about	1375
Andalusite to sillimanite	above	1300
Kyanite to sillimanite	above	1300

Melting Points.

Sillimanite	1816°	Anorthite	1550°
α-$MgSiO_3$	1557	Bytownite (Ab_1An_5)	1516
α-$CaSiO_3$ (pseudo-wollastonite)	1540	Labradorite (Ab_1An_2)	1477
α-Ca_2SiO_4	2130	Andesine-labradorite (Ab_1An_1)	1430
Diopside ($MgSiO_3$,$CaSiO_3$)	1391	Andesine (Ab_2An_1)	1375
Borax	741	Oligoclase-andesine (Ab_3An_1), about	1345
Sodium chloride	800		
Sodium sulphate	884	Albite below	1200
		Microcline below	1200

L. J. S.

Amber from the Galician Carpathians. J. Niedzwiedzki (*Zeitsch. Kryst. Min.*, 1911, **49**, 223; from *Kosmos, Lemberg,* 1908, **33**, 529—535).—Amber occurs in strata of Tertiary age over a wide area in the eastern Carpathians of Galicia and Roumania. The material found in a bituminous shale of Upper-Oligocene age at Delatyn, in eastern Galicia, is transparent and pale yellow, with patches of brownish-yellow and dirty green by reflected light; sp. gr. 1·044; H 2—2½. Analysis by W. Syniewski gave: C, 79·93%; H, 10·03%; O, [10·04]; S, nil. O. Helm determined in a transparent sample 0·74% succinic acid, and in a brownish sample 1·67%. This variety of amber, for which the name *delatinite* is suggested, differs from succinite in containing rather more carbon, much less succinic acid, and no sulphur; and from roumanite in the absence of sulphur.

L. J. S.

Pressure Acting Alone has no Effect in the Transformation of Opal into Quartz. Giorgio Spezia (*Zeitsch. Kryst. Min.*, 1911, **49**, 208; from *Riv. min. crist. ital.*, 1908, **35**, 62—64).—The author showed in 1898 that opal from Baldissero, when heated for seven days at 280—290° in a dilute solution of sodium silicate, became changed into quartz. The same opal was kept for eight years in such a solution at the ordinary temperature (never exceeding 30°), but under a pressure of 1600 atmospheres: in this experiment the opal remained unchanged. L. J. S.

Bauxite. André Gautier (*Rev. gen. Chim. pure appl.*, 1910, **13**, 389—393).—A history of the discovery, with the occurrence, and employment of bauxite in commerce; that its composition varies greatly in different localities is shown by the following analytical results.

	White Bauxite.		Red Bauxite.	
	Dried at 100°.	Undried.	Dried at 100°.	Undried.
Al_2O_3	59·8	59·6	59·9	58·6
Fe_2O_3	1·7	1·2	23·9	24·1
TiO_2	4·4	4·3	3·6	3·7
SiO_2	14·1	14·3	1·5	1·8
H_2O	20·0	20·6	11·1	11·8

F. M. G. M.

Composition of a Radioactive Caucasian Mineral.

N. SOKOLOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 439—440).—A mineral, occurring in the Caucasus in solid, black masses, D^{15} 6·4, and exhibiting marked radioactive properties, was found to contain 76·01% U_3O_8, 1·70% S, and 20·00% of a residue insoluble in nitric acid and in sodium hydroxide solution. The composition of this residue is:

SiO_2.	Pb.	$Fe_2O_3+Al_2O_3$.	MnO.	ZnO.	CaO.	MgO.
5·17	4·50	4·30	0·155	0·166	4·100	0·203

T. H. P.

Zonal Structure and Electrical Properties of Cassiterite.

THEODOR LIEBISCH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 414—422).—Sections cut parallel to the basal plane and parallel to the principal axis of crystals of cassiterite show a well-marked zonal structure. The dark kernel of these crystals is strongly negative thermo-electrically with respect to copper, whilst the paler coloured shell is inactive. When placed between the electrodes of an electric wave detector the dark kernel reacts strongly, whilst the paler shell is inactive. For this reason crystals of cassiterite only act in the detector when the darker coloured pyramid faces, and not the paler prism faces, are in contact with the electrodes. The spark-spectra of cassiterite from various localities, examined by G. Eberhard, show the presence of twenty-one different metals (including scandium; compare Abstr., 1910, ii, 509). Analysis, by R. J. Meyer, of cassiterite from Schlaggenwald, Bohemia, gave the following results: the large well-developed crystal used for analysis was transparent with a reddish colour in fragments from the prism, and it gave a pale reddish powder.

SnO_2.	TiO_2.	SiO_2.	Fe_2O_3,Al_2O_3.	Rare earths.	Total.
99·33	0·44	0·13	0·17	0·10	100·17

L. J. S.

Gajite, a New Mineral.

FR. TUĆAN (*Centr. Min.*, 1911, 312—316).—The mineral was found in limestone near the village of Plešce, district of Gorski kotar, in Croatia. It is snow-white and compact with an irregular fracture, and closely resembles magnesite in appearance. Under the microscope it shows a finely granular texture, with the cleavage and optical characters of the rhombohedral carbonates; sp. gr. 2·619; H. 3½. It is readily soluble in acids with effervescence, and it shows the same colour reactions (of Meigen and Lemberg) as does aragonite. Analysis gave:

CaO.	MgO.	CO_2.	H_2O.	Total.
37·08	23·85	32·34	6·67	99·94

In composition the material thus resembles the rocks pencatite and predazzite (mixtures of calcite and hydromagnesite), but it is apparently homogeneous. L. J. S.

Melanterite and Fibroferrite from the Cetine Mine, Siena.

ERNESTO MANASSE (*Zeitsch. Kryst. Min.*, 1911, **49**, 202—203; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1908, **17**, 51—56).—Perfectly fresh melanterite forming a crystalline crust on massive marcasite was found in the antimony mine of Cetine, near Rosia, prov. Siena. Analysis I. agrees with the usual formula $FeSO_4,7H_2O$. At temperatures higher than 160° the material becomes oxidised:

							Loss at					
	FeO.	Fe_2O_3.	MgO.	SO_3.	H_2O.	Total.	100°.	130°.	160°.	190°.	220°.	280°.
I.	26·92	nil.	trace	28·18	[44·90]	100·00	34·55	35·52	37·30	—	—	—
II.	0·37	32·07	—	31·92	35·24	99·60	23·15	25·24	28·87	31·78	34·98	35·24

Fibroferrite was observed on one specimen of melanterite as very fine, straw-yellow fibres with silky lustre. Between crossed nicols the slender needles give straight extinction, and are fairly strongly birefringent with positive sign in the direction of their length. Analysis II agrees with the formula $Fe_2S_2O_9,10H_2O$ or

$$(SO_4Fe)_2O,10H_2O.$$

The whole of the water is regarded as water of crystallisation; when it is being expelled the colour of the material becomes gradually darker. L. J. S.

Strüverite from the Black Hills, South Dakota.

FRANK L. HESS and ROGER C. WELLS (*Amer. J. Sci.*, 1911, [iv], **31**, 432—442).—The mineral occurs abundantly as small, black crystals resembling columbite in appearance, and is found in a pegmatite-vein in the Etta mine, near Keystone. Associated minerals are columbite (in crystals several pounds in weight, and in masses reaching 600 lbs.), cassiterite, beryl, spodumene, mica, felspar, and quartz. The spodumene is met with as enormous crystals reaching 42 feet in length, with a cross-section of 3 by 6 feet; it is said that 37 tons were mined from a single crystal, the material being used for the extraction of lithia. The strüverite crystals are tetragonal, with angles near to those of rutile; but being twinned on $e(101)$, with elongation in the direction of the pyramid-edge $[(111),(1\bar{1}1)]$, they present an orthorhombic habit similar to crystals of mossite and tapolite.

The mineral is decomposed by fusion with sodium hydrogen sulphate, but only incompletely by fusion with sodium carbonate. It is decomposed by heating in chlorine, and by this means a separation is effected of titanium from the columbium and tantalum. Somewhat variable results were obtained by different methods (details of which are given). The following mean analysis approximates to the formula $FeO,(Ta,Cb)_2O_5,6TiO_2$.

TiO_2.	SnO_2.	FeO.	Ta_2O_5.	Cb_2O_5.	SiO_2.	H_2O.	Total.	Sp. gr.
47·8	1·3	7·3	34·8	6·2	2·0	0·4	99·8	5·25

The mineral thus belongs to the ilmenorutile-strüverite series, and contains more tantalum than the original strüverite from Craveggia, Piedmont (Prior and Zambonini, Abstr., 1908, ii, 398). L. J. S.

The Composition of Helium-containing Minerals.

HANS LANGE (*Zeitsch. Naturwiss. Halle*, 1910, **82**, Reprint, 34 pp.).—A close examination has been made of euxenite from the granite-pegmatite vein of Säterdal, S. Norway. Single crystal fragments show clearly rhombic habit. The hardness is 6·5, and the sp. gr. 4·62, rising after ignition to 5·06. It shows the same behaviour as fergusonite, glowing throughout the mass with a bright brownish-yellow light when heated to dull redness. The analysis showed:

Nb_2O_5.	TiO_2.	SnO_2.	ThO_2.	ZrO_2.	UO_2.	$(LaCeDi)_2O_3$.	$(YEr)_2O_3$.	FeO.
20·81	31·05	0·13	3·32	trace	5·95	2·52	24·68	4·79

CaO.	MgO.	PbO.	K_2O.	H_2O.	CO_2	N_2 and He.	Total.
0·56	0·04	0·64	0·13	3·99	0·08	0·06	98·75%

The analysis shows 1·53% of uncombined titanic acid, the ratio $(TaNb)_2O_5:(TiSn)O_2$ being exactly 1 : 5, in agreement with Broegger's view that euxenite and polycrase are the respective end members of a homoiomorphic series in which the ratio $M_2O_5:TiO_2$ varies in stochieometric proportion between the limits 1 : 2 and 1 : 6. On ignition 1·627 c.c. of helium and 0·246 c.c. of nitrogen are evolved per gram of euxenite. The helium content is estimated to correspond with a period of accumulation of 300 million years.

An examination of the red fluorspar from Ivitgut, Greenland, described by Thomsen, showed that the fluorspar was active to the photographic plate, whilst the surrounding black cryolite was inactive. The fluorspar was separated from the cryolite and divided into a heavier and lighter portion by Thoulet's solution. The lighter part contained 4% of rare earths (equivalent 145) containing ThO_2. The heavy part consisted of a non-fluorspar mineral containing iron and copper, with uranium and lead, which is the source of the helium. The fluorspar, but not the cryolite, appears to be able to absorb and retain the helium.

The remaining sections of the paper deal with the analytical separation of tantalic, niobic, and titanic acids, and the composition of zirconium oxychlorides. The oxychlorides which exist are stated to be $ZrOCl_2$ with 2, 4, 6, 8 molecules of water, and with $5\frac{1}{2}$ molecules of water and 2 molecules of hydrogen chloride, five in all, whilst five others which have been described do not exist. F. S.

The Formation of Minerals during Sintering. LEOPOLD JESSER (*Zentr. hydraul. Zemente*, 1911, 2, 1—6).—Many crystalline minerals may be obtained by heating mixtures of their components to a sintering temperature, without actual fusion. Using amorphous silica, kaolin, calcite, and dolomite as raw materials, and a marl, containing silica, alumina, and lime in the same proportion as melilite, as a flux, sintering is readily brought about in a Portland cement furnace. Dolomite and silica in the proportions required to give diopside yield crystals of a monoclinic pyroxene and of a mineral resembling akermanite, but not identified with certainty. The same result is obtained when the marl is replaced as flux by sodium hydroxide. Mixtures of kaolin and lime of the composition $2SiO_2,Al_2O_3,CaO$ with sodium hydroxide yield some anorthite and much glass. The state of division and the rapidity of heating are important factors in these reactions.

Amorphous iron, obtained from the oxalate, is rapidly converted into the crystalline form by heating with 3% of sodium in a porcelain crucible over a Bunsen burner. C. H. D.

Allophane, Halloysite, and Montmorillonite. STANISLAUS J. THUGUTT (*Centr. Min.*, 1911, 276).—The colour reactions obtained for these minerals with organic colouring matters (this vol., ii, 210) had previously been described by E. Dittler (*Zeitsch. Chem. Ind. Kolloide,* 1909, **5**, 96). L. J. S.

A New Type of Moldavite. ERNST WEINSCHENK and H. STEINMETZ (*Centr. Min.*, 1911, 231—240).—A few specimens of the type described were found in prehistoric burial places in Bohemia and Moravia ; they have the form of small glass beads with peculiar surface markings, and a pale yellow, bluish-green, or brown colour, but they resemble one another in their sp. gr. of 2·656 and refractive index of 1·571.

Analysis of a pale yellow bead from Oberkaunitz, Moravia, gave the results under I. Under the microscope it shows the characters of a colourless glass. The material fuses readily with evolution of abundant gas bubbles, and a loss of weight of 0·22%. When quickly cooled, it solidifies again as a glass, but if the cooling is delayed by only two minutes the material is completely devitrified. In composition this very basic glass is quite unlike any known glasses of volcanic origin, and it is very unlikely that it is an artificial product dating from prehistoric times ; it is probably therefore of meteoric origin and to be classed with the tektites :

	SiO_2.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	Alkalis [diff.].
I.	45·67	6·64	0·79	1·10	27·49	2·60	[15·5] (Na_2O, little K_2O)
II.	68·15	2·66		0·69	12·85	nil	[15·5] (Na_2O).

A bead of somewhat similar appearance found with Roman remains at Regensburg gave analysis II ; this agrees in composition with an artificial Roman glass. L. J. S.

Minerals from Berks County, Pennsylvania. EDGAR F. SMITH (*Proc. Acad. Nat. Sci. Philadelphia,* 1911, **62**, (1910), 538—540).—The following analyses are given of minerals from a railway cutting east of Reading. I, Laumontite, chalky-white with vitreous and pearly lustre. II and III, Apophyllite, colourless to white crystals. IV, Chabazite, colourless to white crystals. V, Scolecite, radiating needles. VI, Garnet : material of various colours—black, green. brown, grey—was found ; that of the material analysed is not recorded, VII., Pyroxene, light green crystals.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Loss on ignition.	Sp. gr.
I	52·12	22·2	—	—	—	11·89	—	—	—	14·12	2·253
II.	52·03	0·28	trace	—	—	25·11	—	5·13	0·71	17·43	2·399
III.	51·95	2·94		—	—	23·68	0·36	4·47	0·34	15·81	2·37
IV.	48·59	18·49	—	—	—	8·78	0·05	0·69	1·41	22·01	2·053
V.	47·04	25·42	—	—	—	9·86	—	—	4·77	13·60	2·27
VI.	34·98	5·82	26·82	0·37	0·08	31·23	0·57	—	—	—	3·6
VII.	52·23	3·58	—	2·45	1·55	20·00	18·31	—	—	1·79	3·187

L. J. S.

Constitution of Zeolites. ENNIO BASCHIERI (*Zeitsch. Kryst. Min.*, 1911, **49**, 201—202; from *Atti Soc. Toscana Sci. Nat.*, 1908, **24**, 133—152. Compare Abstr., 1909, ii, 589).—The following zeolites, were examined by Tschermak's method for the isolation of the silicic acid. Heulandite from Teigarhorn, Iceland (anal. I.): by the action of strong sulphuric acid at 55—60° a silicic acid was obtained which contained 19·31% H_2O at the decomposition point, corresponding with the formula $H_{10}Si_6O_{17}$ (heulandite-acid). Stilbite from Teigarhorn, Iceland (anal. II), gave an acid (D 1·954) containing in different experiments 21·05, 20·93, 20·16% H_2O, corresponding with $H_{10}Si_6O_{17}$. Analcite from Seiser-Alp, Tyrol (anal. III), yielded with concentrated hydrochloric acid, acting for a week at the ordinary temperature, a pulverulent acid (D 1·841) containing 21·31, 22·43, 21·60% H_2O, corresponding with Tschermak's leucite-acid, $H_4Si_2O_6$. Apophyllite from Seiser-Alp, Tyrol (anal. IV), yielded a flocculent acid (D 2·016) containing 12·39, 12·69% H_2O, corresponding with datolite-acid, $H_2Si_2O_5$.

	SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
I.	58·99	15·26	6·80	0·08	2·03	1·15	15·72	100·03
II.	58·56	16·72	6·42	—	0·98	0·30	17·89	100·87
III.	56·49	21·89	0·56	—	11·39	0·53	8·73	99·59
IV.	52·39	—	24·90	—	1·09	4·90	16·22	99·50

The author proposes a classification of the zeolites based on these results, results which are adversely criticised by the abstractor (F. Zambonini). L. J. S.

Fayalite from the Island of Pantelleria. JULIUS SOELLNER (*Zeitsch. Kryst. Min.*, 1911, **49**, 138—151).—Small, well-developed crystals, 1—2 mm. across and of varying habit, are found, together with crystals of cossyrite (Abstr., 1909, ii, 814), quartz, and felspar, in a loose, sandy material in the Cuddia Mida crater. They are wine-yellow to yellowish-green, transparent to translucent, and bright on the surface, but frequently they are covered with a skin of limonite. Axial ratios [$a:b:c=0·46000:1:0·58112$]. Optical constants:

	α.	β.	γ.	$\gamma—\alpha$.	$2V$.
Green (Hg, 0·5461μ)	1·80867	1·84304	1·85104	0·04237	50°31′15″
Yellow (Hg, 0·57795μ)	1·80442	1·83826	1·84625	0·04183	51°1′15″

Analysis by M. Dittrich gave:

SiO_2.	TiO_2.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	Alkalis.	H_2O.	Total.	Sp.gr.
28·89	1·19	5·08	56·05	3·39	0·74	3·11	0·42	1·07	99·94	4·24

Neglecting water and alkalis and calculating the whole of the iron as ferrous oxide (61·90%), this analysis gives the formula

$$10(Fe,Mn)_2(Si,Ti)O_4,1(Mg,Ca)_2(Si,Ti)O_4.$$

These determinations of the optical constants and percentage of ferrous iron fall into their proper place in the table of olivines given by Penfield and Forbes (Abstr., 1896, ii, 373). L. J. S.

Composition of the Mud and Water of Lake Tinaksk, Astrakhan. N. W. SOKOLOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 436—439).—The water of this lake contains, in grams per litre, Br, 0·501; Cl, 182·994; SO_3, 42·352; Mg, 39·5676; K, 0·8651; and Na, 78·308. The percentage composition of the mud of the lake (dried at 120°), which exhibits considerable radioactivity, is: clay and sand (insoluble in hydrochloric acid), 28·7; combustible matter, 20·826; FeS, 3·655; organic sulphur, 0·686; SO_3, 18·810; SiO_2 (soluble), 1·200; CO_2, 4·824; CaO, 14·300; MgO, 4·610; Al_2O_3 + F_2O_3, 2·270; total, 99·881. T. H. P.

Physiological Chemistry.

The Mechanism of the Gaseous Exchange in the Lungs. R. du Bois-Reymond (*Chem. Zentr.*, 1911, i, 90—91; from *Arch. Anat. Physiol.*, *Physiol. Abt.*, 1910, 257—278).—By subjecting cats' and frogs' lungs, filled with nitrogen, to the action of normal blood, the author finds that oxygen passes from the blood into the lung alveoles. Simultaneously, the lobes absorb carbon dioxide from the blood, at first very rapidly, and then with gradually diminishing speed. These observations contradict the view that the gaseous exchange is due to the activity of the epithelial cells. It is to be considered as a purely physical equalisation of the gaseous tensions in the blood and air contained in the lungs.

The Influence of Breathing Oxygen. II. Relationship to Constitution. Otto Warburg (*Zeitsch. physiol. Chem.*, 1911, **71**, 479—484. Compare this vol., ii, 211).—These experiments with young red-blood corpuscles of the bird were carried out on the lines of the author's previous work. The influence of various aldehydes and alcohols on the oxidation was investigated. The aldehyde compound formed which inhibits oxidation (and is much more effective than that of the corresponding alcohol) is dissociable, and the action is reversible; mere washing with Locke's solution restores the oxidative process.

W. D. H.

Carbon Dioxide Output During Decerebrate Rigidity. Herbert E. Roaf (*Proc. Roy. Soc.*, 1911, **83** *B*, 433—434).—The abolition of decerebrate rigidity in cats by means of intravenous injections of curare does not lower the carbon dioxide output, and hence the postural tonus requires very little expenditure of energy. When the tonus of the decerebrate preparation is abolished by decapitation, a marked fall in the carbon dioxide output is produced, and this is not due to the abolition of tonus or to the fall in blood-pressure.

W. J. Y.

Temperature-coefficient of the Rate of the Heart Beat. Charles G. Rogers (*Amer. J. Physiol.*, 1911, **28**, 81—93).—The data obtained are such as would be expected if the heart beat were the result of a chemical reaction, but certain variations indicate that the reaction is not a simple one; one has to deal probably with a series of reactions which are affected differently at different temperatures; possibly enzymic action is involved, as Loeb suggested. W. D. H.

The Residual Carbon in Human Blood under Normal and Pathological Conditions. STEFANO MANCINI (*Biochem. Zeitsch.*, 1911, 32, 164—171).—By residual carbon is meant the carbon still contained in blood after precipitation of the proteins by phosphotungstic acid. This was estimated by Spiro's modification of Messinger's method. The normal human blood contains 0·0765 gram carbon per 100 c.c. A considerable increase was found in cases of Malta fever, bronchopneumonia, cirrhosis of the liver, cancer, interstitial nephritis, and especially in eclampsia and uræmia. The author ascribes the increase to colloidal substances, of which he discusses the origin.

S. B. S.

The Influence of Iodoform, Chloroform, and Other Substances Soluble in Fat on Phagocytosis. HARTOG J. HAMBURGER, J. DE HAAN, and F. BUBANOVIC (*Proc. K. Akad. Wetensch.*, 1911, 13, 982—1002).—The phagocytic effect was measured by determining the percentage of horse leucocytes which take up charcoal particles, the experimental method being the same as that repeatedly described by the authors. A fresh saturated solution of iodoform (containing 0·001%) in 0·9% saline was found to considerably increase the phagocytic effect, especially in the case of those leucocytes in which this effect had been diminished by prolonged keeping (eighteen hours) in saline. The effect was still noticeable when the dilution of the iodoform was 1 in 5 millions. Old iodoform solutions which had been exposed to light and in which the iodoform had been decomposed, exerted, on the other hand, a deleterious effect. The favourable effect is due therefore to the iodoform and not to iodine ions. It was assumed therefore that the effect is due to the solubility of iodoform in lipoids, and similar results were obtained with other lipoid substances investigated, namely, chloroform, benzene, camphor, turpentine. In the case of chloroform and benzene, the favourable effects are most pronounced in more dilute solutions (1 in 100,000), as in the more concentrated solutions the substances exert a toxic (narcotic) effect on the protoplasm. The increased phagocytic effect is ascribed to the diminution of the surface tension of the lipoid membrane of the cell and the consequent increased capacity for amoeboid movement. The influence of these factors on the therapeutic action of iodoform is discussed, and the analogy is pointed out of the effects observed by J. Loeb and by Lillie on certain actions of lipoid soluble substances on artificial parthenogenesis. S. B. S.

Glycolysis. II. The Influence of Phosphates on Oxidative Glycolysis. WALTHER LÖB (*Biochem. Zeitsch.*, 1911, 32, 43—58).—In salt-free sugar solutions, neutral hydrogen peroxide exerts only a very slight oxidative action, which can be increased by increasing the hydroxyl ion concentration. In concentrations equal to that existing in blood, which only differs slightly from pure water, the oxidative capacity can be markedly increased by the presence of phosphates. The optimal hydroxyl ion concentration is between $p_H = 8{\cdot}302$ and $7{\cdot}070$. When $p_H \overset{=}{<} 5{\cdot}600$, even in the presence of phosphates, the glycolysis is not greater than that in pure water. If the hydroxyl ion concentration be kept constant, glycolysis increases with increasing quantities of phosphates. By replacing phosphates by serum, lecithin, disodium glycerophosphate, or phenylethylamine, no glycolysis takes place, whilst guanidine and piperidine increase the action. The phosphate glycolysis is inhibited or completely prevented by serum, lecithin, sodium glycerophosphate, phloroglucinol, potassium iodide, and Witte's peptone, and especially by sodium oleate. S. B. S.

Serological Studies by the Help of the Optical Method. XIV. EMIL ABDERHALDEN and E. RATHSMANN (*Zeitsch. physiol. Chem.*, 1911, **71**, 367—384).—The serum or plasma of normal dog's blood does not invert sucrose. After subcutaneous or intravenous injection of sucrose, an enzyme is found in the blood which has this power. The amount of cleavage is determined polarimetrically. In the present research it is shown that the same result follows abundant feeding on sucrose. W. D. H.

Serological Studies by the Help of the Optical Method. XVI. EMIL ABDERHALDEN and ERNST KÄMPF (*Zeitsch. physiol. Chem.*, 1911, **71**, 421—442).—The plasma or serum of dogs after the injection of blood from an animal of another species is able to split silk peptone, whereas the injection of the blood of the dog produces no such effect. Anaphylaxis was not observed in a guinea-pig by injecting testis or ovary substance from the guinea-pig of either sex. High molecular polypeptides and peptones also did not produce anaphylaxis. W. D. H.

Plastein Formation. VALDEMAR HENRIQUES and J. K. GJALDBÄK (*Zeitsch. physiol. Chem.*, 1911, **71**, 485—517).—If pepsin is added to a concentrated solution of the products of peptic digestion containing hydrochloric acid, a synthetic process occurs which can be measured partly by precipitation with tannic acid, and partly by titration with formaldehyde. The process occurs between 5° and 70°. The synthetic product differs from the original material; the more complete the cleavage of the latter, the less complex is the synthesised substance, and the greater the quantity formed. W. D. H.

The Significance and Measurement of the Acidity of the Gastric Juice. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Chem. Zentr.*, 1911, i, 170—171; from *Zeitsch. exper. Path. Ther.*, 1901, **8**, 398—413).—The usual titration methods do not give the true acidity of the gastric juice, and the author therefore recommends the measurement of the acidity, either by means of the hydrogen ion concentration cell, or by the indicator method (Friedenthal, Abstr., 1904, ii, 288). In the latter method, the colorations produced by the gastric juice with methyl-violet, tropaeolin, Congo-red, and methyl-orange are compared with those obtained with dilute standard hydrochloric acid solutions, the same indicators being used.

The concentration of hydrogen ions in normal gastric juice lies between 0·028 and 0·0015*N*. F. B.

Action of Pepsin. IV. EMIL ABDERHALDEN and FRIEDRICH FRIEDEL (*Zeitsch. physiol. Chem.*, 1911, **71**, 449—454).—As shown in previous papers, pepsin is adsorbed by elastin. It can be dissolved out from the elastin and retains its activity; it may become more active if left long in contact with the elastin. The transport of pepsin to the intestine in this way may be of value. Milk curdled in the stomach will adsorb pepsin in the same way. W. D. H.

The Influence of the Climate of High Altitudes on the Metabolism of Man. GEORG VON WENDT (*Chem. Zentr.*, 1911, i, 411; from *Skand. Arch. Physiol.*, 1910, **24**, 247—258).—Whilst residing at an altitude of 3000—4500 m. above sea level, the author has determined his daily intake and output of nitrogen, sulphur, phosphorus, iron, calcium, magnesium, sodium, potassium, and chlorine, and finds that in the case of nitrogen, sulphur, and iron the balance is positive. The retention of nitrogen often observed in metabolism experiments in the Alps is due to the formation of living material, and not to the formation of intermediate nitrogenous compounds. F. B.

The Dependence of Calcium Metabolism on the Organic Constituents of the Food in a Grown Dog, with Some Observations on Phosphoric Acid and Magnesium Metabolism. II and III. MARTIN KOCHMANN and ERNST PETZSCH (*Biochem. Zeitsch.*, 1911, **32**, 10—42).—The calcium, magnesium, phosphoric acid, and nitrogen were estimated in the ingesta and egesta with various diets of different quantities of meat, with and without additions of carbohydrates, fats, and calcium salts. From the results of the present and former communications, the authors draw the conclusion that it is not possible to attain a calcium equilibrium with definite minimal quantities of this element, the amount necessary for the purpose varying with different diets. By adding protein, fat, or carbohydrate to a given diet, the existing calcium equilibrium is destroyed, and the organism loses considerable quantities of calcium, which appears to be eliminated as calcium phosphate. To restore the equilibrium again, larger quantities of calcium must be added to the diet than those lost by the organism. The added calcium appears to be retained in the body in the form of phosphate, even when it is administered in the form of chloride. The loss of calcium by the organism does not exert any deleterious effect, as it appears to act as a normal protection against toxic metabolism products. The phosphoric acid metabolism is dependent both on the nitrogenous and calcium metabolism, in addition to other factors. No definite conclusions could be drawn as to the magnesium metabolism. S. B. S.

Purine Metabolism. VI. Purine Metabolism under the Influence of Diminished Oxidative Processes of the Organism. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1911, **32**, 101—107).—It has already been shown by the author (Abstr., 1910, ii, 626) that the fermentative destruction of the purine bases is an oxidative process, and also that in the absence of oxygen, uric acid is readily formed by certain organs. For this reason, investigations of the output of uric acid and purine bases, under conditions of diminished oxidation, were undertaken, by exposing animals to an atmosphere containing relatively large quantities of carbon dioxide. The animals employed were the dog (when the uric acid is assumed to owe its origin to an oxidative process) and the duck (where the origin is probably due to synthesis). In the former case, the exposure to the atmosphere rich in carbon dioxide had but little influence on the uric acid output, whilst in the latter case there is a marked increase. S. B. S.

Calcium Metabolism in Lactating Women after Use of Mineral Waters Containing Calcium Hydrogen Carbonate. LORENZO COLESCHI (*Chem. Zentr.*, 1911, i, 501 ; from *Arch. Farmacol sperim.*, 1910, **10**, 254—267).—The calcium, received with the mineral water, is excreted mainly in the milk, and it is therefore possible to influence favourably the nourishment of sucklings by the administration of water containing calcium carbonate to lactating women. F. B.

"Romauxankalk" in Animal Metabolism. OSKAR HAGEMANN (*Pflüger's Archiv*, 1911, **140**, 158—164).—This commercial preparation contains calcium, phosphoric acid, and iron in organic union, and is claimed to be easily assimilable. Metabolic experiments on sheep show that it is easily digestible and assimilable, the addition of it to the diet increasing the putting on of calcium and phosphoric acid very considerably. W. D. H.

Effect of Parathyroidectomy on Metabolism. ISIDOR GREENWALD (*Amer. J. Physiol.*, 1911, **28**, 103—132).—The excretion of nitrogen increased after the removal of the parathyroids in dogs, when tetany developed, but the amount of urea was relatively less. There was an increase in creatine, purine substances, undetermined nitrogen, inorganic sulphates, and neutral sulphur. Ammonia and creatinine were unaffected. Before tetany developed there was retention of phosphorus; after tetany developed the phosphorus excretion rose. The increase in unknown nitrogenous compounds is attributed to lessened activity of the liver. No evidence that tetany is due to poisoning by ammonia or carbonic acid was forthcoming. W. D. H.

Absorption of Aluminium from Aluminised Foods. MATTHEW STEEL (*Amer. J. Physiol.*, 1911, **28**, 94—102).—In dogs, alum is readily absorbed, but does not accumulate in the blood. If aluminium chloride is given intravenously, from 5 to 11% of it passes into the fæces during the next three days, but whether it is excreted by the liver or intestinal wall, or both, was not ascertained. W. D. H.

The Cleavage of Proteins in the Alimentary Canal of Different Kinds of Animals. EMIL ABDERHALDEN, WILHELM KLINGEMANN, and THEODOR PAPPENHUSEN (*Zeitsch. physiol. Chem.*, 1911, **71**, 411—420).—In the stomach-contents of dog, ox, sheep, pig, goose, and hen, no amino-acids or but the merest traces were found. They are in all cases found in the intestinal contents; glycine, alanine, leucine, aspartic acid, glutamic acid, phenylalanine, tyrosine, and cystine were isolated. In the pig and ruminants, small amounts of amino-acids were always found in the stomach, which can hardly be explained in the case of the ruminants by the action of enzymes contained in the food. Certain difficulties met with in the research are commented on. W. D. H.

The Effect of Some Local Anæsthetics on Nerve. W. L. SYMES and VICTOR H. VELEY (*Proc. Roy. Soc.*, 1911, **83** *B*, 421—432). —A comparison of the effects of cocaine, stovaine, and its homologues (compare this vol., ii, 516) on the activity of frog's nerve was made by applying these substances to motor nerves between the stimulating electrodes and the muscle.

As tested in this way, by the effect on the conductivity of the nerve, stovaine and its homologues as well as Fourneau's salt are more active local anæsthetics than is cocaine. The anæsthetic block in individual nerve fibres is complete or else zero, throughout a wide range of intensity, to impulses evoked by maximal single stimuli.

This block is usually also complete for impulses evoked by tetanising stimuli within the same range, but when not complete is largely resistant to summation.

Judged by the effects of these substances, the amplitude of a motor nerve impulse is either maximal or zero within normal limits of stimulation.

The conditions being similar, the amplitude of a muscle twitch depends on the number of fibres involved. W. J. Y.

Lipoids of Animal Organs. ERNEST GÉRARD and M. VERHAEGHE (*J. Pharm. Chim.*, 1911, [vii], **3**, 385—390).—Bang has defined "lipoids" as those constituents of cells which are extracted by ether or other solvents of fats, and they have been classified by Thudichum according to the ratio of nitrogen and phosphorus present. The author has extracted the lipoids of a number of carefully cleaned specimens of animal organs, and has determined the percentage of phosphorus and cholesterol present. The figures quoted in brackets give in order (*a*) the percentage of lipoids in the dry organ named, (*b*) the percentage of phosphorus in the lipoids, (*c*) the percentage of cholesterol in the lipoids, and (*d*) the melting point of the cholesterol: calf thymus (*a* 5·69, *b* 2·29, *c* 9·40, *d* 148°), sheep thyroid (*a* 8·79, *b* 1·81, *c* 2·00, *d* 145°), calf lung (*a* 8·33, *b* 1·90, *c* 13·10, *d* 148°), pig liver (*a* 14·03, *b* 3·82, *c* 3·85, *d* 145·5°), calf pancreas (*a* 34·40, *b* 1·55, *c* 12·50, *d* 146°), calf spleen (*a* 13·38, *b* 3·17, *c* 14·70, *d* 147°), sheep kidney (*a* 6·18, *b* 2·75, *c* 13·5, *d* 145·5°), sheep suprarenal capsules (*a* 22·26, *b* 5·32, *c* 3·00, *d* 145·5°), bull prostate gland (*a* 13·09, *b* 1·58, *c* 4·50, *d* 144°), cow ovary (*a* 6·56, *b* 2·18, *c* 6·50, *d* 143°).

The lipoids were in most cases solid, and bright yellow or yellowish-brown, with the exception of those from the liver, which were black, whilst those from the suprarenal capsules darkened rapidly in air. The cholesterol is identical with that of biliary calculi. All the lipoids contained oxycholesterol, as indicated by Lifschütz (Abstr., 1909, ii, 77). Further, the cholesterols extracted gave rise to this product on exposure to light and air. T. A. H.

The Depressor Action of the Suprarenals. J. STUDZINSKI (*Arch. exp. Path. Pharm.*, 1911, **65**, 155).—The depressor substance in extracts of suprarenal tissue is not choline, but Popielski's vasodilatin. W. D. H.

Monoamino-acids of the Whalebone of the North Whale. EMIL ABDERHALDEN and BERNHARD LANDAU (*Zeitsch. physiol. Chem.*, 1911, **71**, 455—466).—The material contained 13·3% water, 1·03% ash, and 15·47% nitrogen. Other analytical details, especially in relation to the effect of hydrolysis and yield of monoamino-acids in various extracts are given at length. W. D. H.

Mineral Composition of the Bee. FRÉDÉRIC ARONSSOHN (*Compt. rend.*, 1911, **152**, 1183—1184).—The insects dried at 100—110° yielded 4·23% of ash containing the following elements: S 1·413%, Cl 0·294%, I 0·0009%, P 0·953%, As 0·0000015%, Si 0·034%, Cu 0·006%, Fe 0·015%, Mn 0·002%, Zn 0·012%, Al 0·010%, Ca 0·056%, Mg 0·099%, K 0·025%, Na 0·049%, Fluorine doubtful. W. O. W.

The Composition of the Material Spun by Oeceticus platensis. EMIL ABDERHALDEN and BERNHARD LANDAU (*Zeitsch. physiol. Chem.*, 1911, **71**, 443—448).—This South American animal (family *Psychidae*) builds a house with small pieces of wood, united by a web which it secretes. In order to see if this resembles silk, the monoamino-acids which result from hydrolysis were estimated; 100 grams of ash-free material gave glycine 27·1; alanine 18·8, leucine 0·75; aspartic acid 0·25; glutamic acid 2·35; phenylalanine 1·8, and proline 3·2 grams; tyrosine was absent. The material contains 12·56% of nitrogen, and 17·4% of ash. W. D. H.

The Partition of Bromine in the Organism after the Administration of Inorganic and Organic Bromine Preparations. ALEXANDER ELLINGER and YASHIRO KOTAKE (*Arch. exp. Path. Pharm.*, 1911, **65**, 87—119).—After giving sodium bromide, the results obtained confirm those of Nencki and Schumow-Simanowski. Most bromine is found in those parts which are normally richest in chlorine. Very much the same follows the administration of ethyl dibromophenylpropionate. A small part of the bromine in the urine, however, is in organic combination. Some is excreted by the intestinal mucous membrane and is found in the fæces. "Sabromin" in similar doses leads to a much smaller amount of bromine in the blood, and damages the kidneys. It is well absorbed, the chief bromine depôts being the subcutaneous tissue and liver, which is not the case with the other two compounds investigated; the urine contains very little organically united bromine, and the brain practically none. The solubility of organic bromine compounds in lipoids gives no clue to their partition in the body. W. D. H.

Colloido-chemical Analysis of Absorption and Secretion Processes. Absorption from the Peritoneal Cavity. Martin H. Fischer (*Koll-chem. Beihefte*, 1911, **2**, 304—342. Compare this vol., ii, 309).—Experiments are described, in which the author has compared the quantities of liquid absorbed from the peritoneal cavity in a given time after the injection of water, aqueous solutions of methyl and ethyl alcohol, carbamide, glycerol, sucrose, dextrose, and various salts of the alkali and alkaline earth metals. It is found that the absorption phenomena are very closely similar to those which are exhibited in the absorption of water by emulsion colloids.

In reference to these data and the results obtained by other observers, the author discusses the processes of absorption and secretion by functional cells from the colloido-chemical point of view. According to the view put forward, the selective character of the absorption and secretion of dissolved substances is determined by the distribution of the dissolved substances between the three phases, water, secreting and absorbing tissue, blood. The phenomena, which are determined by the tendency towards equilibrium in this system, are in all respects analogous to those which are found in the unequal distribution of a soluble substance between water, a solid, and a liquid colloid. H. M. D.

Variation in the Composition of Cows' Milk with Advance of Lactation. Charles Crowther and Arthur G. Ruston (*Trans. Highland and Agric. Soc. Scotl.*, 1911, [v], **23**, 93—102).—Fortnightly analyses of the milk of each cow of the herd at the Experiment Farm of Leeds University during two years. The records include thirty-three periods of lactation (26 cows).

Whilst the results show that the composition of milk with advance of lactation may differ greatly with different cows, they indicate that, in general, the milk is richest in total solids, fat, and proteins during the earliest and latest periods of lactation, and poorest in these constituents about the second or third month. The sugar content tends to decrease steadily with advance of lactation after the first month or so, whilst the ash remains approximately constant. N. H. J. M.

Effect of Food Deficient in Calcium and Phosphoric Acid on the Secretion of Milk. Gustav Fingerling (*Landw. Versuchs-Stat.*, 1911, **75**, 1—52).—When milk-producing animals receive insufficient calcium and phosphorus for maintenance and for milk production, these substances are for some time provided by the organism without diminishing the activity of the milk glands. As time goes on the milk secretion and the amounts of calcium and phosphoric acid in the milk will fall off. The production of milk will, however, gradually increase as soon as sufficient amounts of the two substances are supplied in the food.

The percentages of calcium and phosphorus in milk are only slightly affected by the deficient feeding, and tend to increase rather than diminish. N. H. J. M.

The Work of Concentration of the Kidneys. L. Lichtwitz (*Arch. exp. Path. Pharm.*, 1911, **65**, 128—154).—In a case of diabetes insipidus it was found that the power of the kidney to concentrate the chlorine ion was destroyed. The power to concentrate chlorine and sugar is independent of that of the other substances investigated. There is, however, a correspondence between concentration of nitrogen and phosphoric acid, and of purine bases. The action of diuretics on the chlorine curve was investigated, but there is no similar effect of such drugs (except calomel) in the curve of nitrogen and phosphoric acid. The warming of the neighbourhood of the kidney is also a factor of importance. W. D. H.

Osmotic Work of the Kidneys. XII. Iodide, Nitrate, Sulphate, and Phosphate are Execreted in the Urinary Tubules. Ernst Frey (*Pflüger's Archiv*, 1911, **139**, 512—531).—Sodium chloride is regarded as the only salt which is separable easily from the blood into the urine by filtration; the bromide behaves in the same way. These salts are also considered to be re-absorbed in the tubules. Iodides, sulphates, and phosphates are separated by secretion only; in the separation of nitrates both processes are concerned. None of these salts is re-absorbed. W. D. H.

Urinary Acidity. Emil von Skramlik (*Zeitsch. physiol. Chem.*, 1911, **71**, 290—310).—The titration acidity, and the electro-chemical acidity of urine are influenced in the same direction by diet, both being highest on a meat diet. W. D. H.

Commencement and Duration of the Excretion of Arsenic in Urine after the Use of Ehrlich-Hata's Preparation, Dihydroxydiaminoarsenobenzene. Karl Greven (*Chem. Zentr.*, 1910, ii, 1764—1765; from *Münch. med. Woch.*, 1910, **57**, 2079—2080).—When the preparation is injected subcutaneously, the excretion of arsenic is more rapidly completed than in the case of intramuscular injections. The simultaneous administration of potassium iodide apparently shortens the duration of the excretion, whilst in the case of mercury the duration appears to be increased. F. B.

The Property of Urine of Reducing the Blood Pressure. L. Popielski (*Chem. Zentr.*, 1910, ii, 1763; from *Zentr. Physiol.*, 1910, **24**, 635—639).—The substance described as vasodilatin (Abstr., 1909, ii, 593) is produced by every injurious influence on the morphotic elements of the blood. A decrease of blood pressure appearing after the introduction of any substance is not necessarily due to the direct action of the substance, but may be caused by the vasodilatin, produced by the injury of the morphotic elements. The lowering of the blood pressure by urohypotensin (Abelous and Bardier, *Chem. Zentr.*, 1910, i, 673) is due to the presence of a substance having hæmolytic properties, which would be better termed urohæmolysin. F. B.

Chylous and Pseudo-chylous Ascites. R. L. MACKENZIE WALLIS and HAROLD A. SCHÖLBERG (*Quart. J. Med.*, 1911, 4, 153—204. Compare Abstr., 1910, ii, 635).—As the result of the examination of two additional cases of pseudo-chylous ascites the conclusions formerly stated are confirmed. A scheme of procedure is given for distinguishing between chylous and pseudo-chylous ascites by chemical and physical methods, as well as an historical summary of all known cases of this nature. R. V. S.

The Breakdown of Fatty Acids in Diabetes Mellitus. JULIUS BAER and LÉON BLUM (*Arch. exp. Path. Pharm.*, 1911, 65, 33—34. Compare Abstr., 1910, ii, 227).—Corrections in two of the curves given in the authors' previous paper. W. D. H.

Protein Metabolism in Phloridzin Diabetes. CHARLES G. L. WOLF and EMIL OSTERBERG (*Amer. J. Physiol.*, 1911, 28, 71—80).—In phloridzinised dogs, creatinine increases in the urine, but not in proportion to the catabolism of protein. The processes giving rise to the acetone group are distinct from these, and there is also no relationship between total sulphur metabolism and acetone compounds, or creatine. W. D. H.

The Action of Chemical Substances on Sugar Excretion and on Acidosis. III. JULIUS BAER and LÉON BLUM (*Arch. exp. Path. Pharm.*, 1911, 65, 1—33).—In phloridzinised dogs the administration of glutaric acid decreases the output of sugar, nitrogen, and the substances which lead to acidosis. The same property is present in a whole series of normal dicarboxylic acids, in which the number of carbon atoms varies from five to eight. The action is not changed by the substitution of $CH{\cdot}OH$-groups for CH_2-groups. The action is present in incompletely hydroxylated acids, and in certain acids which may be changed into such hydroxy-acids. W. D. H.

Chemical Changes Produced in Milk by Bacteria and Their Relation to the Epidemic Diarrhœa of Infants. HAROLD A. SCHÖLBERG and R. L. MACKENZIE WALLIS (*Local Gov. Bd., Med. Officer's Rep.*, 1911, 504—543).—Incubation of milk for fifteen to twenty-four hours at 37° leads to the production of a peptone-like substance, although longer periods of incubation cause it to disappear again. During the summer months, peptones appear even in fresh samples of milk, the quantity of albumoses and peptones present depending on the age of the milk, and on the temperature to which it has been exposed. Investigations on the pancreas of infants show that both the peptone-like substance and the peptones have a toxic effect. The bacteriological results obtained indicate a connexion between the production of these substances and the quantitative and qualitative bacterial content. They are formed by a large number of different sporing and non-sporing varieties, and some of the organisms isolated produce a substance which can replace secretin in pancreatic digestion experiments. R. V. S.

Serological Studies with the Help of the Optical Method. XV. EMIL ABDERHALDEN and BENOMAR SCHILLING (*Zeitsch. physiol. Chem.*, 1911, **71**, 385—410).—Diphtheria toxin and antitoxin produce on admixture no alteration in rotatory power. But either added to a solution of silk peptone (or of the peptone produced by diphtheria bacilli) produces cleavage of the latter in different degrees. A mixture of toxin and antitoxin is inactive. The plasma and serum of a dog which has received an injection of diphtheria toxin possess the same property. Neither substance splits glycyl-*l*-tyrosine. Koch's tuberculin acts like the diphtheria products; so also does the serum from a horse with catarrhal pneumonia. W. D. H.

The Occurrence and Diagnostic Significance of a Peptolytic Enzyme in the Stomach Contents. L. KUTTNER and GEORG PULVERMACHER (*Chem. Zentr.*, 1911, i, 27—28; from *Berl. klin. Woch.*, **47**, 2057—2059).—The authors recommend the use of silk peptone instead of glycyltryptophan for the detection of peptolytic enzymes in the stomach contents.

The gastric juice (5 c.c.), mixed with 5 c.c. of an aqueous solution containing 5 grams of sodium carbonate and 25 c.c. of chloroform, is treated with 2 c.c. of a 20% solution of silk peptone and kept for twenty-four hours at 37°. The mixture is boiled, filtered, and the filtrate concentrated and allowed to remain in ice. The presence of a peptolytic enzyme is shown by the separation of tyrosine. The presence of blood has no influence on the reaction. The test is not a specific sign of gastric carcinoma. F. B.

Ionic Action of the Phosphoric Acids. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1911, **32**, 243—265).—In comparing the physiological action of salts of the different phosphoric acids, and also of organic phosphoric acids, the number of anions and cations present in the solutions must be taken into account. This may be done approximately by employing equivalent and not equimolecular solutions.

The action of orthophosphates is the same qualitatively as that of pyrophosphates, but smaller effects are produced by the former.

The alkali, formed by hydrolysis of the salts in solution, plays a considerable part in the effect produced by intravenous injections of the tetra-, tri-, and to some extent the di-sodium pyrophosphates, which is, however, readily distinguished from the effect produced by the salt.

In subcutaneous injections of pyrophosphate the toxic action is produced by disproportionately large doses.

There is no difference between pyro- and ortho-phosphates when administered *per os*, since the former are transformed into the latter by the gastric juice. The toxicity of metaphosphates, and of glycero- and inositol-phosphates is ascribed to the cations.

In the case of glycerophosphates the whole of the injection is found in the urine within twenty-four hours of the injection, and is almost entirely present as a salt of free phosphoric acid.

Glycerophosphoric acid is not a constituent of normal urine.

W. J. Y.

Inhibition of Transudation and Exudation by Calcium Salts.

Richard Chiari and Hans Januschke (*Arch. exp. Path. Pharm.*, 1911, **65**, 120—127).—The intravenous or subcutaneous injection of calcium salts, especially the chloride (the lactate coming next), either completely or partly inhibits the effusion of pleural fluid which occurs in dogs and rabbits as the result of the administration of sodium iodide, thiosinamine, or diphtheria-toxin; it acts similarly on the inflammatory œdema produced in the eye by the instillation of abrinine or allyl thiocarbimide. This action is not related to the effect of calcium salts on blood-clotting. Calcium treatment in such conditions in man is recommended. W. D. H.

The Behaviour of Gluconic and Saccharic Acids in the Organism.

Eduard Schott (*Arch. exp. Path. Pharm.*, 1911, **65**, 35—37).—P. Mayer (*Zeitsch. klin. Med.*, **47**, 87) stated that in rabbits, gluconic acid given subcutaneously was, in part, excreted in the urine as such, and in part as saccharic acid. Baer and Blum found in diabetic dogs no saccharic acid when gluconic acid was given. In view of a possible difference between herbivora and carnivora, Mayer's experiments on rabbits were repeated, and no saccharic acid was found in their urine. W. D. H.

Behaviour of α-Amino- and α-Ketonic Acids in Animals.

Franz Knoop and Ernst Kertess (*Zeitsch. physiol. Chem.*, 1911, **71**, 252—265. Compare Knoop, Abstr., 1910, ii, 880; also Embden and Schmitz, this vol., ii, 53).—A dog when fed with α-amino-γ-phenylbutyric acid yielded in the urine the *l*-modification of this acid, $[\alpha]_D -29\cdot55°$, the acetyl derivative of the acid, $[\alpha]_D +20°$, and *d*-α-hydroxy-γ-phenylbutyric acid, $[\alpha]_D +12\cdot94°$. In addition, hippuric acid was formed, indicating degradation of the amino-acid through the ketonic acid to the next lower fatty acid.

When fed with the α-ketonic acid the products were *d*-α-hydroxy-γ-phenylbutyric acid, acetylaminophenylbutyric acid, and hippuric acid.

The formation of the same hydroxy-acid in both instances and in larger quantity from the ketonic acid is confirmatory of the conversion of the amino- into the ketonic acid in the animal. The acetylamino-acid is also in each instance derived from a probably inactive intermediate compound, and not by direct acetylation (see also Neubauer and Warburg, this vol., ii, 53). E. F. A.

Pharmacological and Chemo-therapeutic Studies in the Toluidine Series.

Hermann Hildebrandt (*Arch. exp. Path. Pharm.*, 1911, **65**, 59—86).—The author has shown previously that dimethyl-*o*-toluidine is hæmolytic, and blood pigment passes into the urine of rabbits treated with it. Others have shown a similar action is possessed by other members of the series; the present research continues this work. The bromine derivative, *p*-bromodimethyl-*o*-toluidine, is less toxic; the dibromo-derivative is still less hæmolytic. Dimethyl-*p*-toluidine is as strong a hæmolytic as the ortho-compound. Comparisons were made between these and other hæmolysins, and researches on immunity instituted. The rôle of cholesterol as an anti-hæmolysin is discussed, so also are the relationships between the pharmacological reactions and the chemical constitution of these substances. W. D. H.

The [Physiological] Action of Phenolphthalein. FRITZ C. KOEHLER (*Chem. Zentr.*, 1911, i, 579; from *Schweiz. Woch. Chem. Pharm.*, 1910, **48**, 802).—Phenolphthalein has no action on the intestine when the contents of the latter are acid. The action apparently occurs only when the intestinal contents have an alkaline reaction. F. B.

Chemical Constitution and Physiological Action. WOLFGANG HEUBNER (*Verh. Ges. deut. Naturforsch. Aerzte.*, 1911, **11**, 466—469).—It was observed that whereas phenacetin converts hæmoglobin into methæmoglobin, the same result was not produced by the di-*o*-dimethyl derivative. A systematic investigation was therefore undertaken with various benzene derivatives to determine the particular grouping to which the methæmoglobin-forming property is due. It was found that quinol, catechol, and pyrogallol possess the property, whereas resorcinol and phloroglucinol do not. The former substances can be converted into quinone, and as this substance readily converts hæmoglobin into methæmoglobin, it is assumed that those benzene derivatives which oxidise to quinone are methæmoglobin producers. With hæmoglobin in absence of oxygen, methæmoglobin is not formed with these, although this happens with quinone itself; in fact, the latter substance acts more readily on hæmoglobin than on reduced hæmoglobin. The reaction between quinone and methæmoglobin is a molecular one. In presence of oxygen, less than molecular quantities produce the effect, the quinone-forming substance acting in this case catalytically. The difference between the action of methæmoglobin-formers *in vitro* and in the animal were also investigated; *in vitro* the actions on blood of different animals are similar, but differences are observed in animals. This is ascribed to the difference in the metabolism of the injected quinone formers. The results do not explain the differences between phenacetin and its dimethyl derivative, or between various other chloro-substituted anilines which were investigated. S. B. S.

Elimination of Colouring Matters by the Animal Organism. PAUL SISLEY and CHARLES PORCHER (*Compt. rend.*, 1911, **152**, 1062—1064).—Ingestion *per os* of Orange I by dogs is followed in forty-eight hours by the appearance of aniline-*p*-sulphonic acid and 4-amino-α-naphthol in the urine. Crystalline Ponceau and chrysoidine behave in a similar manner. The fact that reduction products do not appear in the urine when these dyes are injected subcutaneously, points to reduction in the former case having taken place in the alimentary canal, probably through the agency of bacteria. Urine decolorises Ponceau with production of α-naphthylamine, but if previously sterilised this reaction does not occur. W. O. W.

Comparative Action of Strophantin and Digitoxin on the Toad's Heart. L. RODOLICO (*Chem. Zentr.*, 1911, i, 246; from *Arch. Farm. sperim.*, 1910, **10**, 233—244).—The action of digitoxin is not identical with that of strophantin. Small doses of the latter produce a vigorous systole, the heart remaining in a state of half contraction. Digitoxin, even after repeated injection, does not have the same action. Strophantin, in doses of 0·12 mg. and less, brings about systolic stoppage; this never occurs with digitoxin.

F. B.

I. The [Physiological] Action of Homocholine. II. The Glycine in Crab Extract. ERNST BERLIN (*Chem. Zentr.*, 1910, ii, 1766; from *Zentr. Physiol.*, 1910, **24**, 587—589).—I. Intravenous injection of small doses of synthetic γ-homocholine in cats causes a strong diminution of the blood-pressure; larger doses also produce a great increase in the salivary and lachrymal secretions, and finally death through stoppage of respiration. In frogs, the heart's rate is diminished. Choline hydrochloride has a similar action.

II. The glycine present in the fraction of crab extract not precipitated by phosphotungstic acid is converted by exhaustive methylation into betaine, and was isolated as such in considerable quantity.

F. B.

Certain Physical and Physiological Properties of Stovaine and its Homologues. VICTOR H. VELEY and W. L. SYMES (*Proc. Roy. Soc.*, 1911, **83** *B*, 413—420).—The substances employed in the experiments were stovaine and its methyl, ethyl, amyl, phenyl, and benzyl homologues, as well as a new salt prepared by Fourneau, namely, propyl dimethylaminobenzoyloxy*iso*butyrate, which may be regarded as intermediate in chemical structure between cocaine hydrochloride and stovaine, but differs from these in that it gives an acid reaction.

The densities of these derivatives show a decrease in each series with increase of molecular weight, but this decrease does not vary uniformly with each CH_2 group added to the molecule.

On the central nervous system and on the circulation, Fourneau's salt is less active, and methylstovaine no more active than stovaine. Amylstovaine is less active on the central nervous system, whilst it produces a somewhat greater depression of blood pressure, which is, however, more gradual in onset.

W. J. Y.

The Action of Morphine and Opium Preparations (Pantopon) on the Digestive Canal. OTTO COHNHEIM and GEORG MODRAKOWSKI (*Zeitsch. physiol. Chem.*, 1911, **71**, 273—289).—In dogs morphine and opium cause no delay in the emptying of the stomach, but inhibit the secretion of gastric juice. In the case of morphine, an abundant spontaneous flow of the juice occurs some hours later, and this is still greater if all the opium alkaloids are given. The amount of pancreatic juice is lessened. The constipation produced is believed to be partly due to the smaller quantity of fluid secreted.

W. D. H.

[Physiological] Action of Chloromorphides. ERICH HARNACK and HERMANN HILDEBRANDT (*Arch. exp. Path. Pharm.*, 1911, **65**, 38—53).—Care should be taken that commercial *apo*morphine should be free from chloromorphides. Chloromorphides act on animals (cold and warm blooded) very like acetyl derivatives of morphine, causing paralysis and reflex tetanus, and are much more toxic than morphine. The α- is more powerful than the β-base. They are not emetics, but anti-emetics. W. D. H.

[Physiological Action of] Thebaine, Morphothebaine, Thebenine, and Some of their Derivatives. Hermann Hildebrandt (*Arch. exp. Path. Pharm.*, 1911, **65**, 54—58).—In dogs, thebaine in certain doses antagonises the emetic action of *apo*morphine. The action of morphothebaine is much weaker. Thebaine is readily converted into thebenine, a phenanthrene derivative with an open-chain containing nitrogen, and in this and similar derivatives there is no anti-emetic action. W. D. H.

Physiological Action of Aromatic Mercury Compounds. I. Ferdinand Blumenthal (*Biochem. Zeitsch.*, 1911, **32**, 59—73).—Numerous experiments on animals were carried out with the sodium salt of diaminodiphenylmercuridicarboxylic acid, $Hg[C_6H_3(NH_2)\cdot CO_2Na]_2$. Animals and rabbits were chiefly employed. The latter, when of 2½ kilos. weight, could tolerate doses of 1 gram of the drug when administered subcutaneously. Mercury is in this form, therefore, about 30 times less toxic than in the form of sublimate. *In vitro* experiments show that the substance has powerful bactericidal and also spirochetocidal properties. S. B. S.

The Increase of the Toxic Action of Potassium Chloride by Low Concentrations of Sodium Chloride. Jacques Loeb and Hardolph Wasteneys (*Biochem. Zeitsch.*, 1911, **32**, 155—163).—The addition of sodium chloride to potassium chloride increases the toxic action of the latter on *Fundulus* when less than 8 or 10 mols. of sodium salt to one of potassium salt are present. If the proportion is increased, however, to 15 mols., the toxic action, as shown in the previous communication (this vol., ii, 420), is diminished. The action is due to the sodium ions, as shown, when sodium sulphate is substituted for the chloride. Concentrations of sodium chloride which increase the toxic action of the potassium salts are themselves non-toxic, and the fish can exist in them for an indefinite length of time.
S. B. S.

Chemical Changes in Phosphorus Livers. Julius Wohlgemuth (*Biochem. Zeitsch.*, 1911, **32**, 172).—The author claims priority for the discovery that the phosphorus-containing nucleoproteins resist destruction more than the other phosphorus-free proteins (compare Slowtzoff, this vol., ii, 315). S. B. S.

The Antagonistic Action of Cholesterol to the Glucosidic Heart Poisons as Determined by Investigations on the Isolated Frog's Heart. Theodor Karaúlow (*Biochem. Zeitsch.*, 1911, **32**, 145—154).—In view of the observation by Windaus, that digitonin combines with cholesterol, and is presumably therefore rendered non-toxic, the effect of cholesterol on the toxic action of various glucosides when perfused in Ringer's solution through the isolated frog's heart was investigated. It is found that the cholesterol acts antagonistically only to the true saponins, such as digitonin, but has no de-intoxicating action on the true heart poisons, such as strophanthin, antiarin, digitalein. Helleborein occupies an intermediate position, in that it is only partly deprived of its toxic action by cholesterol. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Pigments as Product of Oxidation by Bacterial Action. MARTINUS W. BEYERINCK (*Proc. K. Akad. Wetensch.* 1911, **13**, 1066—1077).—The oxidation of quinic acid to protocatechuic acid is brought about by numerous species of bacteria, and the action can be readily demonstrated by the addition to the medium of ferric salts. *Micrococcus calco-aceticus* and *B. fluorescens non liquefaciens* possess this faculty in a high degree. The oxidation of quercitol to pyrogallol is only caused by certain varieties of *Pseudomonas aromatica*, which can be isolated from spontaneously infected ("aromatic") green malt extract and aromatic milk. Melanine can be formed from tyrosine by certain vibrios isolated from sea-water and sewage (*Microspira tyrosinatica*). A vinegar bacterium (*Acetobacter melanogenum*) can produce a caramel-like substance from peptone. The oxidation function does not appear to be a constant property of bacteria, as organisms which are similar in all other respects differ from one another in their capacity for producing pigments. S. B. S.

Phenomena of Fermentation are Actions of Digestion. Study of Denitrification in the Vegetable Kingdom. PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1911, **25**, 289—312).—The reduction of nitrates does not modify the nature of the fermentations produced by denitrifying microbes. Denitrification by anærobic ferments which produce hydrogen may take place without the formation of intermediate products. Hydrogen is the chemical agent employed by anærobic microbes in assimilating the nitrogen of nitrates, the sulphur of sulphuric acid, and possibly the phosphorus of phosphates. The most active denitrifying organisms may be considered as those which are best adapted for assimilating nitric acid.

The higher plants reduce nitrates with formation of nitrous acid and of gaseous derivatives of nitrous acid under some conditions. In 0·1% solutions of potassium nitrite, higher plants give rise to liberation of oxygen in absence of light. Higher plants develop normally when supplied with nitrites as the only source of nitrogen.

N. H. J. M.

The Germicidal Action of Arsenic and Antimony Compounds on Bacillus typhosus. GILBERT T. MORGAN and E. ASHLEY COOPER (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 365—366).—The germicidal action of atoxyl and its derivatives on *Bacillus typhosus*, as determined by the Rideal-Walker test, is very slight, as is that of potassium arsenate and potassium dicamphorylarsinate. The much greater activity of di-iodomethylarsinic acid is due to the presence of iodine. Potassium arsenite is more active than phenol. Triphenylantimony hydroxynitrate is very active. The high germicidal action of compounds of tervalent arsenic may be due to the formation of additive compounds with proteins. C. H. D.

Extraction of Zymase. ALEXANDER VON LEBEDEFF (*Compt. rend.*, 1911, **152**, 1129. Compare this vol., i, 248).—The observations of Kayser (this vol., i, 421) are confirmed by the author in a communication to be published shortly. W. O. W.

Amount of Glycogen in Differently-fed Yeast Cultures. WILHELM HENNEBERG (*Bied. Zentr.*, 1911, **40**, 277—278; from *Zeitsch. Spiritusind.*, 1910, **33**, 242).—Glycogen may occur both in abnormal and normal yeast. It is also stored up in pure sugar solutions and under conditions of insufficient, exclusive nutrition, so that its presence is no indication either of normal yeast or of the normal composition of the nutritive solution.

The production of peptone under some conditions is hindered by poisonous substances, such as organic ammonium salts; ammonium sulphate and, under some conditions, calcium sulphate are very unfavourable.

Yeast cells containing more than about 53% of protein usually contain no glycogen or very little. It is therefore very probable that yeast cells in potato mashes, concentrated mashes, and worts will not, as a rule, accumulate much glycogen. N. H. J. M.

The Influence of Arsenates and Arsenites on the Fermentation of the Sugars by Yeast Juice. ARTHUR HARDEN and WILLIAM J. YOUNG (*Proc. Roy. Soc.*, 1911, **83** *B*, 451).—The addition of sodium or potassium arsenate to a mixture of yeast juice and sugar produces a large acceleration in the rate of fermentation. This enhanced rate differs from that produced by phosphate, in that it continues long after a chemical equivalent of carbon dioxide has been evolved, whilst the arsenate is found in the free state throughout the fermentation. As in the case of phosphate, there is a certain optimum concentration of arsenate, corresponding with which there is a maximum rate of fermentation.

The total fermentation produced depends on the concentration of arsenate employed, and may be either higher or lower than that given in the absence of arsenate.

The dextrose and mannose are similarly affected by yeast juice in presence of arsenate, whilst lævulose differs from these two sugars in that it is much more rapidly fermented, and the optimum concentration of arsenate is much higher. This acceleration produced by arsenate is due to an increase in the rate of hydrolysis of the hexosephosphate of the juice by the enzyme, hexosephosphatase, resulting in an increased supply of phosphate. The action of arsenate is therefore essentially different from that of phosphate, and it has been found that it cannot replace phosphate in the fundamental reaction of alcoholic fermentation.

The rate of auto-fermentation of yeast juice and that of the fermentation of glycogen are considerably increased by the addition of arsenates, and this is mainly due to an acceleration in the rate of action of the diastatic enzyme of yeast juice, whereby a greater supply of sugar is afforded.

Arsenites produce a similar effect to arsenates, but in a much less marked degree.

A total inhibition of fermentation is produced by large concentrations of either arsenates or arsenites. W. J. Y.

Fermentations with Yeast in the Absence of Sugar. II. CARL NEUBERG and L. TIR (*Biochem. Zeitsch.*, 1911, **32**, 323—331).—Yeast has been found to evolve carbon dioxide in the presence of solutions of salts of the following acids: formic, acetic, butyric, glyoxylic, lactic, pyruvic, *l*-β-hydroxybutyric, malic, *d*-*l*-glyceric, *d*-gluconic, methylsuccinic, oxalic, maleic, fumaric, succinic, *d*-tartaric, *d*-saccharic, tricarballylic, aconitic, citric, aspartic, glycerophosphoric, and oxalacetic, and also in the presence of *dl*-alanine, silk peptone, and lecithin.

Since the same effect is produced with these substances by zymin and hefanol in the presence of toluene, the phenomenon is considered as separable from the life of the cell, and as bound up with the process of respiration, of which alcoholic fermentation is probably a special instance. W. J. Y.

The Transformation of Amino-acids into Hydroxy-acids by Moulds. FELIX EHRLICH and K. A. JACOBSEN (*Ber.*, 1911, **44**, 888—897).—The authors have examined the action of a large number of yeasts, moulds, and allied organisms on amino-acids, and find that the majority of the yeasts and even organisms which are only remotely related to them possess the power of fermenting amino-acids, in the presence of sugar with the formation of alcohols. Thus *p*-hydroxyphenylethanol is produced by the fermentation of tyrosine with *Dematium pullulans* (compare Ehrlich, this vol., i, 127).

The nature of the products obtained in the fermentation of amino-acids by moulds varies accordingly as the action proceeds in the presence or absence of carbohydrates. In the latter case, a more or less complete degradation of the amino-acid molecule takes place. A similar degradation also occurs with some moulds during fermentation in the presence of sugars, whilst in other cases the greater part of the molecule remains intact.

The fermentation of amino-acids with *Oidium lactis* in the presence of dextrose, invert sugar or lactose, and of nutritive salts gives rise to the formation of hydroxy-acids in almost quantitative yields, and this therefore furnishes a very convenient method for the preparation of hydroxy-acids in the optically-active form.

d-*a-Hydroxy-β-*p-*hydroxyphenylpropionic acid,*

$$OH\cdot C_6H_4\cdot CH_2\cdot CH(OH)\cdot CO_2H,$$

is obtained together with a small quantity of *p*-hydroxyphenylethanol by the fermentation of *l*-tyrosine with *Oidium lactis* in the presence of invert sugar. It crystallises in long, colourless, silky needles, m. p. 169°, $[\alpha]_D^{20}$ + 18·4°. The corresponding *l*-acid was obtained by Kotake (Abstr., 1910, i, 384) from the urine of dogs suffering from phosphorus poisoning, so that this is the first example of the formation of enantiomorphously related isomerides from one and the same optically active substance by the plant and animal organism respectively.

The fermentation of *d-l*-phenylalanine similarly yields *d*-*α*-hydroxy-*β*-phenylpropionic acid (McKenzie and Wren, Trans., 1910, **97**, 1355), together with small quantities of phenylethanol and *α*-hydroxy-*β*-*p*-hydroxyphenylpropionic acid, the formation of the last-named substance being due to autolysis of the mould with the formation of tyrosine, which is then transformed into the corresponding hydroxy-acid.

l-*a-Hydroxy-β-3-indolepropionic* (l-*indolelactic*) *acid,*

$$C_8H_6N\cdot CH_2\cdot CH(OH)\cdot CO_2H,$$

obtained in a similar manner by the fermentation of *l*-tryptophan, crystallises in felted, silky needles, m. p. 99°, $[\alpha]_D^{20}$ − 5·34°. It gives a yellow precipitate with mercuric sulphate, a brownish-red coloration with Millon's reagent, and a flocculent precipitate with bromine water. With dimethylaminobenzaldehyde and strong sulphuric acid it develops a bluish-green coloration. Aqueous solutions of the acid on evaporation become reddish-violet in colour.

In some cases the fermentation of amino-acids by moulds results in the formation both of the corresponding hydroxy-acid and an alcohol. Thus in the fermentation of tyrosine by *Monilia candida*, half the amino-acid is converted into a-hydroxy-*β*-*p*-hydroxyphenylpropionic acid, the remainder being transformed into tyrosol (*p*-hydroxyphenylethyl alcohol).

In view of the ease with which the fermentation of amino-acids by *Oidium lactis* and other moulds occurs, the authors consider that hydroxy-acids are far more widely distributed in nature than has hitherto been imagined. The aroma of many kinds of cheese would appear to be due to the presence of hydroxy-acids, either free or in the form of derivatives, produced by the combined action of *Oidium lactis* and *Penicillium.* F. B.

The Biochemical Aspect of Carbon Dioxide Assimilation in Green Plants. Viktor Grafe (*Biochem. Zeitsch.*, 1911, **32**, 114—129).—The action of formaldehyde on green plants (*Phaseolus vulgaris*) was investigated by exposing them in pots to the action of formaldehyde vapour under glass shades. The vapour was obtained from pure formaldehyde solutions of known strength and quantity in open basins, and control experiments were made under similar bell-jars with the same quantities of formaldehyde solution, under which no plants were exposed. The formaldehyde left in the vessel after exposure was estimated by Romyn's method. By this means it was found that plants can tolerate formaldehyde vapour to a much greater extent than was formerly believed, and that the formaldehyde was used up by the plants (in maximum, 1 mg. per plant). The amount of formaldehyde which could be tolerated without injury from May to December was found to be about half as small as that which could be tolerated between December and March. The action takes place in presence of chlorophyll and light, for if an etiolated plant is exposed to formaldehyde vapour in quantities which are not injurious to a green plant, and then exposed to light, it shows the symptoms of formaldehyde intoxication. The chlorophyll appears to exert a protective influence against formaldehyde poisoning. The plants exposed to the aldehyde contain more reducing sugar than control plants grown under similar conditions without the aldehyde, but do not contain more starch; in fact, experiments showed that formaldehyde is injurious to the amylase, which is supposed to be the agent concerned in the synthesis of starch from sugar. S. B. S.

Behaviour of Organic and Inorganic Substances in Vegetable Organisms. I. ETTORE VASSALLO (*Gazzetta*, 1911, **41**, i, 342—352).—The author has devised an apparatus for the rapid administration of substances in solution to the roots of plants. By its means as much as 121·3 c.c. of 0·5% sodium chloride solution were absorbed by a plant in forty-eight hours. Robust roots are found to withstand a pressure exceeding 80 cm. of mercury. T. H. P.

Action of Methyl and Other Alcohols on Green Plants and Micro-organisms. THOMAS BOKORNY (*Centr. Bakt. Par.*, 1911, ii, **30**, 53—64).—Phenols are in general less favourable than true alcohols of the fatty series.

Methyl alcohol is suitable as a source of carbon for several bacteria, and is utilised by algæ and flowering plants. Peas and beans grown in water-cultures grew better in presence of 0·5—1·0% of methyl alcohol than without alcohol. Ethyl alcohol is utilised by bacteria, but not by higher plants. The higher monohydric alcohols are also not utilised by flowering plants.

Polyhydric alcohols of the fatty series, such as ethylene glycol, glycerol, and many carbohydrates, are mostly suitable as sources of carbon. N. H. J. M.

The Action of Useful and Harmful Stimulators on the Respiration of Living and Killed Plants. NICOLAUS IWANOFF (*Biochem. Zeitsch.*, 1911, **32**, 74—96).—Experiments were made on the influence of the addition of sodium phosphates on the respiratory processes of both living and killed plants, the material employed being chiefly wheat embryos and the stems of bean plants, which were investigated both in the living condition and after being killed either by acetone or submission to a low temperature. Estimations were made of the carbon dioxide which was evolved in an atmosphere of air in some cases, and in an atmosphere of hydrogen in others. Disodium phosphate stimulates the respiration in the case of wheat embryos both of the living and killed material, and also increases the respiratory quotients. In the case of bean plants, 1—2% solutions of phosphate exert no influence on the respiration of the living plant. In the case of the killed plant, however, the carbon dioxide output is increased 27% by 1% phosphate, and 62% by 2% phosphate. This takes place in an atmosphere of hydrogen, and is at the expense of the primary ærobic processes. Phosphate exerts no action in secondary oxidative processes (namely, after addition of a dextrose solution). Monopotassium phosphate inhibits respiration; the autolysis products of yeast increase it. The influence of quinine, sodium selenate, arbutin, and other substances on the respiratory processes was also investigated; most of these act deleteriously. S. B. S.

The Formation of Hordenine during the Germination of Barley. TORQUATO TORQUATI (*Chem. Zentr.*, 1911, i, 166; from *Arch. Farmacol. sperim.*, 1910, **10**, 62—71, 97—119).—The author has determined the hordenine content at five different stages in the germination of barley. The amount is greatest during the first four days, and then gradually diminishes.

Hordenine is not present in ungerminated barley, neither could it be detected during the germination of wheat, peas, and lupins.

A method for the estimation of hordenine is described. F. B.

Nitrate and Nitrite Assimilation. OSKAR BAUDISCH (*Ber.*, 1911, **44**, 1009—1013).—The author's experiments on nitrate and nitrite assimilation were guided by the idea that the nitrosyl group, $\colon N\cdot OH$ or $\colon N{<}^{O}_{H}$, would behave similarly to the aldehyde group, $\cdot C{<}^{O}_{H}$, in a physiological-chemical sense, since both groups are very reactive.

When a solution of potassium nitrite in a mixture of water and excess of methyl alcohol is exposed to diffused daylight or a mercury lamp, oxygen is split off from the nitrite molecule after a short time; the methyl alcohol is oxidised to formaldehyde, which combines with the $\colon N\cdot OK$-group, giving the salt of formhydroxamic acid, according to the equation: $CH_3\cdot OH + KNO_2 = OH\cdot CH\colon NOK + H_2O$. The formhydroxamic acid was isolated and identified. A solution of potassium nitrate acts similarly, being first reduced to nitrite. After exposure to the light the nitrite-methyl alcohol solution is strongly alkaline, and gives a precipitate of silver hyponitrite with silver nitrate. It also contains formaldehyde, so that "alkali-fission" of the hydroxamic acid has taken place according to the equation: $CHO\cdot NH\cdot OK = H\cdot COH + \colon N\cdot OK$ and $2\colon NOK = K_2N_2O_2$. On prolonged exposure to light both the nitrite and formhydroxamic acid disappear, the final products being ammonia or amines.

Ethyl alcohol gives similar results to methyl alcohol. With both alcohols there is no reaction in the dark, even at the boiling point.

Nitrates and nitrites are readily reduced by aldehydes under the influence of light; hydroxamic acids are intermediate products, but the reduction proceeds rapidly to ammonia or the amines. Probably in this case an "acid fission" takes place: $CHO·NH·OH + H_2O = H·CO_2H + NH_2·OH$. Light also brings about the reduction by carbohydrates, phenols, naphthols, and aldoximes. With lævulose, carbon monoxide is evolved; acetaldoxime gives acetamide.

A pure dilute aqueous solution of potassium nitrate is reduced to ammonia by prolonged exposure to the light from a mercury lamp.

From the above experiments the author draws the conclusion that the nitrate and nitrite assimilation in the green parts of plants is a photo-chemical process. T. S. P.

The Stimulative and Toxic Effects of Various Chromium Compounds on Plants. PAUL KOENIG (*Landw. Jahrb.*, 1910, **39**, 775—916).—A comprehensive study of the action of chromium on plant life; the action of chromium salts, dichromates, and chromates in varying concentrations, either alone or in conjunction with lime, phosphoric acid, and various salts, was observed on characteristic representatives of numerous natural orders, both in soil and water cultures; and the toxic and stimulative concentrations for each family recorded in tables. The results obtained by other workers, that the higher the degree of oxidation of chromium the more toxic its effect, were confirmed, a wheat plant being killed by a 0·0064% solution of sodium dichromate, whereas it required a 0·5% solution of chromium sulphate to give a similar result. The analysis of the soils and plants, with various methods of estimating their chromium content are described, whilst to ensure freedom from varying climatic influences the experiments were repeated several years in succession, and the mean results carefully noted. The red coloration given by sodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate in the presence of chromium was found to be satisfactory for the identification of traces of chromium in plant ash. F. M. G. M.

Investigation of Nitrogen Assimilation by Foliage Leaves. RICHARD OTTO and W. D. KOOPER (*Landw. Jahrb.*, 1910, **39**, 999—1004).—An account of experiments on the assimilation of atmospheric nitrogen by the foliage leaves of higher plants. Leaves of *Aesculus Hippocastanum* were picked in the mornings and evenings of sunny days at intervals covering a period of four months, carefully dried, and the nitrogen content of the morning and evening pickings estimated and compared.

The morning leaves were found invariably to contain slightly more nitrogen, from which it is considered extremely improbable that higher plants are capable of directly assimilating atmospheric nitrogen through their leaves. F. M. G. M.

The Aldehyde of Leaves. HARTWIG FRANZEN (*Verh. Ges. deut. Naturforsch. Aerzte*, 1911, 11, 35—37).—On steam distillation the fresh and finely macerated leaves of the hornbeam give a peculiarly smelling distillate containing an aldehydic compound (compare Reinke, Abstr., 1882, 243). The addition of *m*-nitrobenzhydrazide to the distillate gives a condensation product, which from alcohol or benzene forms slender, yellow needles, which sinter at 160°, and have m. p. 167—168°. Hydrolysis with sulphuric acid gives the free aldehyde as a colourless oil with a peculiar pungent odour, b. p. 47—48°/17 mm. The *hydrazone* prepared from the aldehyde by condensation with benzhydrazide forms colourless leaflets, m. p. 112—113°. Oxidation of the aldehyde with silver oxide by Délepine's method produced an acid of m. p. 32—33°, which was identified as Δ^{α}-hexenoic acid, $CH_3\cdot[CH_2]_2\cdot CH{:}CH\cdot CO_2H$. The aldehyde must therefore be *Δ^{α}-hexenoic aldehyde*, $C_5H_9\cdot COH$, and analyses of the above condensation products confirm this.

The same aldehyde was found to occur in the leaves of the maple, acacia, poplar, vine, chestnut, oak, eagle fern, elder, lupin, black alder, clover, walnut and hazel-nut. From the leaves of the horse-chestnut and the lime much smaller quantities of the aldehyde were obtained, but they were accompanied by another aldehyde which gave a hydrazone with *m*-nitrobenzhydrazide having the m. p. 237—238°.

From the above results the conclusion is drawn that Δ^{α}-hexenoic aldehyde occurs in all plants containing chlorophyll. It is very probable that it stands in genetic relation with glucose, as may be seen by comparing the formula $CH_3\cdot[CH_2]_2\cdot CH{:}CH\cdot COH$ and $OH\cdot CH_2\cdot[CH\cdot OH]_4\cdot COH$. T. S. P.

A Lipolytic Enzyme in Sweet Almonds. MARIO TONEGUTTI (*Chem. Zentr.*, 1911, i, 332; from *Staz. sperim. agrar. ital.*, 1910, **43**, 723—734).—Details of experiments are given, indicating the presence of a lipolytic enzyme in sweet almonds. F. B.

Occurrence of Sucrose in the Dry Roots of Certain Plants of the Aristolochiaceæ, and of a Glucoside Decomposed by Emulsin in those of Asarum europœum. M. LESUEUR (*J. Pharm. Chim.*, 1911, [vii], 3, 399—403).—Trials with invertase and emulsin on aqueous solutions of alcoholic extracts of the roots of *Aristolochia longa*, *A. Serpentaria*, and *Asarum europœum* showed that all three contained sucrose, whilst the third also contained a small quantity of a substance (glucoside ?) which was decomposed by emulsin. The quantity of sucrose present was small except in the first named. T. A. H.

Content and Distribution of Hydrogen Cyanide in the Bamboo. O. WALTER, T. KRASNOSELSKAYA, N. MAKSIMOFF, and W. MALSCHEWSKY (*Bull. Acad. Sci. St. Petersburg*, 1911, [vi], 397—426).—The authors have investigated the occurrence of hydrogen cyanide in different varieties of bamboo, using the Prussian-blue test and Guignard's picrate paper for detecting the acid, and titration with silver nitrate for estimating it. The general results deducible from the numerical data are as follows.

The young shoots of the bamboo contain, in their growing parts, hydrogen cyanide to the extent of 0·145% of their weight, or 1·5% of the dry weight. The distribution of the acid in the shoot is extremely irregular, very little occurring at the nodes or in the upper parts of the internodes, but a considerable quantity in the growing parts. In the initial state of development of the shoot, the bud situated on the root-stock contains a very large store of hydrogen cyanide, which is gradually transferred and consumed as growth proceeds. When the food-supply of the plant is restricted, the amount of the acid in the shoot diminishes considerably, but the diminution rarely occurs in the lower parts of the shoot. The grown-up parts of bamboos (the leaves and stem) are quite free from hydrogen cyanide, and the bamboo is hence distinguished as a special type of cyanogenetic plant.

Hydrogen cyanide occurs in the bamboo, not in the free state, but in the form of a very unstable compound, which is readily decomposed by boiling water, although not by boiling alcohol. T. H. P.

Composition of Bananas. KIYOHISA YOSHIMURA (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 406—411).—In order to ascertain what changes take place in the composition of bananas during the ripening of the fruit, the author made analyses of unripe bananas, and of the same at intervals after they had been stored in a warm room. The dry substance of the unripe fruit contained 68·16% of starch, but no sugar; after the lapse of three weeks, the fruit (dry substance) contained 14·48% of starch, 19·83% of invert sugar, and 49·95% of sucrose. These results, in conjunction with those obtained at the end of one week's and two weeks' storage respectively, show that the starch is first of all converted into sucrose, and that the latter is gradually inverted by the enzyme (invertin) present in the fruit, so that there is no definite ratio between the quantities of sucrose and invert sugar. The quantity of tannin in the dry substance (1·7%) remained constant during the ripening process. W. P. S.

Reversibility of the Enzymatic Action of Castor Oil Seeds. MORITZ KRAUSZ (*Zeitsch. angew. Chem.*, 1911, **24**, 829—831).—Olive oil is completely decomposed into fatty acids and glycerol by the action of the enzyme occurring in castor oil seeds, provided that the glycerol formed be removed from the mixture from time to time. The enzyme is also capable of forming glycerides from a mixture of fatty acids and glycerol; at the end of four days, a mixture consisting of 100 grams of oleic acid, 100 grams of glycerol, 80 c.c. of $N/10$-acetic acid, and 20 grams of the dry ferment was found to contain 11·1% of neutral oil having a saponification number of 180·3, and an iodine number of 88·4. This oil consisted of a mixture of mono-, di-, and tri-olein. W. P. S.

Caulerpa prolifera. HENRI MICHEELS (*Bull. Acad. Roy. Belg.*, 1911, 110—179).—This sea-weed simulates the higher plants in form, and possesses rhizoids (points of attachment), rhizome, and leaves, and has the peculiarity that when parts of it are detached from the plant they form new members.

The present paper gives the results of experiments designed to determine the influence of environment and certain physical conditions on the proliferation of detached leaves of the plant. Critical résumés are also given of the numerous papers, mostly from botanical journals, already published on the physiology of this plant. The experimental results are tabulated in detail in the original.

The chief results obtained are as follows: Proliferation does not take place at the expense of leaf tissue, but represents an actual gain in weight. The sea-water used at the Zoological Station at Naples, containing 42·986 to 43·939 grams of total solids per litre, is more favourable to proliferation than sea-water collected over one kilometre from the coast and containing probably about 38·634 grams of total solids per litre. Natural sea-water is more favourable to proliferation than artificial sea-water. The addition of alkalis to sea-water tends to inhibit proliferation of the leaves, whilst the addition of minute quantities of acids to some sea-waters improves them in this respect, probably by destroying their slight alkalinity. Proliferation takes place in leaves placed in vessels completely filled with sea-water, but to a greater extent when air is also present, or when a continuous stream of sea-water is maintained; it is inhibited to some extent in filtered sea-water. Small quantities of distilled water added to sea-water favour proliferation, but larger quantities tend to reduce it. These effects are due to change in composition, not to alteration of osmotic pressure. The value of Δ for the liquid expressed from the plant is $-0·55°$, whilst that of the surrounding sea-water is $-2·269°$.

Proliferation does not take place in the absence of light, whether air is present or not. The carbon dioxide necessary for proliferation is probably provided by the microplankton of sea-water. The author confirms Winterstein's observations (Abstr., 1909, ii, 746) as to the loss of oxygen when sea-water is exposed to light. With reference to the influence of light of different wave-lengths on proliferation, it is shown that the less refrangible portion of the spectrum inhibits it, and that neither infra-red nor ultra-violet rays are necessary. The plant is not injuriously affected by exposure to ultra-violet rays from a Uviol lamp. Proliferation is retarded, but not stopped, when the temperature is reduced to 4°. The passage of an electric current through sea-water kills the plant, but "cathodic liquors" from sea-water, prepared as described already (Abstr., 1910, ii, 883), favour proliferation, whilst "anodic liquors" kill the plant. T. A. H.

The Fruit of the Cornus paniculatum. GUINNEVERE SHEETS (*Chem. News*, 1911, **103**, 172—173).—The sugars present are lævulose and dextrose, and are stated to constitute 78·98% of the dried fruit. Tartaric, citric, and acetic acids were found, the last named probably resulting from fermentation; 0·56% of nitrogen was present. The oils appear to be palm oil and cocoa-nut oil. Analysis of the ash is also given. E. J. R.

So-called "Lichen quercinus viridis." EMANUEL SENFT (*Chem. Zentr.*, 1911, i, 506; from *Pharm. Post.*, 1910, **43**, 1017—1019).—The drug consists mainly of the lichen *Evernia prunasti*, and contains atranoric, usnic, and evernic acids. The last-mentioned acid is characteristic of the lichen. It crystallises in lustrous, colourless prisms, m. p. 164—170°, dissolves in strong sulphuric acid and alkalis with a yellow colour, gives a red coloration with ferric chloride, and when boiled with barium hydroxide, is decomposed into everninic acid, $C_9H_{10}O_4$, orcinol, and carbon dioxide. F. B.

Fresh Gentian Root, and a Preparation from the Same, "Dialysé Golaz." JAMES BURMANN (*Chem. Zentr.*, 1911, i, 165—166; from *Schweiz. Woch. Chem. Pharm.*, 1910, **48**, 755—758).—The author gives an account of the constituents of gentian root, and describes the preparation and properties of "dialysé Golaz." The latter is a yellow, fluorescent liquid, obtained by dialysing the fresh, crushed root with 65% alcohol in the absence of air. It contains the glucosides, gentiopicrin and gentiamarin. F. B.

Basic Substances in Extract of Mushroom. FRIEDRICH KUTSCHER (*Chem. Zentr.*, 1911, i, 497; from *Zentr. Physiol.*, 1910, **24**, 775—776).—The aqueous extract of mushrooms contains arginine, choline, betaine, and a *substance*, $C_9H_{15}O_2N_3$. The latter compound, isolated in the form of its *aurichloride*, gives Pauly's diazo-reaction, and also the tryptophan and Millon's reaction; it appears to be a trimethyl derivative of histidine. F. B.

Rhamnus Cathartica Bark. ALEXANDER TSCHIRCH and H. BROMBERGER (*Arch. Pharm.*, 1911, **249**, 218—223. Compare Binswanger, *Jahrb. Fort. Pharm.*, 1848, **185**, 470, and Tschirch and Polacco, Abstr., 1900, i, 681).—An alcoholic extract of the bark on standing deposited *rhamnosterol*, $C_{13}H_{28}O_2$, m. p. 83—85°, which was crystalline and colourless and gave the reactions of a phytosterol.

The portion of the extract insoluble in water contained (1) emodin, identical with that present in the bark of *Rhamnus frangula*; (2) an iso*emodin*, $C_{15}H_{10}O_5$, which decomposed above 305°, crystallised in long, red needles, gave a bluish-violet solution with alkali, and furnished an *acetyl* derivative, m. p. 233°; (3) chrysophanol, m. p. 196°, identical with the "chrysophanic acid" obtained from senna (Tschirch and Hiepe, Abstr., 1900, i, 681); (4) *rhamnofluorin*, $C_{14}H_{12}O_6$, which decomposed at 220°, formed ash-grey crystals, gave a greenish-yellow, fluorescent solution in alcoholic ammonia, and did not reduce Fehling's solution, and (5) fat.

The portion of the extract soluble in water yielded tannin, dextrose, and small quantities of emodin and of a brown, microcrystalline *substance*, which reduced Fehling's solution in the cold and gave a deep brown coloration with alkalis. T. A. H.

Some Constituents of Extractum Secalis cornuti. R. ENGELAND and FRIEDRICH KUTSCHER (*Chem. Zentr.*, 1910, i, 1762; from *Zentr. Physiol.*, 1910, **24**, 589—591).—When oxidised with calcium permanganate, agmatine, the base contained in secale extract, gave guanidine, guanidinobutyric acid and succinic acid.

Uracil occurs in the bases of secale extract, which are not precipitated by silver nitrate and ammonia. The extract also contains succinic acid, lactic acid, and a substance giving Millon's reaction. F. B.

Action of Ultra-violet Light on the Green Husks of Vanilla. JEAN POUGNET (*Compt. rend.*, 1911, **152**, 1184—1186. Compare Abstr., 1910, ii, 993).—Heckel (Abstr., 1910, ii, 63) was unable to detect the formation of vanillin when the green husks were treated with anæsthetics, such as chloroform and ether. On exposure to ultra-violet light, however, the odour of this substance became perceptible, the action being accelerated by immersing the pod in a solution of manganous chloride. The odour is more rapidly developed in mature plants which have lost their green colour. W. O. W.

Fruit of Viburnum lentago. C. E. GILLETTE (*Chem. News*, 1911, **103**, 205—206).—On extraction with alcohol the fruits yielded 56—57% of dry matter, and on subsequent extraction with water 2·0—2·5%. In these extracts dextrose and lævulose were detected. The residue on extraction with ether gave 4·25% of oil, expressed on the original fruits. This oil was amber-yellow in colour, dried on exposure to air in thin films, had saponification number 218, and yielded 25% of unsaponifiable matter. The whole fruits contained 0·14% nitrogen. Malic acid and tannin were detected. A detailed analysis of the ash showed phosphoric oxide, potassium, sodium, and aluminium as the predominant constituents. T. A. H.

The Chemistry of Barley Glumes. K. GEYS (*Zeitsch. ges. Brauwesen*, 1910, **33**, 347—349).—The aqueous hydrochloric acid extract obtained from barley glumes yielded a substance found to be identical with phytin; this on heating at 140—150° with 30% sulphuric acid under pressure was hydrolysed according to the equation: $3C_2H_8O_9P_2 + 3H_2O = 6H_3PO_4 + C_6H_{12}O_6$, yielding inositol (m. p. 208°) and phosphoric acid; whilst the ash contained $P = 17·7\%$, Ca 20·5%, and Mg 2·3%.

The work of Posternak (Abstr., 1903, ii, 679, 680) and of Neuberg and Brahn (Abstr., 1907, i, 1097; 1908, i, 394) is discussed.
F. M. G. M.

Chemistry and Analysis of Wines: A Criticism of Methods and Interpretation of Results. C. VON DER HEIDE and W. I. BARAGIOLA (*Landw. Jahrb.*, 1910, **39**, 1021—1081).—A comprehensive physical and chemical study of various wines of Moselle type. The vintages of various soils are compared, and the possible influence of the latter on the products discussed. The organic and inorganic constituents, densities, total acidity, and ratio of acids to bases were estimated, and the probable form of existence of each in the living plant studied from a chemical and physical point of view. F. M. G. M.

How Lead Arsenate is Eliminated at Vintage. L. MOREAU and E. VINET (*Compt. rend.*, 1911, **152**, 1057—1060. Compare Abstr., 1910, ii, 443).—An account of further experiments in support of the observations recorded previously. In consequence of the large amount of lead and arsenic removed with the skins and sediment, wine from grapes treated with lead arsenate contains a proportion of this substance comparable with that existing naturally in the untreated product.
W. O. W.

[Colloids in Relation to Agriculture.] E. RAMANN (*Koll-Chem. Beihefte*, 1911, **2**, 285—303).—An account is given of the connexion between surface energy and the colloidal state, and of the application of the principles of colloidal chemistry to the changes which take place in the soil in relation to plant growth. H. M. D.

Biological-Chemical Processes in Soils. Contribution to the Nitrogen Question. W. Mooser (*Landw. Versuchs-Stat,* 1911, **75**, 53—106).—From the results of experiments on nitrification and on the losses of ammonia in soils containing various amounts of calcium carbonate to which an ammonium salt has been added, the conclusion is drawn that nitrification cannot always be due to the action of nitrifying organisms alone; the amount of free ammonia liberated in very calcareous soils would, it is considered, render bacteriological nitrification impossible.

According to Liechti and Mooser (*Landw. Jahrb. Schweiz.*, 1906, 1), very large amounts of aromatic compounds are applied to the land in liquid manure, the amounts of benzoic acid being at least 400—500 kilos. per hectare, and of phenols, 34—83 kilos.

Experiments on the disappearance of *p*-cresol added to soils indicate that it is due to the chemical action of some soil constituent, possibly a protein in the colloidal state. In any case no deterioration of soil fertility is to be feared as the result of applying substances, such as "carbolineum," containing cresol. N. H. J. M.

Effect of Previous Heating of Soil on the Growth of Plants and the Germination of Seeds. F. Fletcher (*Cairo Scient. J.*, 1910, **4**, Reprint, 6 pp.).—Pot experiments with maize grown in soil yielded 0 to 314 mg. of fresh produce (mean 145·5 mg.). The same soil when previously heated at 95° gave 36 to 353 (mean 151·7) mg. of fresh substance, whilst after heating at 170°, the soil yielded 835 to 1470 (mean 1056) mg. of fresh substance. The higher results obtained with soil previously heated is attributed to toxic plant excreta being rendered insoluble, and consequently innocuous. It is suggested that the toxic substance may be an alkaloid dihydroxystearate (compare Schreiner and Shorey, this vol., ii, 147).

Germination experiments are described in which lupins (5), *Tripolium*, (berseem), and *Sesamum* seeds (30 each) were sown in soil which had been heated at about 185°, and in soil which had not been heated. All the lupins and most of the other seeds failed to germinate in the heated soil, whilst all the lupins and *Sesamum* seeds germinated in soil which had not been heated.

Lupin seeds which were placed in extracts of the two soils showed a much higher rate of imbibition in extracts of soil which had not been heated than in extracts of the heated soil.

The conclusion is drawn that the retarded germination is due to a decrease of imbibition, which is attributed to the production of soluble organic substances and, consequently, increased osmotic activity (compare Pickering, *J. Agric. Sci.*, 1908, **2**, 411). N. H. J. M.

[Composition of Rain-water: British Guiana.] John B. Harrison (*Brit. Guiana Dept. Sci. Agric. Rep.* for 1909-10, 15—18. Compare *ibid.*, Reps. for 1890-1904; Hall and Bovell, Abstr., 1910, ii, 994;

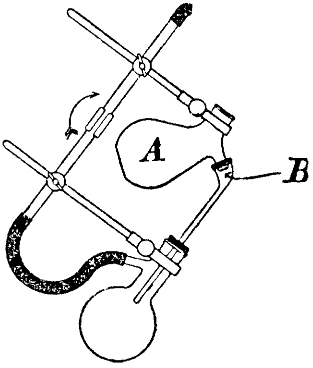
Aufray, this vol., ii, 224).—The amounts of nitrogen as ammonia and nitrates and of chlorine have been estimated in monthly samples of rain-water collected at Georgetown since 1890. The average yearly results since 1904, and the average for the twenty years, are as follows:

		Per million.			Per acre (lb.).			
	Rainfall, inches.	N. as ammonia.	N. as nitrates.	Chlorine.	N. as ammonia.	N. as nitrates.	Total nitrogen.	Chlorine.
1904...	84·98	0·045	0·020	7·02	1·93	0·84	2·77	132·5
1905...	75·66	0·020	0·074	6·58	1·00	3·77	4·77	110·7
1906...	101·25	0·007	0·050	7·18	0·34	2·50	2 84	161·5
1907...	117·65	0·011	0 028	6·05	0·64	1·62	2·26	158·2
1908...	88·72	0·015	0·022	7·96	0·66	0·96	1·62	157·0
1909 ..	105·76	0·015	0 070	6·35	0·78	3·60	4·38	149·2
1890–1909...	99·27	0·018	0·034	5·16	1·01	1·89	2·90	129·2

Of the total nitrogen (average of twenty years) 34·8% was in the form of ammonia, and 65·2% as nitrates. N. H. J. M.

Analytical Chemistry.

A New Arrangement for the Correct Reading of Burettes. GUSTAV GOETZE (*Zeitsch. anal. Chem.*, 1911, 50, 373).—A suitable tube is taken about 4 cm. long, and in the centre is etched, by means of hydrofluoric acid, a complete ring, such as is found on the necks of measuring flasks or the stems of pipettes. The tube is just wide enough to readily slide over the burette when moved up and down by means of the fingers and thumb. The mark is then placed against the lower point of the meniscus, and an accurate reading of the burette scale is thus ensured; in the case of dark-coloured liquids, the top of the meniscus is observed. The two ends of the tube may be also inserted in suitable metallic rings which are fitted with two small springs; these press against the burette tube, and hold the little tube steadily at any desired point. L. DE K.



Simplified Gravimetric Analysis. M. H. PALOMAA (*Chem. Zentr.*, 1910, ii, 1775—1776; from *Annalen Finn. Akad. Wiss.*, A 2. No. 5).—A large number of more or less serious sources of error in ordinary analysis may be avoided by using an apparatus described by the author. The operations, such as precipitation, decantation, filtration, washing, heating, and weighing, are all conducted in a single apparatus. The course of the washing is controlled by determination of the physical constants of the washing liquid. The reagents are dissolved just before they are wanted. The flask *A*, of Jena glass, carries a side-tube, to which at *B* a perforated, round platinum disc has been sealed, which serves as filter bottom, and is covered by means of a small pipette with pulped asbestos. After the substance to be analysed has been placed in the weighed flask and the precipitation carried out as usual, the filtration is carried out by inclining the flask and by suction. As will be seen from the figure, both flask and the vessel intended for receiving the filtrate are fixed on a common, movable arm. L. DE K.

Estimation of Dissolved Oxygen. LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1911, **24**, 831—832).—A 2*N*-sodium chloride solution, saturated with air, may be used as a standard in the process described previously by the author (this vol., ii, 329); 1000 c.c. of this solution, at 0° and 760 mm. pressure, contain 4·69 c.c. of dissolved oxygen; at 5°, 4·24 c.c.; at 10°, 3·85 c.c.; at 15°, 3·51 c.c.; at 20°, 3·23 c.c.; at 25°, 3·00 c.c.; and at 30°, 2·83 c.c. W. P. S.

Method for Measuring the Degree of Vitiation of a Confined Atmosphere. H. HENRIET and M. BOUYSSY (*Compt. rend.*, 1911, **152**, 1180—1181).—By a method based on titration of condensed water with potassium permanganate, the author has only been able to detect the presence of reducing substances corresponding with 1 mg. of oxygen absorbed in the air of a park, and of 21 mg. per 100 cu. metres in that of a workroom containing twenty occupants. In the latter case the volume of the room was 104 cu. metres, and the windows were kept closed for twenty-four hours.
W. O. W.

The Estimation of Halogens According to the Method of Baubigny and Chavanne. HERMANN EMDE (*Chem. Zeit.*, 1911, **35**, 450—452).—The author has subjected the method of Baubigny and Chavanne for the estimation of halogens in organic compounds (compare Abstr., 1903, ii, 510; 1904, ii, 203; 1908, ii, 530) to a thorough test, and recommends it strongly in preference to the Carius method. In many cases in which the Carius method is unsatisfactory, it readily gives good results in a short time, as, for example, in the determination of iodine in iodoglidin.

The author recommends that in the determination of chlorine and bromine in the same compound, they should first be weighed together as the silver salts, and then the silver bromide transformed into silver chloride by means of chlorine, and the total chloride weighed.
T. S. P.

Estimation of Very Small Amounts of Bromine in Presence of Chlorides and Iodides. HENRI BAUBIGNY (*Bull. Soc. chim.*, 1911, [iv], **9**, 352—354).—In connexion with Clausmann's statement (this vol., ii, 329) that it is impossible to estimate satisfactorily bromine in presence of large quantities of chlorides, the author recalls the process previously described, which is sufficiently accurate for the purpose (Abstr., 1897, ii, 385; 1903, ii, 510). W. O. W.

Presence of Bromine in Human Organs. A. LABAT (*Bull. Soc. chim.*, 1911, [iv], 9, 393—398).—After critisising adversely the methods of other investigators for the detection and estimation of small quantities of bromine in presence of iodine, a modification of Baubigny and Rivals' method is described. To 5–10 c.c. of an aqueous solution of the halogen is added 0·1 c.c. of an alcoholic fluorescéin solution (0·25%) and five drops of ammonia. With 0·03 mg. of bromine, a red coloration is developed, whilst with twice this amount the solution shows the characteristic absorption spectrum of eosin. This is distinguished from the fluorescein and iodofluorescein spectra by the displacement of the band between the green and blue towards the right and the appearance of a very narrow band in its place.

In the case of animal organs, the material is calcined with one-fifth its weight of magnesium oxide, extracted with water, and the solution distilled with ferric alum; iodine is estimated in the distillate. The residue is filtered, treated with potassium chromate and sulphuric acid, and distilled in a current of air, the vapours being condensed in a fluorescein solution which is examined as above for bromine.

This method has shown the presence of bromine in the human thyroid gland. W. O. W.

Estimation of Sulphur by the Carius Method. GIUSEPPE ANELLI (*Gazzetta*, 1911, 41, i, 334—341).—The various methods for estimating sulphur in the crude products containing bitumen consist in oxidising the sulphur to sulphuric acid, the bitumen being estimated by difference.

The author has investigated the method in which the oxidation is effected by means of fuming nitric acid in sealed tubes, and finds that this procedure always gives results in excess of the theoretical values, the divergence varying with the nature of the glass of the sealed tube, and amounting, in some cases, to 6%. These high results are found to be due to the attack of the glass by the sulphuric acid formed, but no satisfactory correction could be applied for the silicic acid dissolved. When an organic compound containing a limited proportion of sulphur is being analysed, the error produced in the above manner is negligible, although somewhat high values are usually obtained. With sulphur itself or with compounds containing much sulphur, barium nitrate in slight excess over the theoretical amount must be introduced into the Carius tube with the nitric acid (compare Rupp, Abstr., 1908, ii, 982).
T. H. P.

Estimation of the Proportion of Sublimed Sulphur in a Mixture of Different Sulphurs. TAUREL and GRIFFET (*Compt. rend.*, 1911, 152, 1182—1183).—Sublimed sulphur consists of microscopic globules of crystallised sulphur enclosed in pellicles of the amorphous form insoluble in carbon disulphide. This solvent, however, is able to penetrate the outer layers and remove the interior without altering the size or shape of the globule. The proportion by volume of sublimed sulphur in mixtures may be determined by shaking equal weights of the material with petroleum and carbon disulphide respectively, and observing the volume occupied by the deposits after ten minutes' centrifugation in graduated tubes. W. O. W.

A Rapid Method for the Estimation of Sulphur in Coal Gas, or of Ammonium Sulphate. HERBERT BLAIR (*J. Soc. Chem. Ind.*, 1911, **30**, 397—398).—Ammonia can be determined with rapidity and accuracy by making use of Malfatti's reaction, the formation of hexamethylenetetramine and liberation of acid by treating a solution of an ammonium compound with formaldehyde. The reaction proceeds quantitatively according to the reaction $4NH_4Cl + 6CH_2O = C_6H_{12}N_4 + 4HCl + 6H_2O$, and the acid liberated can be titrated with standard alkali, using phenolphthalein as indicator.

For the estimation of sulphur in coal gas, the liquor obtained in the "Referee's test" is made up to 500 c.c., and 50 c.c. boiled for two or three minutes to remove carbon dioxide. To the hot solution, 10 c.c. of a neutral 30% solution of formaldehyde are added, and the solution at once titrated with *N*/10-potassium hydroxide solution. As the volume of potassium hydroxide solution used is considerable, the method can be utilised for the determination of sulphur in a small volume (1 or 2 cu. ft.) of gas, and the whole operation can be completed in an hour.

In the determination of ammonium sulphate, the sample is dissolved in water, and, as it is always acid, the solution neutralised with potassium hydroxide. An aliquot portion is then boiled for a few minutes, 10 c.c. of neutral formaldehyde solution added, and the liquid allowed to boil for a few seconds. It is then titrated with the standard potassium hydroxide. T. S. P.

Exact Estimation of Nitrogen in Certain Organic Compounds. RUDOLF FABINYI (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 171—173).—Asaraldoxime hydrochloride is oxidised quantitatively by ferric chloride, yielding nitrous oxide :

$$2CHR{:}NOH + 4FeCl_3 + 2H_2O = 2CHR{:}O + 4FeCl_2 + 4HCl + N_2O + H_2O.$$

It is found that this reaction is a general one for aldoximes and ketoximes. Instead of measuring the nitrous oxide evolved, it is advisable to use a volumetric method. 0·2—0·4 Gram of the oxime is oxidised with an excess of a 10—12% solution of ferric chloride, the concentration of which has been determined iodometrically. The oxidation is carried out in hot, slightly acid solution, the gas evolved escaping through a tube which dips into hot water. When oxidation is complete, the flask is allowed to cool, water being drawn back into it. The separated aldehyde is removed by filtration after diluting to a known volume, and a definite fraction of the filtrate is taken, mixed with potassium iodide solution, and titrated with thiosulphate. The nitrogen estimation is correct to 0·05%. C. H. D.

Easy Method for Detecting Nitrites. ARISTIDE DANÉ (*Bull. Soc. chim.*, 1911, [iv], **9**, 354—355).—A solution containing 0·02 gram of synthetic indole in 150 c.c. of 95% alcohol forms a sensitive reagent for the estimation of nitrites. The liquid to be examined is treated with 2—5 c.c. of this solution; on the addition of sulphuric acid a red coloration rapidly appears. The reaction is sensitive to the extent of 1 in 2,500,000, and may be used in water analysis when other methods give doubtful results. W. O. W.

Estimation of Nitrites. ERWIN RUPP and FRANZ LEHMANN (*Arch. Pharm.*, 1911, **249**, 214—217).—The process depends on the oxidation of the nitrite by freshly liberated bromine, and the estimation of the excess of bromine by the addition of an iodide and titration of the iodine liberated.

Sodium nitrite (2·5 grams) is dissolved in water, the solution made up to 500 c.c., and 10 c.c. of this placed in a 250 c.c. stoppered bottle. To this, 50 c.c. of a solution containing 0·8351 gram of potassium bromate and 3 grams of potassium bromide per litre are added, and the mixture, after addition of 10 c.c. of dilute sulphuric acid, is shaken and left in the dark for thirty minutes. Potassium iodide (0·5 gram) is then added, and after two minutes the liberated iodine is titrated by *N*/10-sodium thiosulphate solution. T. A. H.

Simple Method for the Estimation of Phosphorus in Phosphorised Oils. OTTO FREY (*Chem. Zentr.*, 1911, i, 425—426; from *Pharm. Post*, 969—970).—A quantity of the sample equivalent to about 0·01 gram of phosphorus is placed in a 300 c.c. porcelain dish, and fifteen drops of fuming nitric acid are added, one drop at a time. When the action is over, 15—20 c.c. of the same acid are added at once, and the liquid is heated on the water-bath until no more red fumes are evolved. After adding 50 c.c. of water and again warming and adding a little wax or paraffin, the liquid is allowed to cool and filtered.

The solution is then made up to a definite volume, and in an aliquot part of this the phosphoric acid is determined by the volumetric molybdate method (dissolving the yellow precipitate in standard alkali, boiling off the ammonia, and titrating the excess of alkali with standard acid). L. DE K.

Estimation of Phosphorus in Milk. ÉMILE FLEURENT and LUCIEN LÉVI (*Compt. rend.*, 1911, **152**, 1015. Compare this vol., ii, 445).—Although, as pointed out by Bordas and Touplain (this vol., ii, 438) and confirmed by the present authors, the total loss of phosphorus during the calcination of milk ash is inconsiderable, yet if calculated as a percentage of the amount in organic combination, it is found to form 21·3% of this portion of the phosphorus. W. O. W.

Estimation of Phosphorus in Milk. FRÉD. BORDAS and F. TOUPLAIN (*Compt. rend.*, 1911, **152**, 1127—1128. Compare this vol., ii, 438).—A reply to Fleurent and Lévi (preceding abstract). W. O. W.

Colorimetric Method for the Estimation of Phosphoric Acid. NAPOLEONE PASSERINI (*Gazzetta*, 1911, **41**, i, 182—186).—The estimation of phosphoric acid in soils by means of the brown coloration which potassium ferrocyanide produces with a solution of a molybdate or phosphomolybdate (comnare Pagnoul, *Méthode pour l'Analyse de la terre arable*, Paris, 1903, 44) presents the disadvantage that the coloration obtained is unstable and rapidly changes its tone.

The method devised by the author makes use of the colour formed by molybdic acid with gallic acid, this colour being extremely stable and varying from yellow to orange to red according to the proportion of molybdic acid present; the yellow or but faintly orange tint is the most suitable to employ.

Ten grams of the air-dried, powdered rock or soil, placed in a flask of about 200 c.c. capacity, are moistened with water and boiled for an hour on the sand-bath with 30–40 grams of concentrated nitric acid, the larger amount being used for soils rich in lime. The liquid is allowed to settle for a few moments, and the turbid liquid introduced into a 250 c.c. graduated flask; the residue is washed repeatedly with small amounts of water, the whole of the liquid being finally made up to 250 c.c. Fifty c.c. of the filtered solution are evaporated to dryness, and the residue heated for an hour on the water-bath and extracted with nitric acid and boiling water, the volume being made up to 50 c.c. Twenty-five c.c. of this solution, after filtration, are treated with 2 c.c. 75% ammonium nitrate solution and 25 c.c. of molybdate reagent, and left for twenty-four hours. The precipitate, after washing with 1% nitric acid solution until the washings give no yellow coloration with gallic acid, is dissolved in the least possible quantity of ammonia solution (1 : 4), the solution being diluted to about 100 c.c., boiled as long as ammonia is evolved, cooled, made up to 100 c.c., and used for the colorimetric estimation.

The standard phosphate solution contains 0·01 grams P_2O_5 per litre and may be prepared by precipitating 10 c.c. of a solution containing 1·9153 grams $CaHPO_4$ per litre with 2 c.c. 75% ammonium nitrate solution and 25 c.c. of molybdate reagent, and proceeding as above, the volume being made up to 1 litre after dissolving the precipitate in ammonia. This solution remains unchanged for a very long time, and, before it is used, a definite volume is boiled to expel most of the ammonia and made up to volume again. 1—2 c.c. of this solution are stirred into a mixture of 15 c.c. of water and 2 c.c. of cold saturated gallic acid solution, the colour being matched by running into 15 c.c. of water and 2 c.c. of gallic acid solution the liquid to be tested. The gallic acid solution keeps for some days, if prepared with sterile water.

T. H. P.

Estimation of Phosphoric Acid as Magnesium Ammonium Phosphate. GUNNER JÖRGENSEN (*Zeitsch. anal. Chem.*, 1911, **50**, 337—343. Compare *ibid.*, 1906, **45**, 287, 306).—A reply to Bube (Abstr., 1910, ii, 804). The author upholds his own theories as to the formation of true magnesium ammonium phosphate. L. DE K.

Refractrometric Estimation of Phosphates in Urine. J. AMANN (*Chem. Zentr.*, 1911, i, 354; from *Schweiz. Woch. Chem. Pharm.*, **43**, 766—768).—Fifty c.c. of the urine are precipitated with 20 c.c. of magnesium mixture, and after fifteen minutes the precipitate is washed as usual and finally with a little alcohol. After removing the adhering liquid by centrifugal action, the precipitate is dried for fifteen to twenty minutes at 110°, and then placed with the filter in a beaker containing 10 c.c. of 5% sulphuric acid. The solution is examined in the Zeiss immersion refractometer, and also the acid itself. The difference in the observations represent the phosphoric oxide, reference being made to a table constructed by the author. If the amount of phosphoric oxide does not exceed 4 grams per litre, a 5% solution of citric acid may be substituted for the sulphuric acid.

L. DE K.

The Behaviour of Uranyl Salts of Dibasic Phosphoric Acids with Indicators. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1911, **32**, 235—242).—Orthophosphoric acid gives the same titration value with uranyl acetate when either cochineal or potassium ferrocyanide is employed as indicator. On the other hand, glycerophosphoric acid forms a soluble uranyl salt, and can be titrated with uranyl acetate with cochineal as indicator, but not with potassium ferrocyanide, since in this case the colour change, corresponding with the formation of insoluble uranyl ferrocyanide, takes place at once. The two hydrogen valencies replaceable by the uranyl group thus correspond in the case of glycerophosphoric acid with a weaker acid than in that of orthophosphoric acid.

Pyrophosphoric and inositolphosphoric acids behave to uranyl acetate in the presence of cochineal exactly like orthophosphoric acid, but in presence of potassium ferrocyanide give only half the titration value. In these acids, therefore, two of the four replaceable hydrogen valencies correspond in strength with those in orthophosphoric acid, and form an insoluble uranyl salt, whilst the other two are similar to those in glycerophosphoric acid, and cannot be titrated in presence of potassium ferrocyanide.

Metaphosphoric acid forms a soluble uranyl salt containing two molecules of the acid, and thus the titration value in presence of cochineal is only half that of orthophosphoric acid, whilst it cannot be titrated in presence of potassium ferrocyanide. W. J. Y.

Reaction of Pyrophosphates with Luteocobaltic Chloride. M. SESÉ (*Anal. Fis. Quim.*, 1911, **9**, 82—84).—The precipitate yielded by pyrophosphates with luteocobaltic chloride has the form of lustrous, silky plates, that given by metaphosphates being pulverulent, and less deeply red-coloured.

The metaphosphate precipitate is soluble in hydrochloric acid, and insoluble in acetic, the reverse obtaining in the case of the pyro-compound. G. D. L.

Estimation of Arsenic in Urine after the Administration of Salvarsan. ALFRED HEIDUSCKA and THEODOR BIÉCHY (*Apoth. Zeit.*, 1911, No. 15, Reprint 3 pp.).—Five hundred c.c. of the urine are mixed with 12½ c.c. of crystallised aluminium sulphate solution, and dilute ammonia is added to strongly alkaline reaction. After boiling for half-an-hour, the supernatant liquid is drawn off, and again treated with aluminium sulphate and ammonia. If much arsenic is suspected, a third treatment may be advisable. The two precipitates, which contain all the arsenic, are drained, and then distilled with 50 c.c. of 36% hydrochloric acid with addition of 5 grams of ferrous sulphate.

The apparatus consists of a 300 c.c. Schott's distilling flask placed slanting, and the acid vapours are passed through a conical flask containing 100 c.c. of water and 25 grams of potassium hydroxide; the flask is fitted with a two-bulb funnel tube, containing dilute potassium hydroxide solution, thus acting as a seal. After distilling three-fourths of the acid, the alkaline liquid is completely neutralised with hydrochloric acid, and the arsenic is titrated iodometrically as usual.

The distillation process may be applied to "Salvarsan" without any previous treatment, but only very small quantities (6—30 mg.) should be used. L. DE K.

Uniform Method for the Estimation of Carbon in all Iron Alloys. A. STADELER (*Metallurgie*, 1911, **8**, 268—270).—The total carbon in iron alloys which are insoluble in acids may be estimated by the method due to Wüst, of fusing with antimony and tin in a stream of oxygen. 1·5—2·5 Grams of a mixture of 3 parts of antimony and 1 part of tin are mixed with 0·3 to 0 5 gram of the alloy, and placed in a large porcelain boat in a Jena glass tube. The temperature should reach 900°, as the results obtained at 800°, although concordant, are uniformly low, except in the case of spiegeleisen, which gives satisfactory results at the lower temperature. The method is particularly suitable for alloys which are not attacked by chromic acid mixture, and for which the only available method has been hitherto that of attack by chlorine. Brittle ferro-alloys should be finely powdered, but special steels may be used as fine drillings. C. H. D.

A Wet-method for the Estimation of Carbon in Organic Substances. FRANZ TANGL and GEORG VON KERESZTY (*Biochem. Zeitsch.*, 1911, **32**, 266—273).—A description is given of the apparatus and the method of procedure employed by the authors for the estimation of carbon in animal and vegetable products, by a slight modification of the method of Messinger (Abstr., 1890, 1467). The method consists essentially in adding sulphuric acid, drop by drop, to a mixture of potassium dichromate and the substance or liquid to be analysed contained in a special flask. The gases evolved are carried, by means of a current of dry air freed from carbon dioxide, first through a combustion tube containing hot copper oxide, and then over hot lead dioxide to remove halogens; the carbon dioxide is finally absorbed in a solution of baryta, and estimated by titration.

The method gives good results. W. J. Y.

Estimation of Silicon in Vanadium and Molybdenum and in their Iron Alloys. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 635—636).—In the case of vanadium, the sample is dissolved in concentrated hydrochloric acid, and the solution, after dilution, is decanted through a filter. The insoluble residue of silica is washed twice with water, then with 10% hydrochloric acid until it is free from green colour; it is, finally, washed with hot water, ignited, and weighed. For the estimation of silicon in molybdenum and iron-molybdenum alloys, the metal is dissolved in *aqua regia*, the solution evaporated, and the residue treated with concentrated hydrochloric acid containing a small quantity of nitric acid. After being heated, the mixture is diluted, filtered, and any remaining traces of basic iron salts are removed from the residue of silica by treatment with 5% hydrochloric acid. W. P. S.

A New Volumenometer for Determining the Specific Gravity of Cement. N. S. Borch (*Zentr. hydraul. Zemente.*, 1911, **2**, 17—19).—The cement is introduced into a vessel previously filled with light petroleum to a certain mark. By means of an air-bulb, petroleum is then forced out of this vessel into a narrow graduated side-arm, until the level of the original mark is reached in the main vessel. The height of the column is then read to 0·01 c.c. A large ground stopper forms a foot, and is removed for cleaning.

C. H. D.

Racemic Acid as an Analytical Reagent. André Kling (*Bull Soc. chim.*, 1911, [iv], **9**, 355—361).—Racemic acid gives an almost immediate precipitate with solutions of calcium or strontium acetate containing one part of the metal in 10,000, whereas in a barium solution (3—5%) a crystalline precipitate appears only after several hours. Owing to the fact that the precipitate in the first case always contains appreciable quantities of barium if this metal is also present, the process does not admit of quantitative application, even when the precipitation is carried out a second time. Calcium and strontium may be estimated, however, in presence of magnesium if the solution is acidified with phosphoric acid, and the former may be determined in presence of iron or aluminium after the addition of citric acid.

W. O. W.

Laboratory Methods. Ernst Murmann (*Oesterr. Chem. Zeit.*, 1910, **13**, 227—228. Compare Abstr., 1909, ii, 343, 828, 990).—The author recommends that: (1) A somewhat great excess of hydrochloric acid be present and a few drops of alcohol added to facilitate the precipitation of barium sulphate. (2) One drop of ether be added to freshly precipitated potassium perchlorate to aid filtration. (3) When magnesium ammonium phosphate is dissolved in acetic acid and the magnesium estimated as oxalate, high results are obtained, owing to co-precipitation of phosphoric acid; various means of overcoming this difficulty are discussed. (4) The precipitation of ammonium magnesium arsenate is facilitated by the addition of alcohol. (5) Pure lime, carefully hydrated and dried, is recommended in place of soda-lime for the absorption of carbon dioxide. (6) Pure water can be obtained by one distillation if all spraying is prevented by passage of the vapour through a layer of lentil-like aggregates of quartz.

F. M. G. M.

Adaptation of the Tap-Funnel to Rapid Electroanalysis with Stationary Electrodes. T. Slater Price and Alfred W. T. Hyde (*J. Soc. Chem. Ind.*, 1911, **30**, 391—396).—The difficulty in the use of the ordinary tap-funnel with stationary electrodes is that some of the electrolyte remains in the neck of the funnel, thus escaping electrolysis. This difficulty may be overcome by using a funnel with a three-way tap, such as is used at the bottom of a Hempel gas burette, one way being for the delivery of liquid in the ordinary manner, the other being connected with a rubber hand-bellows (or Shenstone water-blower), by means of which air bubbles may be blown through the solution. In this way the electrolyte in the neck of the funnel may be mixed with the rest of the solution from time to time during the electrolysis, and incidentally the stream of bubbles stirs the electrolyte.

The electrodes mainly used consisted of a cylindrical sand-blasted platinum gauze cathode, and a cylinder of similar gauze for the anode. It was found that satisfactory results were obtained in the deposition of copper, nickel, and zinc. In the deposition of copper, a concentration of less than 1 c.c. of concentrated nitric acid per 70 c.c. of electrolyte is inadvisable, whilst a concentration of 2 c.c. of nitric acid may be used with advantage; the salt used was copper sulphate. With a sufficient amount of nitric acid, previous heating of the electrolyte is unnecessary, but a final temperature of 60—70° does not prevent the deposition of the copper with 2 c.c. of concentrated nitric acid per 70 c.c. of electrolyte (compare Frary and Peterson, *Trans. Amer. Electrochem. Soc.*, 1910, **17**, 295).

Nickel gave good results with the ordinary ammonium sulphate-ammonium hydroxide electrolyte.

Zinc was satisfactorily deposited from the sodium sulphate, sodium acetate, acetic acid electrolyte, about 0·5 c.c. of glacial acetic acid per 70 c.c. of electrolyte giving the best results.

Experiments on the deposition of copper, in which a Hildebrand electrode was used as the cathode, and in which the oxygen evolved at the anode was made to pass through the cathode, showed that oxygen has no deleterious effect on the cathode deposit (compare Blasdale and Cruess, Abstr., 1910, ii, 1112).

The authors are of the opinion that rotating electrodes are to be preferred to stationary ones in usual practice. T. S. P.

The Use of Ether in Metal Analysis. FRANZ MYLIUS and KARL HÜTTNER (*Ber.*, 1911, **44**, 1315—1327. Compare this vol., ii, 444).—In order to test the use of ether in analytical separations, experiments have been carried out with the more important metallic chlorides, both in aqueous and hydrochloric acid solution. Silver and lead chlorides, which are practically insoluble in ether, are not appreciably extracted by ether, either in aqueous or hydrochloric acid solution. Copper, zinc, nickel, platinum, and palladium chlorides are only extracted in traces, whereas from strong hydrochloric acid solutions (20%) iridium chloride is extracted in considerable quantities. Iron, arsenic, antimony, tin, and tellurium chlorides are scarcely extracted by ether from aqueous solutions, but readily from hydrochloric acid solutions. From solutions of chloroauric acid, which contain also at least 2% of free hydrochloric acid, ether extracts over 90% (up to 98%) of the salt; mercuric chloride behaves in the opposite manner, ether extracting 69% of the salt from aqueous solutions, but practically nothing from hydrochloric acid solutions. Both in the case of mercury chloride and gold chloride the formation of double salts with lead, copper, sodium, or potassium chloride diminishes the extraction of the mercury or gold by the ether, the diminution being the most marked in the case of the latter metal.

The above results are applied to the use of ether in quantitative separations. Mercury may be separated from traces of silver, lead, zinc, copper, and tin when the metals are present as chlorides in pure aqueous solution, by extraction with ether. For the separation of arsenic, antimony, tin, and tellurium from other metals, the method offers no advantages. It is, however, of importance in the case of gold alloys containing platinum metals; the solution in aqua regia can be directly extracted with ether to remove the gold, which is then estimated in the ethereal extract.

Analysis of German double-crowns ("Doppelkronen"), 1900–1907, gave the following results:

Au.	Cu.	Ag.	Pb.	Fe.	Ni,Co.	As.	Pt.	Pd.	In.
90·0	9·57	0·37	0·01	0·013	trace	trace	0·023	0·01	trace

T. S. P.

The Estimation of Soluble Mercuric Salts at Great Dilutions. Henry R. Procter and R. A. Seymour-Jones (*J. Soc. Chem. Ind.*, 1911, **30**, 404—405).—Advantage is taken of the fact that in the presence of certain organic acids, such as formic or citric, mercuric sulphide is not precipitated on treatment of a mercuric chloride solution with hydrogen sulphide, but remains in the coloured colloidal form in solution. This colour is perfectly definite for definite concentrations of the chloride and acid if the liquid has been saturated with hydrogen sulphide, and is directly proportional to the concentration of the original mercuric chloride solution.

For carrying out the process, a standard solution of mercuric chloride containing 1 part by weight in 10,000 parts of water and also 1% by weight of formic acid is saturated with hydrogen sulphide. The solution to be estimated is made into a 1% formic acid solution, saturated with hydrogen sulphide, and its colour then compared with that of the standard in a Schmidt and Haensch dipping colorimeter, or in a Lovibond tintometer. T. S. P.

Separation of Cerium by Potassium Permanganate. Edwin J. Roberts (*Amer. J. Sci.*, 1911, [iv], **31**, 350—352).—The boiling solution of the rare earths containing nitrates only, is, if necessary, neutralised with sodium carbonate, and solution of potassium permanganate is added until the red colour becomes permanent. An excess of an alkaline solution of potassium permanganate (1 mol. of permanganate, 4 mols. of sodium carbonate) is then added slowly with constant stirring, and should the colour become entirely bleached, a little more of the pure permanganate should be added. After boiling for ten minutes, during the latter part of which time the solution should be kept quite neutral to litmus by means of sodium carbonate solution, the precipitate, consisting of manganese and cerium hydroxides, is collected and washed with boiling water until the filtrate no longer gives a precipitate with ammonia. The filtrate, which is free from cerium, is boiled with a few drops of alcohol, and, after filtering, the other earths are precipitated with oxalic acid.

The cerium precipitate is dissolved in strong hydrochloric acid; the solution is diluted, and precipitated with oxalic acid. The cerium oxalate is re-converted into nitrate, which is then once more submitted to the permanganate process, when a perfectly pure cerium salt is obtained. L. DE K.

The Precipitation of Aluminium Hydroxide in the Granular Form. W. E. TAYLOR (*Chem. News*, 1911, **103**, 169).—Instead of precipitating aluminium hydroxide by ammonia in boiling solution, the author carries out the operation at 66°, subsequently boiling as usual. The precipitate is then granular, and filters both rapidly and easily. E. J. R.

The "Hughes Reaction" of Potassium Iodide on Paper, and its Bearing on the Question of Acidity in Paper. JAMES STRACHAN (*Chem. News*, 1911, **103**, 193—195).—The brownish-violet coloration which is obtained when certain paper is moistened with potassium iodide solution and exposed to light ("Hughes reaction") is due to the mutual decomposition of alum and potassium iodide in the pores of the paper, and is, therefore, a sensitive test for the detection of acidity due to alum. A paper which gives an intense reaction on the application of the test must be regarded with suspicion as to its value for purposes of permanent records. W. P. S.

Detection and Estimation of Small Quantities of Manganese, Particularly in Organic Substances. GABRIEL BERTRAND (*Bull. Soc. chim.*, 1911, [iv], **9**, 361—370. Compare Baubigny, Abstr., 1903, ii, 184, 335, 512).—The material is incinerated at dull redness, the ash warmed with a little hydrochloric acid, treated with sulphuric acid, and the solution evaporated and again ignited at dull redness. The residue is dissolved in nitric acid (D 1·33), and diluted with three times its volume of water. The volume of solution should be 10 c.c.; 5 drops of 10% silver nitrate solution are then added, and at least 0·1 gram of potassium persulphate. On gently heating, the coloration due to permanganic acid appears, and persists after boiling the solution to decompose excess of persulphate. Unless this is done, the solution becomes yellow. The amount of manganese is then estimated colorimetrically. Details are also given for the use of lead peroxide as the oxidising agent. W. O. W.

The Colorimetric Estimation of Iron. HILARY LACHS and HANS FRIEDENTHAL (*Biochem. Zeitsch.*, 1911, **32**, 130—136).—The red colour of ferric thiocyanate is due to the undissociated salt, which is found to be at its maximum in the presence of 2*N*-hydrochloric acid. Under these conditions it is readily extracted from aqueous solution by ether (or amyl alcohol), and can be colorimetrically estimated in the ethereal solution, for, as the removal of the undissociated salt disturbs the equilibrium, re-combination of the dissociated salt occurs progressively until practically the whole of the ferric thiocyanate has passed into the ether in the undissociated condition. As standards, varying fractions of a cubic centimeter of solutions containing 10^{-4} to 10^{-5} grams iron per c.c. were diluted with water to 1 c.c., to which was added 1 c.c. 6*N*-hydrochloric acid (iron-free) solution, and 1 c.c. concentrated potassium thiocyanate solution. The colour was extracted from these with 1 c.c. ether. In milk the iron was estimated by dissolving the ash from 5 c.c. with 1 c.c. 6*N*-hydrochloric acid, to which solution 1 c.c. of water and 1 c.c. thiocyanate solution were added. The extract obtained from this by 1 c.c. ether was compared with the standards. Milk was found by this method to contain 1·3 mg. iron per litre. By centrifuging milk at 8000 revolutions per minute, it could be separated into layers. The upper layers containing the fat, and the lowest layer (precipitate) containing the caseinogen, etc., were found to contain iron, whereas the middle layer (milk-serum) was free from iron.

S. B. S.

A New Reaction for Ferrous Oxide and the Separation of Iron and Aluminium. K. W. CHARITSCHKOFF (*Chem. Zeit.*, 1911, **35**, 463).—A solution of naphthenic acid in light petroleum extracts quantitatively the ferrous oxide from aqueous solutions of ferrous salts. The reaction is as delicate as in the case of copper salts (compare Abstr., 1910, ii, 549), the light petroleum layer becoming coloured chocolate-brown.

This reaction may be used to separate iron and aluminium. The iron salts are first reduced to the ferrous state, and the solution extracted with the naphthenic acid solution; the aluminium remains in the aqueous layer.

T. S. P.

Estimation of Ferrous Iron in Silicates According to the Pebal-Dölter Method. MAX DITTRICH (*Ber.*, 1911, **44**, 990—991).—Minerals and rocks which are strongly basic, poor in silica, and rich in magnesia, as, for example, olivine, do not always readily dissolve in a mixture of hydrofluoric and sulphuric acids when treated according to the Pebal-Dölter method. The difficulty can be overcome by mixing quartz with the powdered mineral. The quartz must not be too finely powdered; precipitated silica cannot be used, since it is completely dissolved by the hydrofluoric acid before the mineral is attacked.

T. S. P.

Estimation of the Amount of Tin in Tinplate used for Canning Preserved Food. WLLFRID W. O. BEVERIDGE (*J. Roy. Army Med. Corps*, 1911, Reprint, 1—21).—The results are given of an investigation carried out with the object of ascertaining the proportions of tin in tinplate which should be used so as to obtain a well-tinned and serviceable can suitable for preserved foods. The process employed for estimating the tin consisted in dissolving the tin from a measured and weighed piece of the tinplate in a warm solution of dry chlorine in carbon tetrachloride, and weighing the remaining unattacked iron plate. The loss in weight gave the quantity of tin present. As the result of examinations of various tinplates and tin cans, it is recommended that for cans to hold preserved meats, the amount of tin per box of 112 plates measuring 14 by 20 inches should be at least 2·5 lb., or 0·0361 gram of tin per sq. inch (both sides of the plate); for making fruit cans, the layer of tin should be not less than 3·5 lb. per 112 plates, or 0·0506 gram per sq. inch (both sides). For biscuit and similar tins probably 2·25 lb. of tin, or 0·0325 gram per sq. inch, would be sufficient. One-twentieth of the surface of the top, bottom, and sides of a can, respectively, should be taken for analysis, and the lowest amount found on a given surface should be quoted. The surface of the tinplate should not be extensively marked by pinholes as shown by the Walker test (an acid solution of potassium ferricyanide), although at the present time a certain number of pinholes appears to be inevitable. W. P. S.

Pertitanic Acid and its Influence on the Volumetric Estimation of Iron in Titaniferous Minerals. EDMUND KNECHT and EVA HIBBERT (*J. Soc. Chem. Ind.*, 1911, **30**, 396—397).—The direct estimation of ferric iron in the presence of titanic salts presents no difficulty if any of the recognised reduction methods (stannous chloride, sodium hyposulphite, or titanous chloride) are employed. If, however, refractory titaniferous minerals or ores have to be dealt with, fusion has to be resorted to, and under certain conditions this operation may give rise to erroneous results.

The quickest method of dealing with such ores is found to be fusion with potassium hydroxide in a nickel crucible or dish; minerals such as rutile or ilmenite can be completely resolved by heating over a Bunsen flame for ten minutes. The fusion is taken up with water, transferred to a beaker, and strongly acidified with sulphuric acid, when both iron and titanium pass into solution. Some pertitanic acid is formed during the fusion, however, and it is necessary to remove this by titrating the solution with permanganate to a slight pink colour before determining the iron by titration with titanous chloride.

The amount of pertitanic acid formed is not inconsiderable, especially if the fusion is continued for any length of time. If silver vessels are used for the fusion, the amount formed is very small. The production of pertitanic acid does not appear to depend on the presence of iron, since pure titanic oxide also gives rise to it.

T. S. P.

Analysis of Ferro-Vanadium and Estimation of Vanadium in the Presence of Arsenic. WOLDEMAR TRAUTMANN (*Zeit. anal. Chem.*, 1910, **50**, 371—372).—The alloy is decomposed by a double fusion with a mixture of equal parts of sodium hydroxide and peroxide. The aqueous extracts of the fusions are then united, and, after adding an excess of sulphuric acid, heated to boiling and fully oxidised with permanganate. After adding a sufficiency of sulphurous acid, the excess of sulphur dioxide is boiled off in a current of carbon dioxide, and the vanadium is then titrated with standard permanganate.

It is stated by the author that arsenic acid, if present, is not reduced by sulphur dioxide in the circumstances. Arsenious acid is quantitatively oxidised by permanganate in presence of a sufficiency of sulphuric acid at the boiling heat, but an attempt to base on this fact an estimation of arsenious acid in presence of vanadium was not successful. L. DE K.

Analytical Methods Employed in the Estimation of Caoutchouc. The Estimation of Caoutchouc as Tetrabromide. OTTO KORNECK (*Gummi Zeit.*, 1910, **25**, 4—9, 42—46, 77—87, 424).—A series of papers devoted to the description and discussion of numerous methods advocated for the analysis of rubbers, with a large number of examples showing that the same rubber gives divergent results under the varying methods employed by different workers. The methods discussed are : (1) By difference ; (2) direct precipitation, and (3) by means of derivatives, whilst the work of Ditmar, Jacobsen, Fendler, Schneider, Spence, Budde, and Harris is reviewed, and the results compared.

The final paper contains a criticism of Budde's method of estimating bromine in caoutchouc tetrabromide, a sketch of the apparatus employed, and description of the author's procedure in this analysis. F. M. G. M.

The Estimation of Caoutchouc as Tetrabromide. TH. BUDDE (*Gummi Zeit.*, 1910, **25**, 269—270).—A reply to O. Korneck's criticism (see preceding abstract) of the author's methods of estimating the various constituents of rubber, especially of caoutchouc as tetrabromide. F. M. G. M.

Examination of Raw Caoutchouc. Reply to Harries. GEORG FENDLER (*Gummi Zeit.*, 1910, **25**, 311—316, 351—353, 530).—An account of the author's methods of estimating caoutchouc, and a reply to O. Korneck's and C. Harries' criticisms of the same, with a discussion of the Fendler-Kuhn method. F. M. G. M.

Examination of Raw Caoutchouc. Reply to Fendler CARL D. HARRIES (*Gummi Zeit.*, 1910, **25**, 425).—A reply to the criticisms of G. Fendler and O. Korneck. F. M. G. M.

Hübener's Caoutchouc Tetrabromide. The Estimation of Mineral Rubber and Similar Products in Rubber. R. BECKER (*Gummi Zeit.*, 1911, **25**, 531, 598).—Exception is taken to the methods employed by Hübener for the analysis of caoutchouc as tetrabromide, it being stated that other resinous bromo-compounds are present owing to his method of purification. The second paper discusses the employment of different reagents, such as pyridine, carbon disulphide, and acetone, in the preliminary extractions before analysis. F. M. G. M.

Application of the Benedikt-Zigmondy Process for the Estimation of Glycerol in Wine. GUIDO VERONA RINATI (*Chem. Zentr.*, 1911, i, 41 ; from *Staz. sperim. agrar. ital.*, **43**, 656—659).—The process of Benedikt-Zigmondy (oxidation of glycerol to oxalic acid with permanganate in alkaline solution) may be applied to wines as follows: 100 c.c. of wine are concentrated with or without addition of sand to syrupy consistence, and the mass is extracted three or four times in succession with 15 c.c. of absolute alcohol. The filtrate is boiled for two minutes with 3—4 c.c. of strong hydrochloric acid, and then made alkaline with barium hydroxide solution. The solution is filtered, and the precipitate washed with warm alcohol. The alcohol is distilled off, and the barium removed with potassium carbonate. To the filtrate 20 c.c. of 25% aqueous potassium hydroxide and a judicious amount of powdered permanganate are added, and the mixture is heated to 40°. The solution, which should still have a rose colour, is then rapidly cooled, and filtered from the manganese peroxide. The filtrate is acidified with acetic acid, and 10 c.c. of a 20% calcium acetate solution are added. The calcium oxalate is converted into oxide and weighed. By multiplication by 1·638, the weight of the glycerol is obtained. L. DE K.

The Action of Iodine on Phenols and its Application to their Volumetric Estimation. I. Phenol, Salicylic Acid, β-Naphthol. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1911, **30**, 398—402).—The method recommended for the estimation of phenol is as follows: To the dilute phenol solution are added equal volumes of *N*/10-iodine and *N*/10-sodium carbonate. After five minutes, excess of sulphuric acid is added, and the residual iodine titrated with *N*/10-sodium thiosulphate. A pronounced fading of the brown colour due to the iodine, or, in extreme cases, the precipitation of 2:4:6-tri-iodophenol, indicates that too little iodine has been added; in such circumstances more iodine and sodium carbonate should be added, and the estimation completed in the usual manner after five minutes. The determination is best carried out in stoppered bottles.

In the above method, the potassium hydroxide recommended by Messinger and Vortmann (Abstr., 1890, 1473) is replaced by sodium carbonate. When the reaction between iodine and phenol in alkaline solution is allowed to proceed for five minutes only, the product formed is wholly tri-iodophenol, whereas after twenty minutes this compound is transformed to the extent of 95% into tetraiododiphenylenequinone (compare Bougault, Abstr., 1908, ii, 738), the iodophenol probably reacting as the ketodihydrobenzene tautomeride in alkaline solution (compare Wake and Ingle, Abstr., 1908, i, 416).

Salicylic acid may be determined similarly to phenol. If the sodium salt is taken, and not the free acid, tri-iodophenol is the sole or predominating product after five minutes' reaction; after a somewhat longer period, tetraiododiphenylenequinone is the main product (compare Bougault, *loc. cit.*). Equally satisfactory results were obtained with the methyl ester, salol, and many other derivatives.

The experimental figures, and also the preparation of 2:4:6-tri-iodophenol from both phenol and salicylic acid, show that this compound is the primary product of the reaction. The acetyl ester of salicylic acid does not absorb iodine if care is taken to avoid hydrolysis. A sodium *p*-phenolsulphonate reacts with four atoms of iodine, the reaction being complete in twenty to thirty minutes; no further absorption of iodine occurs on remaining for days, and no quinone product is formed. This supports the idea that the formation of the quinone product from phenols is due to their tautomerism in alkaline solution.

β-Naphthol gives an almost quantitative yield of 1 : 2-iodohydroxynaphthalene when its aqueous solution is treated with *N*/10-iodine in the cold. In the presence of the slightest excess of alkali hydroxide above that corresponding with the production of the sodium salt, a crystalline colourless product is no longer obtained, but a green, amorphous product (compare Messinger and Vortmann, *loc. cit.*). The estimation is best carried out as follows: To 150 c.c. of the solution containing 0·072 gram of β-naphthol are added 20 c.c. of *N*/10-iodine and two drops of *N*-sodium carbonate. The solution is heated in a stoppered bottle at 60° for fifteen minutes, cooled, sulphuric acid added, and the residual iodine titrated with thiosulphate.

When allowance is made for the moisture content, gallotannic acid is found to absorb twelve atoms of iodine, and not eleven, as stated by Gardner and Hodgson (Trans., 1909, **95**, 1819). T. S. P.

A Sensitive Test for the Detection of Phenol and Salicylic Acid. JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1911, **30**, 402—404).—To the solution of phenol or sodium salicylate are added 10 c.c. of *N*/10-iodine and 10 c.c. of *N*/10-sodium carbonate, and, after five minutes, 5 c.c. of 3*N*-sulphuric acid. On the addition of the acid, a precipitate of 2 : 4 : 6-tri-iodophenol is obtained immediately from solutions containing four parts per million of phenol, after five minutes from solutions containing two parts per million, and after one hour from solutions containing one part per million. In the case of salicylic acid the test can be used for solutions containing as little as one part per 870,000.

In testing for minimal amounts of phenol, it is of no importance whether the prescribed period of five minutes is exceeded, conversion of the tri-iodophenol into the red insoluble tetraiododiphenylenequinone (compare preceding abstract) only taking place slowly at such dilutions. T. S. P.

Response of Gums and Similar Substances to Moore's Reaction. TORALD SOLLMANN (*Amer. J. Pharm.*, 1911, **83**, 176—177).—Gums, such as acacia, tragacanth, and cherry-gum, and also agar, cetraria, and chondrus, give a golden or brownish-yellow colour when heated with sodium hydroxide solution, but they do not reduce Fehling's solution. As many of these gums contain reducing sugar, they must be washed thoroughly before the test is applied. It may be pointed out that all the sugars, etc., which give a coloration with sodium hydroxide also reduce Fehling's solution. W. P. S.

[Estimation of] the Volatile Fatty Acids. JEAN EFFRONT (*7th Intern. Congr. Appl. Chem.*, 1909, Sect. IV AI, 83—85).—The only method at present available for the analysis of a mixture of volatile fatty acids is that of Duclaux, depending on fractional distillation and the estimation of the acidity of the fractions, and this breaks down completely when more than two acids are present. Better results are obtained by converting the acids into esters, which are more readily fractionated. After saponification, each fraction contains at most two acids, which may be separated by Duclaux's method.

One hundred grams of the acid are converted into the sodium salt, dried, powdered, and introduced into a flask containing 110 grams of alcohol and 100 grams of sulphuric acid. After heating for seven hours in a reflux apparatus, the esters are distilled by means of superheated steam, washed until free from acid, and fractionally distilled. Only 75–80% of the original mixture is thus obtained, a part of the acid escaping esterification and part of the esters remaining dissolved in the washing water. The first part may be recovered by distilling the washing water with phosphoric acid, and the second by saponification, after distilling the neutralised solution. The method is subject to errors of as much as 5%, but is useful in the analysis of the mixtures of fatty acids now obtained abundantly from sugar residues.

C. H. D.

Estimation of Citric Acid in Milk. EM. DESMOULIÈRE (*Chem. Zentr.*, 1910, ii, 1951; from *Bull. Sci. Pharmacol.*, **17**, 588—594).—Two hundred c.c. of milk are boiled a short time with 100 c.c. of 2% acetic acid in a reflux apparatus. When cold, the liquid is filtered, and 150 c.c. of the filtrate are concentrated on the water-bath to pasty consistency, and, after adding two to three grams of purified "Kieselgur," evaporated to dryness. When cold, 3 c.c. of dilute sulphuric acid (0·2 gram per c.c.) are added, and the mixture is allowed to remain for two to three hours with frequent stirring; another 3 grams of "Kieselgur" are then stirred in, and the whole is extracted with cold ether saturated with water until 1000 c.c. of ethereal extract have been obtained. The ether is now evaporated at a gentle temperature, the residue is taken up with water, and diluted to a definite volume. In an aliquot part of the liquid, the joint acidity is estimated, and in the same volume any phosphoric acid is determined and allowed for. A third portion is examined for possible volatile acids. Cow's milk contained 2·21—2·04%; goat's milk, average 1·386%; human milk, 0·785%; sheep's milk, 1·075%; mare's milk, 2·198% of crystallised citric acid.

L. DE K.

Clinical Process for the Estimation of Uric Acid in Blood Serum. PAUL ROETHLISBERGER (*Chem. Zentr.*, 1910, ii, 1952—1953; from *Münch. med. Woch.*, 1911, **57**, 344—347).—The method is based on the reduction of silver carbonate by uric acid. A strip of silver paper is impregnated with sodium carbonate, and blood-serum is dropped on to it. According to the amount of uric acid present, a yellow, brownish-red, or dark brown spot is obtained. A check experiment is then carried out with solutions of uric acid of known strength; light should be excluded.

L. DE K.

Analysis by means of Miscibility Curves; Application to the Examination of Cod Liver Oils. ÉMILE LOUÏSE (*J. Pharm. Chim.*, 1911, [vii], **3**, 377—385).—This method depends on the fact that when partly miscible liquids are mixed in such quantities that the mixture when kept separates into two layers, the composition of the two layers remains constant for any one temperature, and that, on warming, the mixture becomes homogeneous at a temperature which depends on the relative quantities of the two liquids present.

In the case of cod liver oil, varying quantities of oil are mixed with a constant quantity of acetone, and the temperature at which a homogeneous solution is effected in each case is noted. A curve expressing the relationship between the temperatures found and the concentrations of oil is then constructed. For the same type of oil, the curve is of the same form, but the method is delicate enough to distinguish between "pale" and "brown" cod liver oils. T. A. H.

Identification of Colza Oil: Its Detection in Olive Oil and in Other Food Oils. MASSIMO TORTELLI and V. FORTINI (*Gazzetta*, 1911, **41**, i, 173—182).—No special reaction is known for colza oil, as it has been shown that tests based on the assumption that sulphur is present in the oil are valueless, the pure oil containing no sulphur, and Palas's colour reaction (*J. Soc. Chem. Ind.*, 1897, **16**, 361) is given by any oil in which occur traces of substances capable of reducing silver nitrate.

A preliminary test may be made by determining the critical solubility temperature of the acids of the oil. Five c.c. of the total fatty acids, separated in the usual way, are mixed with 10 c.c. of 70% alcohol, and the mixture heated in a water-bath and stirred until complete solution occurs. The liquid is then allowed to cool slowly, and its temperature noted when the fatty acids separate. For olive oil, this temperature is 16°; for two foreign samples, 18° and 20°; for an old sample, 36°; for arachis oil, 59°; for colza oil, above 80°; for sesamé oil, 53°; for cottonseed oil, 67°; and for olive oil containing 10% of arachis oil, 45°.

Three other tests are suggested which are based on the presence of erucic acid in colza oil: (1) The iodine number of the fatty acids giving a lead soap almost insoluble in ether, for colza oil this number is 62, and for olive oil about 8. (2) The m. p. of the fatty acids obtained from the lead soap mentioned under (1); for olive oil this m. p. is about 58°, and for cottonseed, arachis, and sesamé oils about the same, whilst for colza oil it is 41°. (3) A 2·5% solution of the sodium salts of the same fatty acids in absolute alcohol precipitates these salts at about 24° in the case of olive oil; at about 20° for arachis, cottonseed, and sesamé oils; at about 48° for colza oil; at 40° for a mixture of colza and olive oils in equal proportions, and at 34—35° for mixtures of these oils containing from 10% to 30% of colza oil.

Detailed methods are given for carrying out the various tests.

T. H. P.

Estimation of Fat in Pathological Urine. SAMURO KAKIUCHI (*Biochem. Zeitsch.*, 1911, **32**, 137—144).—The author gives details of the method employed for estimating higher fatty acids in normal urines, which he found to be of the practically negligible quantity of

0·0236 gram per 10 litres. He separates the benzoic acid (from hippuric acid), etc., obtained in the light petroleum extract obtained after hydrolysis by exposure for some hours at 100° in a vacuum (the apparatus employed for which process is figured). The benzoic acid under these conditions volatilises, whereas the higher fatty acids do not. The fatty acid in chyluric urines were then estimated by the Kamagawa-Suto method, the same process being employed to separate the benzoic acid, etc., in the light petroleum extract; 50 grams of chyluric urine in one case were found to contain 0·2115 gram of higher fatty acids, a number which agreed well with that obtained by the older method of extracting the protein precipitate from the urine by alcohol. S. B. S.

Estimation of the Saponification Number. LUDWIG W. WINKLER (*Zeitsch. angew. Chem.*, 1911, **24**, 636—638).—The use of propyl alcohol is recommended for the preparation of the alcoholic potassium hydroxide solution employed for saponifying the fats and waxes. Propyl alcohol is a good solvent for fats and waxes, and, as a higher temperature may be obtained during the saponification process than when ethyl alcohol is used, even beeswax is saponified completely after ten minutes' boiling. W. P. S.

Simplified Method for the Estimation of the Acid and Saponification Numbers of Waxes. ALEXIS WICHMANN (*Pharm. Zentr.-h.*, 1911, **52**, 363—367).—It is recommended that the saponification of wax be carried out in a closed flask at a temperature of 100°. One gram of the sample is placed in a round-bottomed flask, 10 c.c. of absolute alcohol are added, and the flask is then securely closed and placed in a steam sterilising apparatus; after the lapse of five minutes, during which time the contents of the flask have been shaken once, the flask is withdrawn from the apparatus, and the acidity of the solution is titrated, using phenolphthalein as indicator. A measured excess of *N*/2-alcoholic potassium hydroxide solution is now added, the flask is again closed, placed in the sterilising apparatus, and its contents are shaken at intervals of five minutes. After being heated for twenty-five minutes, the excess of alkali is titrated. Each time the flask is withdrawn from the sterilising apparatus, it must be allowed to cool for three minutes before being opened. W. P. S.

Methods of Estimating Trimethylamine in Urine. Contribution to the Study of Lecithin Metabolism. P. CACCIA (*7th Intern. Congr. Appl. Chem.*, Sect. IV A, **2**, 69—73).—Various sources of inaccuracy in the method of Serono and Percival for the estimation of trimethylamine in urine are pointed out. The procedure of De Filippi is to be preferred. From his experiments the author draws the conclusion that the small quantities of trimethylamine met with in urine are really present as such, and are not formed by secondary reactions during the chemical operations involved in the estimation. R. V. S.

Estimation of Alkylamines obtained from Urine after Kjeldahl Digestion. C. C. ERDMANN (*J. Biol. Chem.*, 1911, 9, 85—92).—The method described in an earlier paper (Abstr., 1910, ii, 1008) for separating alkylamines from ammonia in the Kjeldahl distillate has been applied to the estimation of organic bases in urine. The results show that the amount of alkylamine yielded by urine when treated in this way is fairly constant, but is increased by the administration of methylcarbamide. Creatinine, however, does not cause any variation in the amount of alkylamine, and methylamine hydrochloride produces only a very slight increase. E. G.

Capsaicin, the Pungent Principle of Capsicum, and the Detection of Capsicum. E. K. NELSON (*J. Ind. Engin. Chem.*, 1910, 2, 419—421).—Although capsaicin, the pungent principle of pepper, was isolated by Micko (Abstr., 1899, i, 716), a further study of the pure substance seemed desirable. A process for its extraction from African cayenne is described. The substance forms pearly leaflets, m. p. 64·5° (Micko, *loc. cit.*, gives 64°).

An extended search for chemical tests for the recognition of small quantities of capsicum when present in ginger ale and other pungent beverages leads to negative results; the conclusion is drawn that detection must depend on the physiological action of capsaicin, and a modification of Garnett and Griers' method for its identification is described. F. M. G. M.

Microchemical Studies. V. A. BOLLAND (*Monatsh.*, 1911, 32, 117—131. Compare Abstr., 1910, ii, 748).—A microchemical examination of the compounds obtained from the usual alkaloidal reagents and the following 34 alkaloids: anagyrine, alstonine, anhalonine, mescaline, pellotine, quebrachine, aspidospermine, *apo*atropine, homoatropine, methylatropine, atroscine, belladonine, bebeerine, hydroberberine, oxyacanthine, boldine, carpaine, conessine, corydaline, bulbocapnine, ditaine, cephaeline, erythrophleine, gelsemine, lupinine, *apo*morphine, *apo*codeine, hydrocotarnine, ethylnarceine, pereirine, pilocarpidine, oxysparteine, sabadine, and sabadinine. A very large majority of the compounds are amorphous. C. S.

Estimation of Aconitine with Silicotungstic Acid. H. RIBAUT (*Chem. Zentr.*, 1911, i, 431; from *Bull. Sci. Pharmacol.*, 17, 634—639).—The following points were observed. The composition of the aconitine precipitate depends on that of the liquid from which the precipitation takes place. The richer the liquid is in nitric acid or silicotungstic acid, the more silicotungstic acid does it contain. The solubility of aconitine silicotungstate depends on the amount of nitric or silicotungstic acid, particularly the former. If the liquid contains 2·3% of nitric acid and 0·5% of free silicotungstic acid, and if all the conditions given in the Codex are observed, the factor 0·793 proposed by Ecalle gives satisfactory results without any correction for solubility. L. DE K.

Estimation of Atropine. Titration of the Alkaloids in Belladonna Extracts MAURICE JAVILLIER (*Chem. Zentr.*, 1911, i, 430; from *Bull. Sci. Pharmacol*, 17, 629—634).—To the alkaloidal solution, which should not be too dilute, is added so much hydrochloric acid that the liquid contains 2% of the same. While stirring, a 10% solution of silicotungstic acid is dropped in in slight excess, and after twenty-four hours the precipitate is collected, washed with 1% hydrochloric acid, and burnt to ash. The weight of this × 0·4064 represents the atropine. As the atropine compound is not quite insoluble in water, a correction should be made of 0·0048 gram of atropine for every 100 c.c. of the mother liquor. Some samples of belladonna extracts examined by this method, which the author states to be correct, gave considerably less atropine than indicated by the usual titration process. L. DE K.

Estimation of Nicotine in Concentrated Tobacco Juices. JOHANNES SCHRÖDER (*Chem. Zeit.*, 1911, **35**, 382. Compare this vol., ii, 163, 345).—Attention is again called to the most unsatisfactory processes used for the assay of nicotine in commercial tobacco extracts. Portions of the same extracts having been forwarded to different analysts, one working by Schlœssing's and another by Kissling's process, they respectively reported 6·41% and 6·23% of nicotine. Two other analysts (processes used unknown) reported 9·40% and 8·80%. L. DE K.

Assay of Coca Leaves. ANNE W. K. DE JONG (*Arch. Pharm.*, 1911, **249**, 209—214).—A reply to Bierling, Pape, and Viehöver (this vol., ii, 344), who criticise and suggest modifications in the author's process for the assay of coca leaves (Abstr., 1905, ii, 778 ; 1909, ii, 276).

The emulsion formed when the acid liquors are shaken with light petroleum is easily broken up by running the acid solution with the emulsion into a beaker, and passing a current of air through it. The use of hydrochloric acid stronger than the 0·5% solution recommended by the author presents no advantage in preventing the formation of emulsion. Light petroleum gives a slightly higher result for "total alkaloids" than ether. The author deprecates the use of methods in which the solvent is allowed to remain in contact with the leaves in place of extraction in a Soxhlet aaparatus, since in the former type of process some alkaloid is always left in the leaves. The higher results furnished by Panchaud's method are probably not due to the use of less water, but to the fact that the ether is not cooled, and consequently evaporates to some extent, so that the aliquot part taken contains more alkaloid. Higher results are got by the author's method if ether at the atmospheric temperature is used in place of ice-cold ether, especially in the Tropics. T. A. H.

Substances which Mask the Colour Reactions of Strychnine. EFISIO MAMELI (*Gazzetta*, 1911, **41**, i, 329—334).—The two principal colour reactions for strychnine are : (1) Otto's reaction : violet streaks being formed in sulphuric acid in contact with potassium dichromate crystals ; (2) Mandelin's reaction : a bluish-violet coloration with a sulphuric acid solution of ammonium vanadate, changing to reddish-violet, and then to red gradually, or more rapidly on addition of water.

The author has investigated the effect on these reactions of a large number of organic compounds, including phenacetin, *o*- and *p*-phenetidine, *p*-aminophenol, salacetol, phenol, glycerol, anethole, phenetole, *β*-naphthol, acetonylacetone, salol, aniline, quinoline, *o*-toluidine, hexamethylenetetramine, acetic, tartaric, citric and salicylic acids, antipyrine, aspirin, menthol, etc.

Of the compounds commonly used as drugs, the only ones which have no influence on these two colour reactions are: caffeine, salophen, amygdophenin, theobromine, "saccharin," saligenin, sulphonal, trional, tetronal, veronal, and antithermin.

In order to get rid of disturbing compounds, advantage is taken of the slight solubility of strychnine in water and in all organic solvents except chloroform. Extraction with chloroform, evaporation, and repeated washing of the dry residue with ether is sufficient to free strychnine from the majority of admixed substances. T. H. P.

Colorimetric Estimation of Strychnine. E. SCANDOLA (*Chem. Zentr.*, 1911, 1, 593; from a Reprint from *Boll. Soc. Med.-chirurg. di Pavia*, 1910).—The solution, which should not contain any other alkaloid but strychnine, is evaporated to dryness, and 2 c.c. of Mandelin's reagent are added; this is made by dissolving 1 gram of ammonium vanadate in 200 grams of monohydrated sulphuric acid. When the solution has turned red, 10 c.c. of water are added, and the whole is then introduced into a graduated cylinder and diluted to 100 c.c. The coloration is then compared in a suitable apparatus with that obtained from solutions of strychnine sulphate of known strength.

L. DE K.

Estimation of Indole. HARALD SEIDELIN (*J. Hygiene*, 1911, 11, 118—121).—Dilute solutions of indole of known strength are treated with Ehrlich's solution (*p*-dimethylaminobenzaldehyde), alcohol, hydrochloric acid, and potassium persulphate, and, when the red colour so produced has reached a maximum, these are extracted with chloroform; the chloroform extracts form a colour scale for the subsequent estimation of indole. Fading due to oxidation is prevented by covering the chloroform with sterile physiological salt solution, and the tubes are closed with cotton wool and paraffin or rubber caps.

W. D. H.

A New Spectro-colorimetric Method of Estimating Indican in the Urine. ST. KOZŁOWSKI (*Bull. Acad. Sci. Cracow*, 1911, 47—56).—The method of estimation depends on the measurement of the coefficient of extinction of the product of oxidation for monochromatic light of two different wave-lengths. To test the method, experiments were made with solutions of pure indigotin and indirubin, both of which are formed in the oxidation process, and the extinction coefficients were determined for the sodium and the green mercury lines. For indigotin the absorption constant was found to be 0·0273 and 0·1106 respectively, the values for indirubin being 0·0586 and 0·0242.

On the basis of Vierordt's law, these data can be applied in the estimation of the quantities of indigotin and indirubin in a solution containing both, if the extinction coefficients for the sodium and mercury lines are determined for the mixed solution. Actual measurements show that the values obtained in this way are in moderate agreement with the true concentrations, the values for indigotin being, however, too high and those for indirubin too low. H. M. D.

Estimation of Indican in the Presence of Iodides, and their Estimation. C. J. REICHARDT (*Pharm. Zeit.*, 1911, **56**, 321).—Before applying the usual test for indican (by means of bleaching powder and chloroform), it is advisable to remove substances that interfere by means of lead acetate. The author, however, noticed that iodine, if present, is but imperfectly removed, and may be detected both in the filtrate and precipitate. An experiment is described where a person took a dose of 0·3 gram of sodium iodide, and after four hours 150 c.c. of urine were passed. Fifty c.c. of the urine were mixed with 30 c.c. of 10% solution of lead acetate, and the filtrate and washings were rendered alkaline with potassium hydroxide. After removing the lead hydroxide by filtration, the liquid was mixed with a little starch solution, and ferric chloride was added until the colour became black One c.c. of *N*/10-thiosulphate was now added at once, and the reddish-brown liquid again titrated to black colour with *N*/10-iodine; 0·75 c.c. of thiosulphate was used = 0·028575 gram of iodine in 150 c.c. The precipitate was then treated with solution of ammonium chloride to dissolve the lead iodide, and the solution treated as before, when 0·3 c.c. of thiosulphate was used = 0·01143 gram of iodine in 150 c.c. From the 0·24 gram of iodine administered, 0·04 gram passed into the urine after four hours. L. DE K.

Experiments with the Biuret Reagent [Detection of Protein. etc.]. S. L. KANTOR and WILLIAM J. GIES (*Proc. Amer. Soc. Biol. Chem.*, 1910, xvii—xviii; *J. Biol. Chem.*, **9**).—Paper and other forms of cellulose completely decolourise the biuret reagent (and also Fehling's solution), a copper cellulose product being formed. Such paper may be used for the detection of protein or of reducing substances.
W. D. H.

Liebermann's Protein Reaction. W. ALBERDA VAN EKENSTEIN and JAN J. BLANKSMA (*Chem. Weekblad,* 1911, **8**, 313—315. Compare Abstr., 1910, i, 461, 762).—An investigation of the colour reactions produced by tryptophan with hexoses, methylpentoses, and pentoses. At the ordinary temperature tryptophan gives with ω-hydroxymethylfurfuraldehyde and concentrated hydrochloric acid a red coloration, which changes to reddish-violet and then to violet. The change is accelerated by heat, and the intensity of the coloration depends on the proportion of hydroxymethylfurfuraldehyde present. Since hexoses with hydrochloric acid yield hydroxymethylfurfuraldehyde, they also produce a similar series of colour changes on warming with hydrochloric acid and tryptophan.

When a mixture of hydrochloric acid and tryptophan is warmed with δ-methylfurfuraldehyde or rhamnose, a violet-tinted red coloration is produced.

Proteins with a tryptophan residue, but lacking a hexose group, undergo scarcely any change when heated with concentrated hydrochloric acid. A trace of hydroxymethylfurfuraldehyde produces the red to violet coloration. 2-Methylfurfuraldehyde and hydrochloric acid impart a rose to purple-red colour to proteins and to methylpentoses, such as rhamnose.

When warmed with ω-hydroxymethylfurfuraldehyde, 2-methylfurfuraldehyde, or furfuraldehyde, proteins lacking a tryptophan residue give no coloration. But when a protein contains both a tryptophan residue and a hexose group, warming with concentrated hydrochloric acid converts this group into hydroxymethylfurfuraldehyde, which reacts with the tryptophan to produce the violet coloration. These facts explain Liebermann's protein reaction.

No coloration is developed when tyrosine or phenylalanine is heated with hydrochloric acid and hydroxymethylfurfuraldehyde, or 2-methylfurfuraldehyde, or furfuraldehyde. When scatole is heated with concentrated hydrochloric acid and ω-hydroxymethylfurfuraldehyde or hexoses, a violet coloration is produced; with 2-methylfurfuraldehyde or methylpentoses, the colour is dark-red to purple-red; with furfuraldehyde it is muddy, reddish-brown (compare Weehuizen, Abstr., 1907, ii, 308).

When heated with concentrated hydrochloric acid and hydroxymethylfurfuraldehyde, indole gives a light yellow to orange-red coloration, the tint depending on the concentration; with furfuraldehyde it produces a brownish-red tint (compare Fleig, Abstr., 1908, ii, 1077). A. J. W.

The Quantitative Chemical Analysis of Mixtures by Utilising Differences of Specific Gravity. Hans Friedenthal (*Ber.*, 1911, 44, 904—908).—The author recommends the more extended utilisation of differences of density for the separation and estimation of mixtures.

Bromoform or methylene iodide, diluted to the requisite density by the addition of toluene or xylene, are serviceable liquids for the separation of salts, carbohydrates, and proteins by this method.

Where necessary, the separation may be effected by means of a centrifuge, a special separating funnel, with no projecting parts, having been devised for use in this case.

A second method of utilising the differences in density for the quantitative analysis of solutions consists in increasing the centrifugal force. By means of a centrifuge making 10,000 revolutions per minute, casein can be completely separated from milk in three hours, and milk fat separated into a solid and a liquid layer.

The differences of density may be accentuated by bromination or treatment with iodine, and the separation of unsaturated compounds thereby more readily accomplished. By treating milk fat with iodine, and subsequently centrifuging, the unsaturated fats may be readily separated.

With centrifuges of high revolution, it has been found possible to separate many colloids from solution. F. B.

Action of Metals in the Presence of Hydrogen Peroxide on the Reagents for Blood. FRANZ MICHEL (*Chem. Zeit.*, 1911, **35**, 471).—The following scheme is recommended in order to determine whether a substance consists of inorganic or organic oxidisers, or contains organic catalysts:

(1) The substance gives a green coloration with the leucomalachite-green reagent, without the addition of hydrogen peroxide. Oxidisers, such as ferric salts, halogens, manganese dioxide, etc., are present. These substances also give a red colour with an aqueous solution of 2 : 4-diaminophenol hydrochloride. (2) With the above reagent alone, the substance gives no coloration, but on the addition of hydrogen peroxide a more or less intense green colour gradually develops. Metals, such as iron or copper, the compounds of which readily give up oxygen, may be present, as also blood or pus. A few c.c. of a colourless 1% solution of diaminophenol hydrochloride are now added to the green solution. If a red colour is immediately produced, an inorganic catalyst is present. If the green colour is unaltered, an organic catalyst, such as blood, is present. T. S. P.

New Chemical Reaction for Blood. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1911, **50**, 57—67).—The reagent is prepared from Baeyer's eosin hydrate (this Journ., 1877, i, 200), which is produced by dissolving 0·2 gram of eosin in 200 c.c. of 20% potassium hydroxide solution at the boiling point. After cooling, 55 c.c. of hydrochloric acid (D 1·19) are added, and the orange-coloured precipitate obtained is collected and dried. The reagent consists of an alcoholic solution of this substance, which, just before use, is rendered alkaline with potassium hydroxide and treated with a few drops of 10% hydrogen peroxide. The blue liquid obtained rapidly becomes yellow in contact with blood, the reaction being apparently specific for hæmoglobin and its derivatives containing iron. The only other substances found to give it are potassium ferricyanide and potassium permanganate, but these turn the blue solution yellow in the absence of hydrogen peroxide, whilst blood does not.

Convenient modifications of the test are described for the recognition of blood-stains, and of blood in urine and fæces. R. V. S.

Peroxydase of Cow's Milk and the *p*-Phenylenediamine Reaction. ÉMILE NICOLAS (*Bull. Soc. chim.*, 1911, [iv], **9**, 266—269).—Boiled cows' milk, or the casein precipitated therefrom by alcohol, magnesium sulphate, or acetic or lactic acid, gives a blue coloration with *p*-phenylenediamine and hydrogen peroxide, provided that sufficient hydrogen peroxide is used. The coloration is due to the interaction of casein with an oxidation product of the amine. Such milk or casein does not give any reaction with guaiacol and hydrogen peroxide, unless a peroxydase is added. In distinguishing between raw and boiled milk, therefore, by the *p*-phenylenediamine test, one drop only of hydrogen peroxide solution (1 vol.) per c.c. of milk should be used, as this quantity gives a blue coloration if peroxydase is present, but no coloration with boiled milk or the casein precipitated from this (compare Bordas and Touplain, Abstr., 1910, ii, 57, 226).

T. A. H.

General and Physical Chemistry

The Theory of Refraction Constants. Otto Wiener (*Ber. K. Sächs. Ges. Wiss. Math.-phys. Kl.* 62, 1910, 256—277).—Mathematical; the author obtains for the dielectric constant of a mixture consisting of one substance imbedded in another a generalised Lorenz-Lorentz expression which involves a "form-number" u. This number is determined by the shape of the imbedded particles, and is greater than 2 when the particles are not spherical. The values of u in different cases are discussed; it is shown also how they may be derived from optical data. The results obtained for different substances correspond in general with their relative molecular complexities. The advance with respect to previous empirical improvements of the Lorenz-Lorentz formula consists in the mode of deduction and the theoretical interpretation of the quantity u. F. M. G. M.

Refractive Index of Water. Gregory P. Baxter, Laurie Lorne Burgess, and Herbert Wilkens Daudt (*J. Amer. Chem. Soc.*, 1911, 33, 893—901).—In connexion with a study of the refractive indices of salt solutions and the refractive constants of dissolved salts (following abstract), a knowledge of the exact value of the index of refraction of water at 25° was required. Determinations of the constant have, therefore, been made at this temperature, and also at 20° and 30°, special attention being devoted to the purity of the water and the careful regulation of the temperature. The values obtained for $[n]_D$ are 1·33299 at 20°, 1·33248 at 25°, and 1·33190 at 30°, when referred to air at the same temperatures, and 1·33335 at 20°, 1·33284 at 25°, and 1·33225 at 30°, when referred to vacuum. These values are probably correct within 0·00002. E. G.

Refractive Power of the Halogen Salts of Lithium, Sodium, and Potassium in Aqueous Solution. Gregory P. Baxter, Arthur C. Boylston, Edward Mueller, N. Henry Black, and Philip B. Goode (*J. Amer. Chem. Soc.*, 1911, 33, 901—922).—Much work has already been done on the refractive indices of solutions of electrolytes, but the accuracy of most of the results is regarded as doubtful, insufficient care having been taken, in many cases, to ensure the freedom of the substances from probable impurities, especially moisture.

The densities and refractive indices of solutions of the chlorides, bromides, and iodides of lithium, sodium, and potassium have been determined at 25° at various concentrations.

The increase in density of the solutions with increasing concentration is nearly, but not quite, proportional to the quantity of salt in unit volume. The values obtained by dividing the differences between the densities of the solutions and of water by the molal concentrations have been calculated. These increments decrease slowly with increasing concentration, except in the case of lithium iodide. This decrease is due to the contraction which takes place during the solution of most salts in water, lithium bromide and iodide being exceptions to the rule and showing expansion during solution.

Similar increments have been calculated for change in the refractive index, and these also decrease slowly as the concentration increases. The increments are closely additive at equivalent concentrations, especially at low concentrations, indicating that the ionic, but not the molecular, increments are nearly constant. The increments for potassium salts are uniformly lower than those for sodium salts, whilst those for lithium salts are the lowest; this peculiarity is doubtless closely connected with the contraction or expansion which takes place when the salts are dissolved.

It is pointed out that a refractive constant for one component of a solution cannot be entirely satisfactory, if calculated on the assumption that the specific refraction of the other component remains constant in solution and equal to that of the pure substance, since, in general, specific rotation changes with even slight changes of conditions. The specific refractions of the nine salts are nearly constant, but increase slightly as the dilution increases. The molecular refractions are nearly additive at all concentrations.

E. G.

Second Spectrum of Hydrogen in the Extreme Red. F. Croze (*Compt. rend.*, 1911, **152**, 1574—1576).—The position and relative intensity of 72 bands in the secondary spectrum of hydrogen in the extreme red have been measured for wave-lengths beyond λ 6836 Ångström units. The results, which are given in tabular form, show no well-defined regularities in the distribution of the lines. The most intense are situated at λ 7072, 7325, 6916, and 7056. W. O. W.

Spectroscopy of Oxygen. Walter Steubing (*Ann. Physik*, 1911, [iv], **34**, 1003—1010).—Polemical against Kayser (this vol., ii, 237). H. M. D.

[Spectroscopic Investigations.] Johannes Stark (*Ann. Physik*, 1911, [iv], **34**, 1011—1014).—Polemical against Kayser (this vol., ii, 237). H. M. D.

Spectrum of Air Given by the Initial Discharge of the Spark with Self-induction. Gustave A. Hemsalech (*Compt. rend.*, 1911, **152**, 1471—1474. Compare this vol., ii, 449).—The true spark spectrum of air has been shown to differ from the spectrum produced by the oscillations following the spark. The former may be rendered more intense by blowing air across the electrodes, thus raising the potential. The intensity of the spectrum due to the initial discharge of a self-induction spark varies inversely as the capacity of the condenser and directly as the self-induction.

W. O. W.

Mineral Constituents of a Dusty Atmosphere. W. Noel Hartley (*Proc. Roy. Soc.*, 1911, *A*, **85**, 271—275).—Photographs of spark spectra between cadmium electrodes have been taken with exposures varying from one to sixty seconds. In the case of the longer exposed plates, the solar spectrum is overlaid by exceedingly fine dark lines, which are due to solid matter suspended in the atmosphere. Twenty-two such lines have been identified as those of elements known to be contained in atmospheric dust, namely, calcium, lead, copper, iron, manganese, nickel, magnesium, and carbon. Spectra of the spark discharge in hydrogen showed no trace of these lines. Determinations of the weight of material necessary to give the lines of these spectra have also been made. From these it appears that the calcium and copper reactions are more delicate than the test for sodium by the yellow flame or even by the photography of the ultimate lines of sodium in the oxyhydrogen flame and spark. The reactions of lead, manganese, and magnesium in the spark are much more sensitive than those of sodium, calcium, or copper. H. M. D.

Regularities in the Spectrum of Neon. HERBERT E. WATSON (*Proc. Camb. Phil. Soc.*, 1911, **16**, 130—135).—From an examination of the spectrum of neon it is found that, if the bright lines only are considered, the spectrum exhibits three groups of lines which diminish in general intensity towards the ultra-violet end of the spectrum.

The first group, which extends from the extreme red to $\lambda = 4071$, consists of one very bright line, one weaker line, three quadruplets, and three triplets. The second group, extending from $\lambda = 3754$ to $\lambda = 3370$, contains one very bright line, one weaker line, three quadruplets, and four triplets, whilst the third group, extending from $\lambda = 3167$ to $\lambda = 2736$, contains two bright lines, three quadruplets, and six (or possibly only five) triplets. The differences between the frequencies of the first and second, first and third, and first and fourth lines in the systems of quadruplets are respectively 1070, 1429, and $1847 \times 10^8/\lambda$.

The arrangement of the lines resembles closely the blue portion of the red argon spectrum investigated by Rydberg. H. M. D.

The Separation of the Spectral Lines of Calcium and Strontium in the Magnetic Field. B. E. MOORE (*Physikal. Zeitsch.*, 1911, **12**, 443—445).—From measurements of the separation of the lines of calcium and strontium under the influence of a strong magnetic field, it is found that Preston's law is not satisfied in the majority of cases. For both elements, however, the lines of the second subsidiary series and the first lines of the first subsidiary series are resolved in accordance with the requirements of this law.

H. M. D.

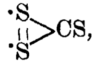
Vacuum Tube Spectra of Mercury. FRANK HORTON (*Proc. Roy. Soc.*, 1911, *A*, **85**, 288—302).—Experiments with mercury vacuum tubes are described, which show that several spectra can be obtained which depend on the electrical conditions of the discharge. The particular spectrum appearing in a given case depends on the energy of the discharge in relation to the mass of vapour through which it passes. The simplest spectrum consists of five lines, and this is always obtained when both limbs of the tube are fairly hot and the discharge is running easily. As the energy of the discharge is increased or the pressure of the vapour diminished, more complicated spectra make their appearance. All the lines of each spectrum appear at the same moment as the electrical conditions become suitable to its production.

Two of the methods employed for producing different spectra of mercury are referred to as being of particular significance for spectroscopic purposes. In one of these, discharge takes place under a low potential difference with the aid of a glowing lime cathode, whilst in the other, discharge is effected in an electrodeless ring by electro-magnetic induction. H. M. D.

The Absorption Spectra of the Vapours of Some Sulphur Compounds. John E. Purvis (*Proc. Camb. Phil. Soc.*, 1911, **16**, 155—160. Compare Trans., 1910, **97**, 2287).

—Observations relating to the absorption spectra of the vapours of ethyl trithiocarbonate, diethyl thionthiolcarbonate, ethyl thioloxalate, and propyl dithioloxalate are recorded which show the influence of temperature between about 15° and 100°, and of pressure between about 760 mm. and 950 mm.

Each of the vapours exhibits one large absorption band which widens as the temperature and pressure are increased. This band is comparable with that previously found in alcoholic solution, although the latter lies nearer the less refrangible end of the spectrum. There is no formation of series of narrow bands analogous to those found in the vapour of carbon disulphide. The broad absorption band is supposed to be due to a ring structure, and the four compounds examined are represented as containing respectively the ring forms: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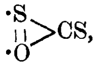
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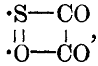
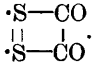

$\begin{matrix}\cdot S-CO\\ \|\quad\;|\\ \cdot O-CO\end{matrix}$, and


$\begin{matrix}\cdot S-CO\\ \|\quad\;|\\ \cdot S-CO\end{matrix}$.

H. M. D.

Investigation of Emission Spectra of Solid Aromatic Substances by means of the Ultra-violet Filter. Eugen Goldstein (*Ber. Deut. physikal. Ges.*, 1911, **13**, 378—392. Compare Abstr., 1904, ii, 689, 690; 1910, ii, 469, 671).

—The ultra-violet filter described by Wood can be conveniently employed in the investigation of the emission spectra of substances which are excited by radiation of very short wave-lengths. It is found that a large number of aromatic compounds, under the influence of the ultra-violet rays thus obtained, exhibit discontinuous emission spectra which are identical with the initial spectra which appear as the first and transient result of the action of cathode rays. Excitation by ultra-violet rays affords therefore a means of studying the detailed structure of the initial spectra. When aromatic ketones or aldehydes are acted on by cathode rays, the chief spectrum is developed immediately, and no evidence of an initial spectrum is obtained. A similar result is found in the action of the ultra-violet rays on these substances.

As with the cathode rays, many aromatic compounds give rise to after-glow spectra (solution spectra) when the ultra-violet rays cease to act. These spectra, the intensity of which increases as the temperature falls, are in all probability due to the presence of traces of impurities. Fractionation experiments are described in support of this view.

When the chief spectrum of a substance has been developed by the action of cathode rays, and the substance is then acted on by ultra-violet rays, these give rise to the chief spectrum instead of the initial spectrum. This indicates that the original substance is modified by the action of the cathode rays, and that the chief spectrum is due to the transformed substance.

The fact that certain substances give emission spectra when acted on by cathode rays, but not when subjected to ultra-violet rays from the filter, is probably due to the remote position occupied by the region of selective absorption in the ultra-violet. Rays of such small wave-length are not transmitted by the filter. H. M. D.

Some Causes of the Formation of Colour in Inorganic Compounds. C. Reichard (*Pharm. Zentr.-h.*, 1911, **52**, 591—597).—A discussion of the colour of inorganic compounds as compared with the colour of the elements from which they are built up. The effect of temperature, state of division, etc., on the variation in colour is dealt with, but no explanation of the colours is given.

T. S. P.

The Colorimetric Dilution Law and its Application to Triphenylmethyl. Jean Piccard (*Annalen*, 1911, **381**, 347—351).—According to Beer (*Ann. Phys. Chem.*, 1852, **86**, 78), the observed intensity of a coloured solution as observed by looking down on the solution placed in a cylinder does not alter during the addition of more of the solvent. The same law holds good when the dissolved material consists of two isomeric modifications in equilibrium with one another. The ratio of the concentrations of the two forms is constant, and hence the colour is constant and independent of the dilution $C^1/C^2 = K$. When, however, the one modification is a dissociating polymeride of the other, the relationships are different; then $C/c^n = K^1$. With increasing dilution the value of C diminishes more rapidly than the value of c.

When solutions of triphenylmethyl in absolute ether are examined in the colorimeter, it is noticed that the yellow colour of the solution increases in intensity during dilution up to a certain maximum value. The colourless triphenylmethyl is presumably a polymeric form of the yellow unimolecular form (compare Schmidlin, Abstr., 1908, i, 623).

J. J. S.

Absorption of Light of Some Corresponding Ethane, Ethylene, and Acetylene Derivatives. Hans Stobbe and Erich Ebert (*Ber.*, 1911, **44**, 1289—1294).—The authors have investigated the ultra-violet absorption spectra of the following groups of compounds in alcoholic solution, and find that the replacement of a single linking by a double or triple linking causes, in all groups, a displacement of the absorption bands (or, in the case of continuous absorption, of the absorbed region) towards the visible spectrum, but the effect in the case of a triple linking is not so great as that of a double linking: (1) Ethylbenzene, styrene, phenylpropiolic acid; (2) β-phenylpropionic, phenylpropiolic and the stereoisomeric cinnamic acids; (3) phenyl phenylethyl ketone, phenyl styryl ketone and phenyl phenylacetylene ketone; (4) dibenzyl, stilbene and tolane; (5) diphenylbutane, diphenylbutadiene, diphenyldiacetylene and diphenylbuteninene.

The formation of reduction or additive products from acetylenic compounds, whereby the triple linking is converted into an ethylenic linking, is therefore accompanied by a deepening of the colour, and the same is true of the formation of polymerisation products.

The polymerisation of phenylpropiolic acid to 1-phenylnaphthalene-2 : 3-dicarboxylic acid causes a displacement of the limits of absorption towards the visible spectrum, by about 700 oscillation frequencies.

F. B.

Fluorescence and Radioluminescence of Some Hydrocarbons with Ethane, Ethylene, and Acetylene Residues. HANS STOBBE and ERICH EBERT (*Ber.*, 1911, **44**, 1294—1297).—The fluorescence and radioluminescence of (1) dibenzyl, stilbene and tolane, and (2) of diphenylbutane, diphenylbutadiene, diphenylbuteninene and diphenyldiacetylene have been investigated, and it is found that in the same series, hydrocarbons containing only single or triple linkings have approximately the same luminescence, whilst those containing double linkings show a much higher luminescent power. Thus, in the second series, the intensity of luminescence increases from the butane and diacetylene derivatives to a maximum with the butadiene compound, the luminescence of diphenylbuteninene having an intermediate value.

The effect accompanying the replacement of a single by a double linking is therefore much greater than that produced by the triple linking, which raises the power of luminescence to only a small extent.

The authors point out a connexion between the intensity of luminescence and the position and form of the ultra-violet absorption bands; increase in the intensity of luminescence is accompanied by a deepening of the absorption bands and their displacement towards the visible spectrum (compare preceding abstract). F. B.

Stokes' Law and a General Relation between Absorption and Phosphorescence. L. BRÜNINGHAUS (*Compt. rend.*, 1911, **152**, 1578—1580. Compare Abstr., 1910, ii, 88, 89).—A comparison of all the known absorption and emission spectra of organic and inorganic phosphorescent substances has shown that each group of bands of the emission spectrum is nearer the red than the corresponding and adjacent group of the emission spectrum. In this respect phosphorescent substances are in accord with the requirements of Stokes' law.

W. O. W.

Triboluminescence. P. N. VAN ECK (*Pharm. Weekblad*, 1911, 48, 581—588, 611—614, 654—665).—A summary of published work on triboluminescence. A. J. W.

Electrical Double Refraction of Carbon Compounds. RICHARD LEISER (*Chem. Zentr.*, 1911, i, 622—624; from *Abhandl. Deut. Bunsen Ges.*, 1910, No. 4, 1—71).—According to Kerr's formula the difference in path, Δ, expressed in terms of wave-lengths, between the ordinary and extraordinary rays in the case of electrical double refraction is given by the formula $\Delta = BlE^2$, where l is the distance in centimetres between the condenser plates used in the interference method of measurement, E is the strength of field, and B is the characteristic constant for the substance under investigation. In the case of carbon disulphide, which is used as the standard substance of comparison in this investigation, as well as for many other substances, B is approximately proportional to $1/\sqrt[3]{\lambda^4}$, where λ is the wave-length.

About 150 organic liquids have been investigated, the ratio of B to B_0 (the latter being the constant for carbon disulphide), being determined under different conditions of field strength, temperature, kind of light used, etc. A full description of the apparatus and method of measurement is given. Most of the data hold for room temperature, but in a few cases measurements were made over a temperature interval of 20°. The great variation in the behaviour of isomerides is illustrated by the following table, which gives the values of $100\ B/B_0$:

n-Butyl alcohol	−113	Benzyl alcohol	−477·0
*iso*Butyl alcohol	−137	*m*-Cresol	+657·0
tert.-Butyl alcohol	+154	Anisole	+ 35·5

No other physical property of organic liquids varies between such wide limits, and it is impossible to determine the atomic values of this property, as, for example, in the case of refractivity, etc. The value of B is very sensitive towards temperature, generally decreasing about 0·5% per degree, so that a comparison of the values obtained at room temperatures is somewhat arbitrary. Nevertheless, the value of B/B_0, excepting in the case of compounds such as nitroform, is fairly independent of the temperature. In some cases, for the purpose of comparison, the molecular electrical double refraction, MB/B_0d, is calculated, but generally the author deals only with the ratio $100\ B/B_0$.

For the hydrocarbons this ratio is always positive, generally small, and increases with the molecular weight; the symmetrical compounds give the smallest values. The following values of $100\ B/B_0$ have been obtained: benzene, 12·1; toluene, 24·3; ethylbenzene, 25·6; *o*-xylene, 41·2; *m*-xylene, 24·4; *p*-xylene, 22·6; ψ-cumene, 30·7; and mesitylene, 18·7. The saturated paraffins have especially small constants, which diminish as the chain becomes more branched; open and cyclic paraffins show very little differences. Each double linking increases the constants 6—9 units. Substitution of a hydrogen atom by a negative group greatly increases the constant: fluorobenzene, 191; chlorobenzene, 385; bromobenzene, 574; iodobenzene, 288; nitrobenzene, 10070; methyl iodide, 209; nitromethane, 330.

The following numbers for different alcohols illustrate the large effect of the introduction of the OH-group: methyl alcohol, 30; ethyl alcohol, about 0; *n*-propyl alcohol, −78; *n*-butyl alcohol, −113; *iso*propyl alcohol, 73; benzyl alcohol, −477; *tert.*-butyl alcohol, 154; *m*-cresol, 657.

The ethers are generally more negative than would be calculated from the means of the alcohol values; in most cases the constants are small, whereas those of the aldehydes and ketones are very large and positive: acetone, 505; acetophenone, 2060; benzaldehyde, 2490. Paraldehyde has a negative constant, −713, indicating the presence of ether linkings.

The fatty acids have small positive constants, the values of which are practically independent of the molecular weight in the higher members of the series; there is also a periodic rise and fall in the constants, similar to that observed in the case of the freezing points. This periodicity is found in several classes of compounds, as, for example, in the substituted aromatic hydrocarbons, whilst in the poly-substituted aromatic compounds definite regularities are observed. With increasing substitution in the paraffins, the constant first increases greatly, then diminishes rapidly to a large negative value, and finally approaches the original small positive value, as illustrated by: methane, about 12; methyl chloride, 200—300; methylene chloride, −36; chloroform, −100; carbon tetrachloride, 2·3.

Substances with high constants are the most reactive, those with low constants being slow to react. There are exceptions, however, as in the case of phenylhydrazine, the constant for which is almost zero. The constants are of great use in determining questions of constitution, and they show also a connexion with the dielectric constant.

The author connects his results with the electron theory of electro-optical effects. There is much to indicate that the individual molecules are anisotropic structures, which, contrary to what holds in the case of crystals, can assume all possible positions with respect to each other

T. S. P.

Radiations Decomposing Water and the Extreme Ultra-violet Spectrum of the Mercury Arc.

A. Tian (*Compt. rend.*, 1911, **152**, 1483—1485. Compare this vol., ii, 452).—The radiations decomposing water with formation of hydrogen and hydrogen peroxide are localised in the extreme ultra-violet, beyond λ 1900 Ångström units. The light from a quartz mercury lamp brings about this decomposition principally through the presence of the rays λ 1846, 1848, and 1851. An electric spark between aluminium electrodes emits the rays λ 1854, 1857·5, and 1862, and is also able to decompose water in the same way.

W. O. W.

Photocatalysis. Action of Light on Mixtures of Uranium Salts and Oxalic Acid.

Ludwik Bruner and J. Kozak (*Zeitsch. Elektrochem.*, 1911, **17**, 354—360).—Solutions containing uranyl nitrate and oxalic acid are exposed to strong daylight, a number of solutions being exposed simultaneously so as to obtain comparable results. The reaction is too slow in artificial light. Two reactions take place: $C_2O_2(OH)_2 = CO_2 + CO + H_2O$ and $C_2O_2(OH)_2 = CO_2 + H \cdot CO \cdot OH$, about 27% of the decomposition being due to the second. The addition of strong acids to the solution has no effect on the reaction. The rate of decomposition of the oxalic acid is independent of its concentration within wide limits. It increases with the concentration of the uranyl salt, but more slowly than this, tending asymptotically to a maximum. The effect of temperature on the rate of decomposition is too small to be measured. An attempt is made to measure the effect of varying the intensity of the light by wrapping the tubes containing the solutions with different numbers of layers of thin paper. The results indicate that light of less than a certain intensity produces little or no reaction; above this intensity the rate of change is almost proportional to the intensity. The analogy between this result and the electrolysis of a solution with increasing *E.M.F.*'s is pointed out.

No indication of the existence of a photochemical extinction could be observed. T. E.

An Apparatus for the Measurement of Radioactivity. BÉLA SZILARD (*Chem. Zeit.*, 1911, **35**, 539—540).—A delicately suspended magnetic needle in metallic communication with a metal band, within which it lies at the zero position, is contained on an insulator inside a flat circular box with glass top etched with a circular transparent scale. The position of the needle is read by a lens in the axis of the needle support. By means of a side plunger a charge can be given to the needle and its metal band. It is adjusted to zero uncharged by rotating the whole instrument, and then charged. The rate of movement of the needle on its return to zero in presence of a radioactive substance is used to measure the activity. For work with emanations, the instrument is mounted on a cylinder bearing a central electrode in connexion with the needle. F. S.

The Presence of Helium in Autunites and the Period of Life of Ionium. ARNALDO PIUTTI (*Le Radium*, 1911, 8, 204—205).—An examination of one of the specimens of Portuguese autunite investigated by Soddy (this vol, ii, 6) showed that the helium was largely present in the portion insoluble in hydrochloric acid. The spectrum of the gas from 3 grams of the original mineral containing 40% of autunite, obtained by calcining the mineral, was compared with that obtained by the calcination of 4·2 grams of the insoluble residue remaining after prolonged treatment with cold concentrated hydrochloric acid. The spectrum of helium was of similar intensity in the two specimens of gas. Since in dissolving the mineral in hydrochloric acid some of the helium in the insoluble residue may be evolved, calculations of the age of the autunite and of the life-period of ionium from this datum may be vitiated. F. S.

A Method of Making Visible the Paths of Ionising Particles through a Gas. CHARLES T. R. WILSON (*Proc. Roy. Soc.*, 1911, *A*, **85**, 285—288).—By using a suitable expansion apparatus the track of individual α- or β-rays, or of ionising rays of any kind, through a moist gas may be made visible by condensing water on the ions set free. The expansion chamber is cylindrical with flat, horizontal roof and floor, 7·5 cm. diameter, and between 4 and 5 mm. high before, and 6·2 mm. high after, expansion. The roof is coated below with a thin layer of clear gelatin, and the floor also with gelatin blackened by Indian ink, which prevents the deposition of dew on the chamber and forms an electrically conducting surface. Before expansion, a field of 16 volts per cm. acts to remove ions as fast as produced. The only ions "caught" on expansion are those produced within 0·025 second before expansion. For eye observation, a Nernst lamp and condensing lens, and for photography, a Leyden jar discharge through mercury vapour at atmospheric pressure (the mercury being boiled in a quartz tube) were employed, the spark being passed from 0·1 to 0·2 second after the expansion had taken place. The radium-tipped metal tongue of a spinthariscope is placed inside the chamber, and the individual trails of the α-rays are then clearly seen. Some of these show evidence of having divided into two trails, due to positive and negative ions under the influence of the field, prior to the moment ot exposure. Those photographed before diffusion has had time to occur are remarkably sharply defined lines. With β-rays, absolutely straight thread-like lines are generally seen radiating from the source, while similar lines due to secondary or reflected β-rays cross the field in other directions. With γ-rays, the cloud is localised in streaks and patches, and consists mainly in fine straight thread-like lines traversing the chamber in all directions, due to the β-particles from the walls of the vessel. With *X*-rays, the cloudlets are mainly thread-like objects, varying in length from a few millimetres to a fraction of a millimetre, rarely straight, and many showing a peculiar beaded structure. The results are in agreement with Bragg's view that the whole of the ionisation by *X*-rays may be regarded as due to cathode-rays or β-rays arising from the *X*-rays. The question as to the form of the *X*-ray wave-front remains undecided. F. S.

The Variation of Ionisation with Velocity for the β-Particles. W. Wilson (*Proy. Roy. Soc.*, 1911, *A*, 85, 240—248).—Separate determinations (1) of the charge carried, (2) of the ionisation produced by the β-rays of radium *B* and *C*, separated by means of a magnetic field into bundles of rays of different velocities, have afforded data for the determination of the relative amount of ionisation produced by the individual β-particle at different velocities. The determination of the charge carried by the rays, and therefore the number of β-particles worked with, was made by allowing the rays, after being sorted out by the magnetic field, to enter a box, closed except for a small hole where the rays enter, and to measure the charge gained by the box in a vacuum by means of the deflexion of an attached gold-leaf system. To measure the ionisation, a box of exactly similar character was employed in the same place in the apparatus as ionisation chamber, the pressure of the air being between 0·1 to 5 cm. of mercury. The increase of ionisation due to multiple reflexion of the rays from the walls of the box was separately determined and corrected for. As a result, it was found that the ionisation in free air per cm. of path produced by the β-particle varies inversely as the square of the velocity between velocities of 1·4 and 2·9 ($\times 10^{-10}$ cm. per second). This result should follow if the same amount of energy is required for the production of each ion, since the average time spent by the β-particle within the atom is inversely proportional to the velocity, and the work done by the electron within the atom is proportional to the square of the time. In thick metal vessels, owing to the complicated manner in which the β-particles are scattered, no simple connexion exists, the ionisation I in a thick copper vessel being approximately represented by the equation : $I = K(c - v)$, where v is the velocity, and K and c are constants. F. S.

Observation of β-Rays from Radium-*D*. OTTO VON BAEYER, OTTO HAHN, and LISE MEITNER (*Physikal. Zeitsch.*, 1911, **12**, 378—379).—A photograph of the magnetic spectrum of the β-rays of a product containing radium-*D*, -*E* and -*F* showed two groups of easily deviable β-rays due to radium-*D*. The velocity of these new rays is 0·37 and 0·31 (that of light = 1). These rays are therefore of the same order of velocity as the cathode rays. Only two of the members of radioactive series, actinium and mesothorium-1, remain in the disintegration, of which no rays have yet been observed. F. S.

The β-Rays of the Active Deposit of Thorium. OTTO VON BAEYER, OTTO HAHN, and LISE MEITNER (*Physikal. Zeitsch.*, 1911, **12**, 273—279).—The photographic examination of the magnetic spectrum of the β-rays of the active deposit of thorium distinguishes three homogeneous groups of rays, that from thorium-*A* with velocity 0·63, and two very easily deviable groups with velocities 0·34 and 0·28 (velocity of light = 1). There is another feeble group of homogeneous rays of velocity 0·72. The β-rays of thorium-*D* are not homogeneous, and range in velocity from 0·93 to 0·95. These results, taken in conjunction with others, lead to the general conclusion that β-rays above 70—80% of the velocity of light are more or less heterogeneous, whilst β-rays of lower velocity are homogeneous. The slower β-rays in passage through matter suffer reduction of velocity without loss of homogeneity. Thus the two groups of velocity 0·63 and 0·72, after passage through 0·045 mm. of aluminium, had velocities 0·57 and 0·68. The faster β-rays through passage of 0·3 mm. of copper, and 0·1 mm. of platinum, did not experience a change of velocity of 1%. The degree of heterogeneity was not affected. The heterogeneity is probably impressed upon the beam in the immediate neighbourhood of the point of expulsion of the rays through a reflexion or secondary radiation effect. The former conclusion that the exponential law of absorption of β-rays indicates homogeneity is modified in consequence of these results. F. S.

The Influence of Radium Rays on the Photo-electric Sensitiveness of Metals. H. DEMBER (*Ber. Deut. physikal. Ges.*, 1911, **13**, 313—327).—The influence of α-, β-, and γ-rays on the photo-electric activity of metals has been examined. With a copper plate in a high vacuum, the photo-electric activity is unaltered when the plate is acted on by α-, β-, and γ-rays. With a platinum plate in similar circumstances, the photo-electric activity increases under the influence of α-rays, but this is due to the secondary effect, which consists in the removal of the adsorbed gases when the surface of the plate is bombarded by the α-particles. In air at atmospheric pressure the phenomena of photo-electric fatigue, first observed by Crowther, are exhibited, but this is shown to be due to the ozone which is generated by the acting rays, and not to an action of the rays on the metal itself. H. M. D.

The Production of Characteristic Röntgen Radiations. R. WHIDDINGTON (*Proc. Camb. Phil. Soc.*, 1911, **16**, 150—154*).—When an element is acted on by primary Röntgen radiation of sufficiently high penetrating power, it emits a characteristic secondary radiation. In order to determine the nature of the primary radiation which is just sufficiently penetrating to cause an element to emit its characteristic secondary rays, the author has made experiments with cathode rays of different velocities. The critical velocities, which correspond with the commencement of the emission of the characteristic rays, were found to be as follows: aluminium 2·8, chromium 5·1, iron 5·7, nickel 6·1, copper 6·18, zinc 6·24, selenium $7{\cdot}25 \times 10^9$ cm. per second. These numbers show clearly that the critical velocity is nearly proportional to the atomic weight of the emitting element.

It has also been found that the energy of the Röntgen radiation for cathode rays of given velocity is proportional to the magnitude of the cathode ray current. H. M. D.

The Intensity of Secondary Homogeneous Röntgen Radiation from Compounds. J. CROSBY CHAPMAN and E. D. GUEST (*Proc. Camb. Phil. Soc.*, 1911, **16**, 136—141).—Measurements have been made of the characteristic secondary Röntgen radiation which is emitted by strontium in the form of chloride and sulphate, and by tin as free metal and in the form of the nitrate. Standardised rays from an *X*-ray bulb were allowed to fall on a thin sheet of the metal or compound under investigation, and the secondary radiation measured by means of a Wilson tilted electroscope. The experimental data show that the intensity of the characteristic secondary radiation is solely dependent on the quantity of the emitting element present, and is therefore a purely atomic phenomenon. This result supports the view that the characteristic secondary radiation does not result from the subsequent bombardment of atoms by ejected electrons, for, if this were so, the intensities of the radiation from a metal and its compounds could not be equal. H. M. D.

The Doppler Effect of Hydrogen Canal Rays. JOHANNES STARK (*Ber. Deut. physikal. Ges.*, 1911, **13**, 353—356).—The interpretation of observations on the Doppler effect exhibited by canal rays in hydrogen by Gehrcke and Reichenheim (this vol., ii, 166) is said to be inconsistent with experimental results obtained by other authors.
H. M. D.

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* and *Proc. Roy. Soc.*, 1911, *A*, **85**, 323—332.

The Action of Cathode Rays on Certain Minerals, and the Nature of the Mineral Colorations. CORNELIO DOELTER (*Monatsh.*, 1911, **32**, 299—318).—The colour changes produced by the action of cathode rays and in some cases of ultra-violet rays on rock salt, sylvine, corundum, zircon, ruby, topaz, kunzite, barytes, and celestine, have been examined. In the case of rock salt, the behaviour of the naturally-coloured blue mineral was compared with that of rock salt coloured artificially by means of sodium and that coloured by the action of cathode rays. The three forms exhibit considerable differences in regard to the effect of high temperature and of ultra-violet light on the coloration.

As yet no satisfactory explanation of the colour changes can be given. H. M. D.

The Behaviour of Radium Emanation at Low Temperatures. R. W. BOYLE (*Phil. Mag.*, 1911, [vi], **21**, 722—732).—The volatility of radium emanation at low temperatures (−130° to −180°) has been investigated by a new method, in which the emanation was contained in a bayonet-shaped tube drawn out to a fine tip at one end, where the emanation could be condensed, and closed at the other end with a very thin mica window, thin enough to allow α-rays to pass through. In this way the α-rays escaping from the window furnish a measure of the amount of emanation in the vapour phase, the α-rays from the condensed emanation not being able to impinge upon the window. The tip of the tube was cooled in pentane, surrounded with liquid air, which slowly evaporated, allowing the temperature to rise gradually while the ionisation produced by the α-rays was observed. With large quantities of emanation and insensitive measuring apparatus, volatilisation appeared to take place sharply at about −160°, but with smaller quantities of emanation and more sensitive measuring instruments, the volatilisation appeared to commence earlier, in one case as low as −170°. The volatilisation appears to be normal, and occurs to a varying extent over a wide range of temperature. F. S.

Typical Cases of Secondary Emanations Produced by Uranium-*X*. W. B. HUFF (*Ion*, 1910, **2**, 360—367).—Schmidt has established that the intensity of β-rays set up in metals by the action of uranium-*X* follows the order of their atomic weights, and the author by direct methods of comparing secondary emanations has confirmed this result. F. M. G. M.

The Complex Nature of Radium-*C*. KASIMIR FAJANS (*Physikal. Zeitsch.*, 1911, **12**, 369—378).—Recoil experiments with pure radium-*C*, deposited from the sulphuric acid solution of the active deposit from a large quantity of radium, on a nickel plate have established the view of Hahn and Meitner that radium-*C* is complex. The recoil product (radium-C_2) gives out β-rays only, within the experimental error of the same absorbability as the total β-radiation of the active deposit. The product radium-C_2 has a half-period of 1·38 minutes, its radioactive constant being 0·084[sec.]$^{-1}$. Since the α-radiation of the active deposit does not come from radium-C_2 or from its product, it must come from radium-C_1; but the amount of radium-C_2 recoiled from radium-C_1 is very small, and is much more than to be expected of a β-ray recoil than of an α-ray recoil. The β-activity of the recoiled radium-C_2 is only 1/20,000th of that of the source. Experiments on the recoil of radium-D from the same source showed that about 25% of the atoms of radium-D formed are recoiled. It follows in consequence that radium-D must be the direct product of radium-C_1, and not of radium-C_2, and that the production of radium-C_2 from radium-C_1 is the first case of a multiple disintegration experimentally observed. The series therefore runs:

$$\begin{tikzcd} & & & & & \text{Ra-}C_2 & & & \\ \text{Ra} \arrow[r] & \text{Em} \arrow[r] & \text{Ra-}A \arrow[r] & \text{Ra-}B \arrow[r] & \text{Ra-}C_1 \arrow[ur] \arrow[dr] & & & & \\ & & & & & \text{Ra-}D \arrow[r] & \text{Ra-}E \arrow[r] & \text{Ra}F \arrow[r] & {} \end{tikzcd}$$

It is suggested that radium-C_2 may be the parent of actinium. It is probable that only a small part of the β-rays of the active deposit are due to radium-C_2. The question as to what radiations the two kinds of disintegration of radium-C_1 are accompanied by remains to be investigated. The recoiled radium-C_2 is always accompanied by a minute amount of radium-C_1, which may be due to the volatility of the latter.

In an appendix [with WALTER MAKOWER] the phenomenon of the recoil of radium-C_2 in a high vacuum is investigated. No greater quantity of radium-C_2 was obtained, than at atmospheric pressure in an electric field, but the quantity of radium-C_1 was increased about fifty times.

F. S.

The Radioactivity of Some Igneous Rocks from Antarctic Regions.

ARNOLD L. FLETCHER (*Phil. Mag.*, 1911, [vi], 21, 770—773).—The radium and thorium contents of 13 specimens of rock from the Antarctic region of S. Victorialand have been determined. The richest was a Kenyt lava, coloured red by infiltration of geyser water, which contained 4·02 × 10^{-12} radium and 1·84 × 10^{-5} of thorium (grams per gram). Three other specimens contained above 2 and 1·3, two above 1·3 and 0·7, and the remainder below 1·0 and 0·5 respectively for the radium and thorium in the above units. Remarkable constancy occurred in both radium and thorium in specimens from the same locality, independently of the chemical or petrographical character of the rock, the ratio of the radium to the thorium being remarkably constant in all the specimens at about 1·7 × 10^{-7}. Tests to see whether the presence of thorium interfered with the method employed to estimate the radium gave negative results.

F. S.

The Association of Lead with Uranium in Rock-Minerals, and its Application to the Measurement of Geological Time.

ARTHUR HOLMES (*Proc. Roy. Soc.*, 1911, *A*, **85**, 248—256).—For minerals of the same age, the ratio of lead to uranium should be a constant if the lead originates from the uranium. By working on certain minerals, such as thorite, zircon, and certain apatites and sphenes, which segregate within themselves on crystallisation a much larger proportion of uranium than is contained in the magma, the amount of lead initially present may be neglected. If changes in the amounts of lead and uranium occur, due to external chemical agencies, it is improbable that the two elements will be equally affected, so that if constancy of ratio of these two elements is found, it may be assumed that the mineral has not undergone appreciable alteration. These considerations limit the investigation to fresh, stable, primary rock-minerals, and those from the Christiania district of Norway, a geologically depressed area of 4000 square miles separated on every side by faults from the surrounding Pre-Cambrian gneiss, have been selected, the minerals being a series of thorite-bearing nepheline-syenites, probably of lower Devonian age. The uranium was estimated by means of the radium emanation and the lead gravimetrically as sulphate, and also colorimetrically by Harcourt's method (Trans., 1910, **97**, 841), the amount of copper and bismuth being negligible. In seventeen minerals arranged in the order of uranium content, the Pb/U ratio of the first fifteen varied from 0·041 to 0·068. With few exceptions the ratio increased somewhat as the uranium decreased, possibly due to the lead initially present in the magma having a gradually increasing relative importance. For the last two minerals, nepheline and felspar, the amount of uranium was only 0·001 and 0·0006%, the Pb/U ratio being 0 4 and 0·5. The mean value taken for the age-estimation was Pb/U = 0·046, which gives the age as 370 million years. The analyses collected by Boltwood of the uranium and lead in minerals are discussed with reference to the probable ages of the minerals. Wherever the geological evidence is clear, it is in agreement with that derived from the Pb/U ratio. The ages indicated by the latter are as follow: Carboniferous 340; Devonian 370; Pre-carboniferous 410; Silurian or Ordovician 430; Pre-Cambrian, (*a*) Sweden 1025 and 1275; (*b*) U.S.A., 1310 and 1435; (*c*) Ceylon 1640; in millions of years. F. S.

The Emission of Negative Electrons by Heated Potassium and Sodium, and the Conductivity of the Vapours of These Metals. KARL FREDENHAGEN (*Physikal. Zeitsch.*, 1911, **12**, 398—408).—Measurements have been made of the electrical conductivity of the vapours of sodium and potassium heated in highly exhausted tubes. When the exhaustion of the tubes is sufficiently high, the galvanometer indications at gradually increasing voltages indicate the existence of saturation currents. This is more clearly marked in sodium than in potassium vapour. The magnitude of the saturation current increases with the temperature in accordance with the exponential formula deduced by Richardson.

By means of experiments with the superheated vapours, it has been found that the current is almost entirely due to the emission of electrons by the heated metals. If, in addition, the vapours have a specific conductivity, the magnitude of this at temperatures below 350° is so small as to elude detection. H. M. D.

Radiation of Rubidium. ÉMILE HENRIOT (*Compt. rend.*, 1911, **152**, 1384—1386. Compare Abstr., 1910, ii, 678).—The radiation from rubidium is more intense, but less penetrating, than that from potassium. The rays are almost homogeneous; their coefficient of absorption by paper diminishes as the thickness increases, and is given by the equation: $K_\rho/K_o = 0{\cdot}90e^{-162\rho} + 0{\cdot}10e^{-950\rho}$, where K_ρ is the intensity of radiation traversing ρ, the weight of paper per square cm.

A close proportionality exists between the radiation and the proportion of rubidium in the salts of the metal. W. O. W.

The Velocity of the Ions of Alkali Salt Vapours in Flames. HAROLD A. WILSON (*Phil. Mag.*, 1911, [vi], 21, 711—718).—The results of earlier experiments on the conductivity of flames containing vapours of salts of the alkali-metals indicate that the positive ions are atoms of the alkali-metals carrying single atomic charges, but this is difficult to reconcile with the fact that the velocities of these ions are the same for all the alkali-metals. The results are re-examined from the point of view that the alkali-metal atoms in the flames exist as ions for only a fraction of the time, the experimental values found for the velocities being then the true velocities multiplied by these fractions. These fractions, deduced from the experimental data, are found to vary from 0·21 for the lithium ion to 0·99 for the cæsium ion, on the assumption that the fraction varies as the square root of the atomic weight. This assumption is found to be in approximate agreement with the experimental data. F. S.

Velocities of the Electrons Produced by Ultra-violet Light. A. LL. HUGHES (*Proc. Camb. Phil. Soc.*, 1911, 16, 167—174).—The influence of the nature of the surface layer on the velocity of emission of electrons by metals when excited by ultra-violet light has been investigated. Experiments were made with nickel, copper, zinc, cadmium, and mercury, and the effect of using the metal as anode and cathode, of allowing the metal to remain in different gases, and of preparing metal surfaces by distillation in a vacuum, was examined.

The results obtained show that these various forms of treatment give rise to considerable differences in the velocity of emission of the electrons. The surfaces obtained by distillation in a liquid air vacuum are more likely to be free from surface films than those which have been treated by a discharge. In support of this view, it is found that the increased velocities obtained for the fresh surfaces are much more constant and remain steadier than the values obtained after a discharge. With ordinary polished metal surfaces, the low values of emission appear to be due to the presence of a retarding surface film. H. M. D.

The Influence of Changes of Temperature and Pressure in Gases on the Movement of the Ions Shown by Ultra-violet Light. ALOIS F. KOVARIK and C. ZAKRZEWSKI (*Ion*, 1910, 2, 289—314).—A description of the apparatus and methods employed in an investigation to determine the influence of temperature and pressure on the size of the negative ions in plates of metal in dry and wet air and in carbon dioxide.

The results indicated that the mobility of ions is greater in dry than in wet air, greater in air than in carbon dioxide, and independent of the nature of the metal. Down to pressures of 200 mm. the product of the mobility and pressure remain constant; below 200 mm. the product increases as the pressure decreases, especially rapidly at very low pressures.

With rising temperatures, the mobility increases, and at very high temperatures is inversely proportional to the density of the gas. At liquefaction temperatures, the mobility is much less than would correspond with the density of the gas, so that here the assumption of larger molecular aggregates appears to be justified. F. M. G. M.

The Question of Valency in Gaseous Ionisation. R. A. Millikan and Harvey Fletcher, (*Phil. Mag.*, 1911, [vi], 21, 753—770. Compare this vol., ii, 175).

—Direct unmistakable evidence has been obtained that the act of ionisation of air molecules by both primary and secondary *X*-rays of widely varying degrees of hardness, and by β- and γ-rays, consists, under all conditions examined, uniformly in the detachment of a neutral molecule of one single elementary charge. The method employed was to measure by a cathetometer the velocity of an illuminated single drop of oil under the joint action of gravity, and an opposed electric field, when it was kept near the upper, negative, plate of a condensor, while a sheet of *X*-ray ionisation was produced parallel and near to the lower, positive, plate. The drop was first so charged that the action of gravity nearly balanced that of the field; the *X*-rays were applied until a sudden start indicated that an ion had been caught by the drop, when the *X*-rays were stopped, the velocity was measured, the *X*-rays again applied until there was another sudden change of velocity, and so on, the movement of the same drop being often observed for several hours. The whole of the observations, with a very few doubtful exceptions, which are probably due to the simultaneous arrival of two ions, indicate that the charge of the drop changes its value by single atomic charges. Under the conditions, all but a few per cent. of the "catches" are of positive ions, and the smallness of the number of catches of negative ions is regarded as conclusive evidence that the greater part of the ionisation of the gas by *X*-rays is due directly to the primary rays, and not to secondary *X*-rays generated from them. The evidence derived from the work of Townsend and others that the positive ions produced by *X*-rays, particularly soft secondary *X*-rays, are doubly charged, is reviewed. The present experiments differ from earlier ones in that the charge on the ion is not measured after the ion has been formed for a considerable time, but is the charge at the moment of formation. The atomic structure of electricity is beautifully demonstrated by these experiments. For a single drop, three or four totally different velocities, due to an increment of the positive charge by one, two, three, or sometimes four, atomic charges, are observed, and no intermediate velocities ever occur. The different velocities are so characteristic that they can be distinguished by the eye unaided by a watch or chronometer. F. S.

A Special Case of Distribution of Ionisation in a Gas. Thin Superficial Layer Containing Ions of Both Signs. Maurice de Broglie (*Compt. rend.*, 1911, 152, 1298—1299. Compare this vol., ii, 356).

—The production of a thin layer of ions on the surface of quinine sulphate in process of hydration is somewhat analogous to the phenomena observed when Röntgen rays impinge tangentially on a metallic plate, except that in the latter case only negative ions are produced, and the layer has an appreciable thickness owing to secondary radiations. The extreme tenuity of the layer over the quinine sulphate crystals is sufficient to account for the difficulty in arriving at saturation, since the electrical field acts by diminishing the initial re-combination of the ions. W. O. W.

Electric Dispersion of Water and Ethyl Alcohol for Very Short Waves. H. MERCZYNG (*Bull. Acad. Sci. Cracow*, 1911, 123—133).—The refraction of electric waves by water and ethyl alcohol has been measured for wave-lengths ranging from 3·5 to 4·5 cms. For these waves the refractive index is appreciably different from the value for infinitely long waves, and the measurements afford information therefore as to the form of the dispersion curve. In the case of water, it is found that the refractive index increases with the wave-length. Both liquids exhibit anomalous dispersion.

H. M. D.

The Electrical and Optical Behaviour of the Chlorine Flame. J. FRANCK and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1911, **13**, 328—334).—When the electrical conductivity of a hydrogen chlorine flame is measured between unsymmetrical electrodes, a unipolar effect is observed, which is of opposite character to that exhibited by hydrogen or coal gas flames burning in air. This difference in behaviour is found whether a continuous or an alternating current is sent through the flame. In a similar manner, the dependence of the polarity on the temperature of the electrodes in the chlorine flame is the reverse of that found in the hydrogen or coal gas flames. With two equal electrodes, the temperature of the cathode is the chief factor which determines the conductivity in the latter, whereas the anode temperature is of primary importance in the chlorine flame.

These observations indicate that the mobility of the positive ions in the chlorine flame is much greater than that of the negative ions. Free electrons are therefore absent, and this is no doubt due to the great affinity of the molecules of electro-negative gases for electrons.

The absence of the yellow colour of sodium when this is introduced into the chlorine flame is probably connected with the absence of electrons. If, however, an oscillatory spark discharge is passed through the flame containing a bead of sodium chloride, an intense *D*-line emission is at once obtained. H. M. D.

The Relation of the Electrical Conductivity of Some Silver Amalgams to Temperature. ANTONIO REYES CALVO (*Ion*, 1910, **2**, 409—410).—The author measured the electrical resistance of very dilute silver amalgams (up to 0·06% Ag) between the temperatures of 0° and 20°, and found that at all concentrations it was merely a function of temperature.

At constant temperatures the resistance decreased with the rise of concentration, and yielded a curve which was concave to the concentration axis. F. M. G. M.

The Conductivity of a Cadmium Amalgam. ANTONIO REYES CALVO (*Ion*, 1910, **2**, 408—409).—The tabulated results of experiments on the conductivity of various cadmium amalgams measured at different temperatures. With more than 1% of cadmium present, conductivity increased with the temperature, first quickly, then more slowly, until a transition point was reached and it became rectilinear. Increased concentration raised the temperature of the transition point. For very dilute amalgams, the conductivity between 0° and 20° may be represented by quadratic equations. F. M. G. M.

Liquid Helium. C. The Change of Electric Resistance of Pure Metals at Very Low Temperatures. IV. The [Electrical] Resistance of Pure Mercury at Helium Temperatures. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1274—1276. Compare this vol., ii, 368, 487).—The electrical resistance of pure mercury at liquid helium temperatures has been measured by the aid of a helium cryostat. At 13·9° (absolute) the resistance is 0·034 of that of solid mercury at 273° (obtained by extrapolation); at 4·3° it is 0·0013, and at 3° it is less than 0·0001. This shows that the resistance of mercury, like that of gold, becomes zero at a temperature which is experimentally attainable and appreciably higher than the absolute zero. The observations agree with the behaviour predicted by the author on the basis of Planck's theory. H M. D.

Electrical Resistance of Antimony Selenides. HENRI PÉLABON (*Compt. rend.*, 1911, **152**, 1302—1305. Compare Chrétien, Abstr., 1906, ii, 550).—The specific resistance of mixtures of antimony and selenium increases with the proportion of selenium until this corresponds with the compound Sb_2Se_3. For mixtures containing less selenium than the compound SbSe, the specific resistance increases regularly with the temperature, and, on cooling, diminishes to the same extent. With higher proportions of selenium, it reaches a maximum as the temperature is raised, and then diminishes until fusion. If the mixture is then cooled, the values for the resistance are much higher than the original numbers, and the maximum occurs at a lower temperature. W. O. W.

Electromotive Force Produced by the Flow of Copper Sulphate Solution through a Capillary Tube. L. RIÉTY (*Compt. rend.*, 1911, **152**, 1375—1376).—A difference of potential of about 0·03 volt is observed between the ends of a capillary tube when an aqueous solution containing 1% of crystallised copper sulphate passes through, under a pressure of 90 atmospheres. The difference is proportional to the pressure, and diminishes as the proportion of copper sulphate increases. W. O. W.

The Temperature-coefficient of Concentration Cells, in which the Same Salt is Dissolved in Two Different Solvents. ARTHUR P. LAURIE (*Proc. Roy. Soc. Edin.*, 1911, 31, 375—396. Compare Abstr., 1908, ii, 1007).—The *E.M.F.* of the cell: Pt|0·025KI + 0·0138I_2 in water |0·025KI + xI_2 in alcohol |Pt, gradually changes from a positive value to a negative one as x varies from 0·043 to 0·345, both at 14° and 25°, current in the direction of transferring potassium iodides from alcohol to water being defined as positive. This is in accord with the theory of such cells, as developed by Luther (Abstr., 1896, ii, 461) and Abel (Abstr., 1906, ii, 722). The curves showing the relation between the *E.M.F.* and x are roughly logarithmic, with approximately the same temperature-coefficients. Similar results were obtained with cells in which the alcohol was replaced by nitrobenzene, and with alcohol–water cells with potassium iodide in solution and silver–silver iodide electrodes. Using Abel's results as a starting point, it is shown theoretically that there is a connexion between the latent heats of solution and the observed results, of the form $E = \lambda' - \lambda + T.de/dt$, where λ' and λ are the latent heats due to the solution of one gram-mol. of potassium iodide in water and alcohol respectively (calling heat absorbed positive), E is the *E.M.F.*, and de/dt is the temperature-coefficient.

Starting with the cell Ag,AgI|0·001KI in water|0·001KI in alcohol|Ag,AgI, the concentrations of the aqueous solutions were varied from 0·001 to 0·1 and the *E.M.F.*'s measured. As the concentration of the aqueous solution increases, the *E.M.F.* changes from positive to negative, and the results are in accordance with the equation $E = RT(\log.C \times x - \log.C')$, where x is a constant, and C and C' are the concentrations of the alcoholic and aqueous solutions respectively.

It is further shown that the condition of electrical equilibrium in the potassium iodide–water–alcohol cell is not when both solutions are saturated with the salt, but is when the strength of the water solution is such that diffusion produces no salt precipitation when it is in contact with alcohol saturated with potassium iodide. This equilibrium is reached when the strength of the water solution is about 2 mols. of potassium iodide per 1000 c.c. T. S. P.

Electrochemical Behaviour of Tin. FRITZ FOERSTER and J. YAMASAKI (*Zeitsch. Elektrochem.*, 1911, 17, 361—374).—The following potentials, referred to the normal hydrogen electrode, are measured at 18°:

Sn|0·9 mol. $SnCl_2$ per litre = −0·188 volt; Sn|0·49 mol. $SnSO_4$ per litre = −0·190 volt; Sn|0·49 mol. $SnCl_2$ in *N*-HCl = −0·204 volt.

Pt|0·25 mol. Sn^{II} + 0·25 mol. Sn^{IV} in *N*-NH_4Cl = +0·131 volt; Pt|0·25 mol. Sn^{II} + 0·25 mol. Sn^{IV} in 0·5*N*-HCl = +0·158 volt: Pt|0·25 mol. Sn^{II} + 0·25 mol. Sn^{IV} in 2*N*-HCl = +0·138 volt.

The effect of adding ammonium chloride or sulphate to the stannous solutions is also studied. The results indicate that the stannous salts exist largely in the complex forms in aqueous solution. The stannous–stannic potentials only become constant after several hours; the change is attributed to the diminution of the concentration of the stannic ions by hydrolysis; it hardly occurs in strongly acid solutions.

The electrolytic reduction of stannic to stannous chloride at platinised platinum cathodes is studied. At the ordinary temperature the change is a slow one, so that a comparatively small increase of current density changes the cathode potential so much that tin is deposited (in 2*N*-acid solutions) or hydrogen is evolved (in 6*N*-hydrochloric acid).

The retardation of the reduction disappears almost entirely at higher temperatures (50—75°), and it is diminished by increase of the concentration of the stannic chloride or of the hydrochloric acid in the solution. T. E.

Thermodynamics of the Cell; Hg, HgCl, $PbCl_2$, Pb. ROBERT LUTHER (*Zeitsch. Elektrochem.*, 1911, **17**, 293—294).—From measurements of the *E.M.F.* of the above cell, the heat of the reaction $Pb + 2HgCl = PbCl_2 + 2Hg$, is calculated to be +21900 cals., direct thermochemical measurements having given 20100 cals. T. E.

Mercurous Perchlorate Voltameter. FRANK C. MATHERS and ALBERT F. O. GERMANN (*Indiana University Studies*, 1910, 41—49).—An acid solution of mercurous perchlorate is made by electrolysing a strong solution of perchloric acid with a mercury anode and a small platinum cathode. Conductivity measurements show that a solution of perchloric acid containing 0·43 gram per c.c. has the best conductivity. The conductivity of solutions of mercurous perchlorate increases slowly with the concentration, but the addition of free acid increases it greatly. For the voltameter, a solution containing 0·642 gram of mercurous perchlorate, 0·2836 gram of perchloric acid, and 0·04 gram of sodium perchlorate per c.c. was used. Without the sodium salt, a part of the mercury is deposited in the form of a black powder. In the voltameter the anode consists of 20 or 30 grams of mercury supported by a layer of glass wool on the bottom of a Gooch crucible, which is suspended in the electrolyte. The mercury cathode is placed below the anode, and is contained in a capillary tube with marks upon it, so that after a determination the mercury deposited may be run off exactly and either weighed or measured. A number of comparisons with silver and copper voltameters show that the error does not exceed about ±0·4%. T. E.

The Dissociation of Amphoteric Electrolytes. LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1911, **33**, 182—189).—If ρ be the proportion of undissociated molecules of an amphoteric electrolyte, then $\rho = 1/(1 + k_a/[H^{\cdot}] + k_b/[OH'])$, where k_a is the acid, and k_b the basic dissociation constant. The form of the curve when the hydrogen ion concentration is plotted as abscissæ, and ρ as ordinates, will depend on the magnitude of the product $k_\alpha^{*}.k_\beta$, which is characteristic for any particular amphoteric substance. The maxima of these curves are the isoelectric points. The smaller $k_a.k_b$, the higher is the maximum above the abscissæ. When it reaches 10^{-14}, the maximum reaches 1 (that is, the substance is entirely undissociated). In electrolytes of smaller value, there is a broad zone of hydrogen ion concentrations in which the substance is not dissociated. This is the case with tyrosine, leucine, and arsenious acid. Substances where $k_a.k_b \geqq 10^{-14}$ do not appear to be capable of existing. S. B. S.

Alterations in the Concentration of the Solution of a Magnetisable Salt in a Non-Homogeneous Magnetic Field. WOLDEMAR VOIGT [with STATESCU] (*Chem. Zentr*, 1911, i, 862—863; from *Nachr. K. Ges. Wiss. Göttingen*, 1910, 545—553).—Theory demands that concentration differences should be brought about in the solution of a magnetic salt placed in a non-homogeneous magnetic field. If a solution of such a salt is placed in a containing vessel so that the concentration of the solution varies in the vertical direction, an almost horizontal beam of light is deviated through the angle a, where $a = DK(n^2 - n_0^2)dH^2/4n^2\rho BT.dz$, and D is the thickness of the vessel, K the magnetisation number, n and n_0 the refractive indices of the solution and solvent respectively, B the Boyle's constant for the solution, which is considered to obey the gas laws, T the absolute temperature, ρ the density of the dissolved salt, H the intensity of the magnetic field.

For a 20% solution of ferric chloride, a was found to be $3{\cdot}5 \times 10^{-6}$, whilst according to the above formula it should have been 5×10^{-6}. If the dissociation of the ferric chloride is taken into account a better agreement is obtained. T. S. P.

The Thermo-electric Effects (Thermo-electric Forces, Thomson Effect) and the Thermal Conductivity of Certain Elements and Compounds and the Experimental Examination of the Electron Theories. JOHANN KOENIGSBERGER and J. WEISS (*Ann. Physik*, 1911, [iv], 35, 1—46).—The thermo-electric properties and the thermal conductivity of silicon, molybdenite, iron pyrites, magnetite, ilmenite, manganite, ferric oxide, and graphite have been investigated. A method of measuring the thermal changes corresponding with the Thomson effect is described, in which short rods of the material are employed instead of long wires. The thermo-electric differences of potential at 50° of the various substances in contact with copper vary from $+770 \times 10^{-6}$ volt in the case of molybdenite to -700×10^{-6} volt for impure silicon. The experimental data are discussed in detail in reference to various deductions from the theory of electrons. H. M. D.

Kinetic Theory of Gases and Thermodynamics. A. BERTHOUD (*J. Chim. Phys.*, 1911, 9, 352—381).—Considered thermodynamically a gaseous system is in equilibrium when its entropy is at its maximum. By the kinetic hypothesis, if all the molecules were at the same temperature at any moment, they would immediately assume a variety of temperatures from zero to infinity. This process being accompanied by a decrease of entropy is impossible thermodynamically. To meet this difficulty, the author assumes that each group of molecules of any particular velocity behaves as a "temperature isomeride" and distributes itself uniformly throughout the whole system as if it were chemically unlike all similar groups of different velocity or temperature. Using this hypothesis the law relating the mean temperature to the proportion of molecules comprised between any two given temperatures was deduced on the principle of maximum entropy with the additional assumption that a rise in the mean temperature is accompanied by a proportional rise in velocity of all the molecules in the system. The relation deduced is identical with that deduced from Maxwell's formula in the case of monatomic gases. With polyatomic gases Maxwell's formula and the thermodynamic reasoning are not in accord unless Maxwell's formula is modified by substituting for the exponent 3 (the heat capacity of a monatomic gas) the value C_v of the heat capacity of the gas considered.

The author holds that Maxwell did not take into account the participation of internal molecular energy in the redistribution of energy which follows each molecular collision. Hence Maxwell's formula only holds for monatomic gases which have no internal energy. R. J. C.

Dynamics of a Gas in Motion According to the Theory of Relativity. FERENCZ JUTTNER (*Ann. Physik.*, 1911, 35, 145—161.)—A mathematical paper in which the author deduces the thermodynamic functions of a monatomic gas in motion on the basis of the theory of relativity. H. M. D.

Thermal Conductivity of Liquids. ROBERT GOLDSCHMIDT (*Physikal. Zeitsch.*, 1911, 12, 417—424).—The method of measurement employed is similar to that used by Schleiermacher (*Ann. Physik,* 1888, 34, 623) in the determination of the thermal conductivity of gases at low pressures. A platinum wire of 0·05 mm. diameter is stretched by means of a spring along the axis of a silver capillary tube, 2 mm. wide, which is in direct contact with a massive cylinder of brass which completely surrounds the capillary. This arrangement ensures constancy of the temperature of the silver capillary throughout its whole length. The brass cylinder is supported in a Dewar tube which contains the liquid under investigation. The liquid fills the capillary tube, the main object of which is to eliminate to a large extent the disturbances which would otherwise result from convection. The errors which occur from the heat exchanges at the ends of the heated platinum wire can be avoided by the use of a shorter compensating wire which is fitted up in an exactly similar manner.

A current of known strength is passed through the platinum wire until a stationary condition is reached. The resistance of the wire in this condition is measured, and from the current intensity and the wire resistance, the temperature of the wire and the thermal conductivity of the surrounding liquid can be calculated.

Measurements have been made for a number of organic liquids. From the data for the alcohols it appears that the conductivity decreases as the molecular weight increases and as the structure becomes more symmetrical. For pentane, measurements were made over an interval of 210°, and for ethyl ether and toluene over 94°. In all cases the temperature-coefficient is negative, and varies from 0·2 to 1·5% per degree. H. M. D.

The Specific Heat of Water. WILLIAM R. BOUSFIELD and W. ERIC BOUSFIELD (*Phil. Trans.*, 1911, *A*, **211**, 199—251; *Proc. Roy. Soc.*, 1911, *A*, **85**, 302—304).—The mechanical equivalent of heat has been determined in terms of the mean calorie from 13° to 55° by a continuous flow calorimetric method in which a current of water was passed through a Dewar vessel of three litres capacity containing an electric heater. The water entered at about 13° and left at about 55°. The heater consisted of a spiral glass tube of small bore, into the end of which were sealed platinum electrodes. The mercury in this tube is connected with a thermometer tube, so that the spiral forms a thermometer bulb. Such a mercury resistance is free from a "thermoid" effect exhibited by ordinary resistances when a large current is passed through them. When this effect is present, the electric resistance is not only dependent on the temperature, but also on the strength of the current. The passage of this appears to induce a state of strain which temporarily alters the resistance by an amount which may reach several hundredths of a per cent.

The continuous flow experiments gave $J_{13}^{55} = 4{\cdot}182$ for the value in joules of the mean calorie between 13° and 55°. By heating a known quantity of water in successive stages, the values of J_{0}^{13}, J_{13}^{27}, J_{27}^{55}, and J_{55}^{80} were obtained. From these data the value of J at any temperature θ is found to be given by the equation: $J = 4{\cdot}2085 - 0{\cdot}003022\theta + 0{\cdot}00007833\theta^2 - 0{\cdot}000000490\theta^3$. This yields 4·179 as the joule equivalent of the 15° calorie, and indicates a maximum specific heat corresponding with 4·174 joules at about 25°.

H. M. D.

Specific Heats of Solids at Low Temperatures. HERMANN BARSCHALL (*Zeitsch. Elektrochem.*, 1911, **17**, 341—345).—The substance is cooled to the temperature of liquid carbon dioxide and allowed to fall into liquid oxygen at its boiling point, the quantity of gas evolved is measured, and the specific heat calculated by means of the latent heat of evaporation of oxygen. The values of the specific heat between about −75° and −183·3° measured in this way are: Lead, 0·0294; silver, 0·0492; cadmium, 0·0503; sulphur, 0·116 to 0·121; mercury, 0·0316; bromine, 0·073; mercuric iodide, 0·0375; lead iodide, 0·0377; lead bromide, 0·0463. T. E.

The Atomic Heats of the Elements. JOHANN KOENIGSBERGER (*Zeitsch. Elektrochem.*, 1911, **17**, 289—293).—The effect of free electrons on the atomic heat is discussed. A free electron has the same atomic heat as the atom of a monatomic gas. In metals the electrons remain free even at very low temperatures, whilst in bad conductors of electricity they are mostly combined. It is pointed out that at low temperatures the atomic heats of bad conductors are much less than 3, whilst those of the metals are greater than 3. At high temperatures the atomic heat of a metal is made up of the part due to the free electrons and that due to the motion of the atoms. The latter, according to Einstein's views, is about 6, whilst the former is 3 when the metal contains one free electron per atom; as a matter of fact, the atomic heats of many metals are nearly 9 at high temperatures. T. E.

Molecular Heat of Fusion. ÉMILE BAUD (*Compt. rend.*, 1911, **152**, 1480—1483).—Traube has shown that the co-volume of a liquid expands as a gas, proportionally to T, the absolute temperature. The variation in molecular volume at the moment of solidification, Δ_v, is the difference between the co-volume of the liquid, V, and the co-volume of the solid, V', supposing that the atoms of liquid and solid occupy the same volume. At constant temperature, t, it follows that: $\Delta_v = (V - V').T/(273 + t)$. Substituting this expression in Clapeyron's equation and integrating, this gives $p = Q/T.(273 + t)/(V - V')t$, where Q is the molecular heat of fusion. At constant pressure $Q/T = k(V - V')t$, or, since $V - V'$ is proportional to T, $Q = k(V - V')_t$. The molecular heat of fusion of a substance should then be proportional to the variation in volume at the temperature of fusion. This conclusion has been found to agree with recorded observations in the case of ethylene dibromide, the three xylenes, naphthalene, and antimony trichloride. W. O. W.

Gaseous Mixtures. Freezing-point Curves of Gaseous Systems. GEORGES BAUME (*J. Chim. Phys.*, 1911, **9**, 245—289).—An apparatus has been constructed for the purpose of obtaining the liquidus curves of gaseous mixtures. The mixtures are synthesised volumetrically.

Successive litres of gas at 0° and a known pressure, which may be less than 760 mm., if necessary, are distilled into the cryoscopic tube, which is cooled in liquid air. The gravimetric composition of the mixtures is estimated from the densities of the gases, all the usual corrections being applied. The cryoscopic tube is provided with a magnetically operated platinum stirrer and an *iso*pentane thermometer.

The error in the estimation of the masses is probably 1 in 3000, but is certainly not more than 1%. The temperatures are accurate to about 0·25°.

The liquidus curve of the system methyl ether–hydrogen chloride was determined. Hydrogen chloride melted at $-111·4°$ and methyl ether at $-138·5°$. The curve exhibits two maxima at $-97·1°$ and $-102·8°$, the mixtures having the compositions Me_2O,HCl and $Me_2O,4HCl$ respectively. Between these maxima, mixtures containing 27 to 38% of molecules of methyl ether are highly viscous, giving vitreous solids, so that the curve cannot be determined.

Extrapolation suggests an eutectic at about 30% of molecules of ether, but if the high viscosity indicates a third molecular compound there would be three maxima and four eutectic points in the complete liquidus curve. R. J. C.

The Depression of the Freezing Points of Sodium and Calcium Chlorides. FRANCIS E. E. LAMPLOUGH (*Proc. Camb. Phil. Soc.*, 1911, **16**, 193—196).—The following values were obtained for the molar depression of the freezing point of calcium chloride: strontium chloride, 240; lithium chloride, 340; sodium chloride, 362; barium chloride, 380; potassium chloride, 448. From the depression of the freezing point of sodium chloride, the calculated molecular lowerings are: sodium bromide, 81; potassium chloride, 166; lithium chloride, 164; calcium chloride, 180; strontium chloride, 176; barium chloride, 202; sodium carbonate, 180; sodium sulphate, 204.

A complete series of freezing-point measurements for the binary system, sodium and calcium chlorides, was also made. The freezing-point diagram is of the simplest type, and exhibits a eutectic corresponding with about 50 mols. % of the two chlorides and about 495°. It is probable that the components separate out in the pure condition from all fused mixtures. H. M. D.

Heat of Evaporation of Oxygen. HERMANN BARSCHALL (*Zeitsch. Elektrochem.*, 1911, **17**, 345—348).—A known quantity of heat was added electrically to liquid oxygen at its boiling point, and the quantity of gas evolved was measured. Full details of the precautions taken to avoid error are given. The results of six experiments gave values lying between 51·23 and 51·38, mean 51·3 calories per gram at 763 mm. pressure. T. E.

Influence of Water Vapour on Measurements in a McLeod Gauge. MARCEL GUICHARD (*Bull. Soc. chim.*, 1911, [iv], **9**, 435—438). —Aqueous vapour behaves like a gas when its tension is low, so that its pressure in a McLeod gauge is given by the ordinary formula $h = a.v/V - v$, where h is the initial pressure at volume V, and a the increase in pressure necessary to reduce V to v. When the tension of aqueous vapour is high, then under compression the vapour attains its maximum tension, f, for the temperature of the surrounding atmosphere, and under these conditions $a = f - h$. Further, a reaches its maximum when $h = fv/V$, and decreases again for higher values of h. Consequently, when the tension of aqueous vapour in an apparatus rises from *nil* to its value at saturation point, the values of a read on the gauge increase to a maximum where $h = fv/V$ and then diminish, so that every value of a corresponds with two initial tensions. Experimental data confirming these conclusions are given. T. A. H.

Optical Method of Measuring Vapour Pressures: Vapour Pressure and Apparent Superheating of Solid Bromine. CLIVE CUTHBERTSON and MAUDE CUTHBERTSON (*Proc. Roy. Soc.*, 1911, *A*, **85**, 306—308).—The refractivity of bromine vapour has been measured by means of Jamin's interferometer, the refractometer tube of the instrument being in communication with a reservoir containing solid bromine at a definite temperature. The temperature of the cooling bath was slowly raised, and the number of interference bands crossing the field of view was counted. Assuming that the refractivity and the pressure are proportional to the density of the vapour, the refractometric observations can be used for the calculation of the vapour pressure at any temperature if the vapour pressure for one particular temperature is known. The calculated pressures can be represented by means of the equation $p = a.b^{\theta}$, in which $a = 2{\cdot}485 \times 10^{-8}$ and $b = 1{\cdot}0834$.

With slowly rising or falling temperature, irregularities are observed at the melting point, which seem to show that superheating and super-cooling take place. H. M. D.

Binary Liquid Solutions. C. MARILLER (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 774—776).—The depression of the vapour pressure of ethyl ether by the addition of foreign substances can be satisfactorily expressed by the equation $100f/f' = 1 - KN$, in which f is the vapour pressure of ether, f' that of a solution which contains N-gram-molecules of the dissolved substance in 100 of the binary mixture, and K is a constant, approximately equal to unity, which is approximately independent of the nature of the dissolved substance.

H. M. D.

Hydrofluorides of Alkali Fluorides. ROBERT de FORCRAND (*Compt. rend.*, 1911, **152**, 1556—1559. Compare this vol., ii, 488).—A review of salts of the type MF,HF from the thermochemical point of view. The following numbers express in Calories the heat of fixation of a molecule of solid hydrogen fluoride on a molecule of solid alkali fluoride: NaF + 8·3, KF + 12·76, RbF + 13·78, CsF + 14·77. It will be seen that, as in the case of the heats of dissolution of the normal salts studied previously, the sodium salt stands somewhat apart from the rest of the series. Although the stability of the normal fluorides increases in the order given above, the contrary is found to be the case with the hydrofluorides.

Rubidium and cæsium fluorides are capable of absorbing excess of hydrogen fluoride to form compounds containing 2HF and 3HF.

W. O. W.

Derivatives of Styrene; Rectification of Some Experimental Errors. PAUL LEMOULT (*Compt. rend.*, 1911, **152**, 1402—1404).—The author has determined the heats of combustion of styrene and a number of its derivatives, and has obtained the following values (expressed in Calories), the first three of which differ considerably from those given by Auwers, Roth, and Eisenlohr (Abstr., 1910, ii, 586). Styrene, 1059·1, α-methylstyrene, 1217·3; αβ-dimethylstyrene, 2510·3, di-*p*-methoxystilbene, 2018. These numbers agree with the theoretical values calculated on the assumption that the hydrocarbons are unsaturated compounds, whereas those obtained by Auwers, Roth, and Eisenlohr are abnormal and correspond more closely with saturated compounds. The increase in the heat of combustion when freshly distilled styrene is kept for a few hours, referred to by these authors, could not be confirmed. W. O. W.

The Value of the Critical Quantities. JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1211—1231).—A theoretical paper in which the author discusses the variation of the term b in van der Waals' equation with the total volume occupied by the substance. H. M. D.

The Value of the Volumes of the Co-existing Phases of a Simple Substance. JOHANNES D. VAN DER WAALS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 13, 1253—1262).—The deviations exhibited by saturated vapours from the requirements of the van der Waals' equation are discussed in reference to the phenomenon of quasi-association. H. M. D.

Weight of a Falling Drop and the Laws of Tate. IV Standardisation of a Tip, and the Calculation of the Surface-Tension and Molecular Weight of a Liquid from the Weight of its Falling Drop. J. LIVINGSTON R. MORGAN (*J. Amer. Chem. Soc.*, 1911, 33, 643—657).—In the earlier papers (Abstr., 1908, ii, 356, 668; this vol., ii, 372) the standardisation of the tip of the capillary tube, that is, the determination of the normal molecular temperature-coefficient, k, of all non-associated liquids falling from it, was effected by means of Ramsay and Shields' formula, connecting surface-tension with capillary rise. It is now shown that by this method the experimental error is multiplied to such an extent as to render the results misleading, and a new method has therefore been adopted which is based solely on the equation $w(M/d) = k(t_c - t - 6)$. The surface-tension in dynes of any liquid at any temperature can be calculated by multiplying its drop weight in mg. from the tip at that temperature by the ratio of the k value of surface-tension to the k value for the tip, both being found by the use of benzene ($t_c = 288{\cdot}5°$) as the standard. Any liquid, which, with the normal (benzene) value of k (k_B), gives the same calculated value of t_c at all temperatures of observation must be regarded as a normal non-associated liquid, since this proves that the normal k is also the correct change per degree of its molecular function. The calculated value, t_c, need not always agree with the observed value of the critical temperature, and this indicates that whilst some liquids are in corresponding states when equally removed from their critical temperatures, others are only so when equally removed from another, fictitious, temperature.

Aniline, pyridine, and quinoline are shown from this point of view to be perfectly normal in molecular weight.

The application to drop weight of the empirical formula for calculating t_c without a knowledge of the molecular weight as given by Walden (this vol., ii, 97) leads to results which differ but little from those calculated by means of k_B. E. G.

Weight of a Falling Drop and the Laws of Tate. V. Drop Weights of Fifteen Non-associated Liquids as Found by the Use of the New Form of Apparatus, and the Molecular Weights Calculated for Them. J. LIVINGSTON R. MORGAN and EDGAR G. THOMSSEN (*J. Amer. Chem. Soc.*, 1911, 33, 657—672).—It is shown, according to the new definition of molecular weight (preceding abstract), that is, that the constant k_B gives for the liquid a constant value of t_c independent of the temperature of observation, t, in the relation $w(M/d)^{\frac{2}{3}} = k_B(t_c - t - 6)$, that ether, ethyl butyrate, anisole, phenetole, ethylene dibromide, chloroform, benzonitrile, and carbon disulphide must be regarded as non-associated. The same conclusion can be reached from the results of capillary rise. The calculated values of t_c agree closely with the observed critical temperatures in the cases of ether and chloroform, but the fictitious values of the critical temperatures found for the other liquids agree with those calculated from the capillary rise. The values of t_c, both true and fictitious, found by the modified Walden method without the use of the molecular weight, agree as closely as could be expected. The calculated value, t_c, for a mixture of equal weights of benzene and carbon tetrachloride is the mean of the values found for the two liquids separately. E. G.

Weight of a Falling Drop and the Laws of Tate. VI. Drop Weights of Twenty New Non-Associated Liquids and the Molecular Weights Calculated for Them. J. LIVINGSTON R. MORGAN and G. K. DAGHLIAN (*J. Amer. Chem. Soc.*, 1911, 33, 672—684).—It is shown, by using the new criterion of normal molecular weight (preceding abstracts), that the following liquids are as completely non-dissociated as benzene: bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, *o*-, *m*-, and *p*-xylenes, mesitylene, ethylbenzene, iodobenzene, fluorobenzene, cymene, ethylene dichloride, methylaniline, ethylaniline, *iso*butyl acetate, carbon disulphide, and diphenylmethane. In the case of dimethylaniline, a somewhat abnormal value was obtained for the molecular weight, but this was probably due to partial decomposition of the substance.

The calculated values of t_c agree closely with the observed values of the critical temperature in the cases of bromobenzene, bromine, ethylidene chloride, toluene, phosphorus trichloride, and *o*-, *m*-, and *p*-xylenes, whilst the difference between the calculated and observed values is less than 1% for mesitylene and but little greater for ethylbenzene and iodobenzene. The calculated values of t_c from drop weight determinations agree well with those obtained from capillary rise in the case of eleven liquids which have been studied by the latter method, but the mean values from capillary rise for mesitylene and *m*-xylene do not accord with those calculated from the drop weight.

The values of t_c, calculated by the Walden method without the aid of molecular weight, agree well in only eight cases, out of sixteen to which it could be applied, with those calculated from k_B, and it therefore seems that the relation is probably not so general as was at first supposed. E. G.

Apparatus for Determination of Viscosities, Especially of Serum and Other Animal Fluids. LEO VON LIEBERMANN (*Biochem. Zeitsch.*, 1911, 33, 218—221).—An apparatus is figured, in which a gilded disk is allowed to vibrate in the liquid under investigation, and the time and amplitude of the vibrations are determined by means of reflexion of a beam of light on to a scale from a mirror attached to the wire suspending the disk. The comparative viscosities of two liquids can be calculated from the formula:

$$\eta_1/\eta_2 = d_2/d_1 . T_2/T_1 . (\lambda_1 - \lambda_0/\lambda_2 - \lambda_0)^2,$$

where η_1, η_2 are the viscosities, d_2, d_1 the specific gravities, T_2, T_1

the times, λ_2, λ_1 the logarithmic decrements of the amplitudes, and λ_0 the logarithmic decrement of the amplitude in air. The advantages and disadvantages of the method as applied to serum are described. S. B. S.

Viscosity of Cellulose Nitrate Solutions. C. Piest (*Zeitsch. angew. Chem.*, 1911, **24**, 968—972. Compare Abstr., 1910, i, 464).—An account of an investigation on the viscosity of solutions of cellulose nitrates. The viscosities were measured by (1) Engler's apparatus, (2) Cochius' viscometer, and (3) a viscometer, similar to that of Cochius, in which the time taken by a hollow, glass bulb to rise through a given depth of liquid is measured. A description and sketch of this new form of viscometer is given.

It is found that the ratios of the viscosities determined by the three methods vary with different solutions; in other words, the viscosities obtained by the three methods cannot be compared with one another.

The viscosity of a solution of cellulose nitrate is dependent on (1) the presence of impurities, such as acetic acid, aldehyde, etc., (2) the duration and temperature of nitration of the cellulose, and (3) the presence of oxycelluloses and hydrocelluloses in the cellulose employed. All these factors produce a marked reduction of viscosity. Solutions of gun-cotton and collodion-wool also become less viscous when kept, although the change takes place very slowly.

It is the author's opinion that the viscosity of a colloidal cellulose nitrate solution is not determined by the magnitude of the cellulose nitrate molecule, but rather by the nature and size of the colloidal particle. W. H. G.

Viscosity of Emulsions Bancelin (*Compt. rend.*, 1911, **152**, 1382—1383. Compare Perrin, this vol., ii, 480).—The viscosity K' of an emulsion of mastic is found to agree with the equation $K' = K(1 + 2{\cdot}9\phi)$, when K is the viscosity of the liquid containing in suspension solid spheres, of total volume ϕ, in unit volume of emulsion. Einstein (*Ann. Physik*, 1906, [iv], **19**, 289) on theoretical grounds deduced the expression $K' = K(1 + \phi)$, but has now altered this to $K' = K(1 + 2{\cdot}5\phi)$ (private communication). The viscosity of sucrose and glycerol solutions is represented by an analogous formula, but carbamide and metallic salts show smaller coefficients of viscosity. Extrapolation from the first formula and from that expressing the coefficient of diffusion of an emulsion gives the value 70×10^{22} for N, the number of molecules in a gram-molecule. W. O. W.

Dissociation of the Compound $ThCl_4,18NH_3$. Edouard Chauvenet (*Ann. Chim. Phys.*, 1911, [viii], **23**, 275—280. Compare Abstr., 1910, ii, 872).—Dry ammonia gas was passed through a tube reaching to the bottom of a small distillation flask containing anhydrous thorium chloride, a long manometer tube containing a mercury index being sealed to the side-tube. The air being displaced, the flask was immersed in acetone and snow until a quantity of liquid ammonia had accumulated. The excess was then evaporated by placing the flask in liquid methyl chloride. The (previously constricted) neck was then sealed off, at the same time the necessary mercury being poured into the gauge. Four observations of the dissociation pressure between 250·5 and 281° abs. were made, the results being plotted on a curve against the absolute temperatures.

From the difference between the heats of formation of $ThCl_4,18NH_3$ and $ThCl_4,12NH_3$ previously determined by the author, the heat of fixation of $6NH_3$ on the latter has been found to be 8·83 cals. per mol. NH_3. Dividing this quantity (Q) by the absolute temperature at which the dissociation pressure equals 760 mm. (determined from the above-mentioned curve) gives practically the same value of Q/T as that found by Matignon (Abstr., 1899, ii, 273) with other ammoniacal metallic chlorides. Moreover, substitution for p of the observed value of the dissociation pressure at 281° abs. in the reduced form of Clapeyron's formula: $Q = 2/1000.273T/T - 273.\log.p/p_0$ (p_0 being the dissociation pressure at 273° abs.; $T = 281$) gives a value for Q closely agreeing with that observed. J. D. K.

Capillary Rise of Amines, Phenols, and Aromatic Hydroxy-Acids. ZDENKO H. SKRAUP and ERNST PHILIPPI (*Monatsh.*, 1911, **32**, 353—372. Compare Abstr., 1909, ii, 868; 1910, ii, 191, 934; this vol., ii, 21).—The capillary rise of weak hydroxides is smaller than that of strong. One purpose of the present paper is to ascertain whether the abnormal rise of ammonia and ethylamine, which is greater than that of the strongest alkali hydroxides, is exceptional or is characteristic of all amines. It is found in the case of aqueous ammonia (and of some amines) that the rise is very different according as the indicating strip is used without any enclosure or is suspended in a tube closed at its upper end and adjusted almost to the level of the basin containing the solution under examination. All the experiments, therefore, have been conducted under the latter conditions. The results are as follows: Aqueous ammonia shows a rise which diminishes with decreasing concentration. Hydroxylamine and hydrazine exhibit rises considerably greater than those of the strong alkali hydroxides. At equivalent concentrations, methylamine, ethylamine, and amylamine show almost identical rises; the same is true of the corresponding quaternary bases, the rise being somewhat smaller. Methylamine and dimethylamine exhibit the same rise, which is considerably higher than that of potassium hydroxide at the same concentration; trimethylamine, like ammonia, gives very different rises according to whether the strip is enclosed or not. Ethylenediamine, tetramethylethylenediamine, and hexamethylethylenediammonium hydroxide exhibit rises only slightly smaller than those of the corresponding monoamines at the same concentrations. In the case of aromatic mono- and di-amines the regularities are not so pronounced as the preceding, but here again the monoamines (aniline and the toluidines) exhibit greater rises than the diamines (the phenylenediamines, *m*-tolylenediamine, 1 : 8- and 1 : 5-naphthylenediamines); in all cases, except the naphthylenediamines, the rises are much greater than those of potassium hydroxide at the same concentration. The position of the amino-group affects the rise; thus of the toluidines the ortho-compound shows the greatest rise, whilst in the case of the phenylenediamines the ortho- and the meta-isomerides exhibit equal rises, that of the para-compound being considerably smaller. The hydrochlorides of some aromatic amines have been examined. The rise, tested by a colour reaction for the base, is the same for the salt as for the free amine, but the height of the acid zone is considerably smaller.

Some phenols and aromatic hydroxy-acids have been examined under the preceding conditions. The diminution in the rise with decreasing concentration is very much slower with phenols than with amines. Phenol, catechol, and quinol exhibit approximately equal rises, those of resorcinol, pyrogallol, and phloroglucinol being somewhat smaller.

Salicylic, *p*-hydroxybenzoic, protocatechuic, and gallic acids have also been examined. When tested by ferric chloride paper the rise almost equals that of the wet zone (100 mm.), and consists of an upper faint zone and a lower strong zone, a behaviour due to the ash in the paper which forms salts with the acid; it has been shown previously that salts are very slightly adsorbed. The acid zone is very much lower and decreases rapidly with increasing dilution.

Hexamethylethylenediammonium iodide, $C_2H_4(NMe_3I)_2$, decomp. 250°, is obtained by treating ethylenediamine in methyl alcohol with methyl iodide (2 mols.) and then with potassium hydroxide in methyl alcohol, repeating these two operations on the liberated base, and finally adding a third portion (2 mols.) of methyl iodide, whereby the diammonium iodide separates in needles. The *platinichloride*,

$$(C_2H_4N_2Me_6)PtCl_6,$$

is described. *Tetramethylethylenediamine* is obtained by distilling an aqueous solution of hexamethylethylenediammonium hydroxide; its *platinichloride* crystallises in orange-red plates. C. S.

Historical Data Relating to Osmotic Force. Rectification of Authors' Names. AUGUSTE ROSENSTIEHL (*Compt. rend.*, 1911, **152**, 1305—1308).—This note relates to the origin of the theory that the phenomena of dissolution are analogous to those of the vaporisation of substances. W. O. W.

Osmotic Pressure of Colloids. JACQUES DUCLAUX and Mme. E. WOLLMAN (*Compt. rend.*, 1911, **152**, 1580—1583. Compare Bayliss, *Kolloid Zeit.*, 1910, **6**, 23).—The osmotic pressure of a colloidal solution of cellulose nitrate in acetone has been measured at different concentrations, using a semi-permeable membrane of denitrated collodion. The ratio of the pressure to concentration, which should be constant if the solution obeyed the ordinary laws, varies markedly, even at low concentrations. The ratio, which is 0·53 in a 0·116% solution, becomes 6·83 for a 1·41% solution. Application of van der Waals' equation for compressed gases does not bring the results into concordance.

It would seem, therefore, that the abnormal osmotic pressures of colloids must be regarded as depending on the peculiar nature of the colloid molecule. W. O. W.

Rate of Dissolution in Gas-Liquid Systems. Tor Carlson (*J. Chim. Phys.*, 1911, **9**, 228—244 *).—The velocity with which a gas dissolves in a liquid at rest depends on the rate of diffusion of the gas into the bulk of the liquid from the saturated surface. According to Fick's law the rate of diffusion is proportional to the concentration gradient in the layer of solution considered.

Hence if c is the concentration of gas dissolved at any time t, and S be the concentration at saturation, $dc/dt = K(S-c)$, where K is a constant depending on the diffusion coefficient, D, at the given temperature and the area, a, and thickness of the saturation layer. This leads to a logarithmic dissolution law similar in form to the unimolecular reaction law. When the liquid is stirred at n revolutions per minute, the saturation layer is diminished in thickness proportionally to $\sqrt[3]{n^2}$, just as Brunner found when dissolving benzoic acid in water; hence $K = K'n^{\frac{2}{3}}Da$. The constant K' is characteristic of the apparatus employed. The author has measured the velocity of dissolution of oxygen and of carbon dioxide in water, estimating the former by Winkler's iodine method, and the latter by Pettenkofer's baryta method. The unimolecular law is found to hold in both cases. The ratio of the diffusion constants, $D_{O_2} : D_{CO_2} = 1{\cdot}158$, determined from the rates of dissolution under similar conditions approximates to the ratio determined by diffusion measurements, namely, 1·166. The concordance lends support to the above theoretical views.

With oxygen and carbon dioxide, the rates of dissolution and liberation from water are practically the same, the latter being sometimes 3—4% higher. The amount dissolved in a given time is proportional to the partial pressure of the gas, but the velocity constant is independent of pressure.

The Arrhenius exponential law appears to hold for the effect of temperature on the rate of dissolution, but no theoretical conclusion is drawn from this. R. J. C.

Possible Solid Solution of Water in Crystals. Theodore W. Richards (*J. Amer. Chem. Soc.*, 1911, **33**, 888—893).—Analyses of cadmium sulphate by Perdue and Hulett (this vol., ii, 397) have shown that the amount of cadmium present in both the crystalline and anhydrous forms is less than that theoretically required on the basis of the atomic weight of cadmium as determined by Baxter. It is now pointed out that this discrepancy is probably due to the presence of solvent in the crystals of cadmium sulphate in the form of a solid solution, and to the retention of traces of the solvent in the dried sulphate either as solid solution or by mechanical inclusion. The presence of a solid solution of the solvent in crystals cannot be easily detected or easily eliminated, and it is therefore evident that solids obtained from an environment containing other substances, such as a solution, cannot be safely employed for exact quantitative work without further treatment. E. G.

Changes in Volume on Solution in Water of the Halogen Salts of the Alkalis. Gregory P. Baxter (*J. Amer. Chem. Soc.*, 1911, **33**, 922—940).—When a salt is dissolved in water, the volume of the solution is usually less than the sum of the volumes of the salt and the water, although in some cases it is greater. Buchanan (*Amer. J. Sci.*, 1906, [iv], **21**, 25) has shown that in saturated solutions of the cæsium haloids, the molecular volumes of the dissolved salts are greater than those of the solid salts, whilst the reverse is the case with the corresponding potassium and rubidium salts. Attempts to correlate the sum of the volumes of the salt and the water with the volume of the resulting solution have previously been hampered by the lack of sufficiently accurate density determinations. The data furnished by Baxter, Boylston, Mueller, Black, and Goode (this vol., ii, 557) for the haloids of lithium, sodium, and potassium, allow the magnitude of the changes of volume which occur during the solution of these salts to be calculated with considerable precision. The results obtained from these data, and also for the rubidium and cæsium salts from those recorded by Buchanan (*loc. cit.*), are tabulated.

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* and *J. Amer. Chem. Soc.*, 1911, **33**, 1027—1032.

Of the fifteen salts, five, namely, the three cæsium salts and lithium bromide and iodide, undergo expansion during solution, whilst the others suffer a contraction.

The causes of these changes in volume have not hitherto been adequately explained. An explanation is now advanced which is based on Richards' hypothesis of the compressibility of atoms and on hydration. It is assumed that during solution and dissociation, a salt is freed to a large extent from compression due to chemical affinity and to molecular cohesion, and that, when the ions or molecules combine with water, both the hydrated substance and the water undergo compression. The latter effect varies regularly with the compressibilities of the substances and with their mutual affinities. It is shown that the change in volume in the formation of the ions from the elements, as measured by the sum of the change in volume in the formation of the solid salt and the change in volume during solution, is an additive property. The part played by the polymerisation of water in the change of volume is discussed, and it is considered probable that this effect varies with varying temperature, but that at the temperature of the experiments quoted it is very small.

E. G.

The Internal Frictions of Colloidal and Non-colloidal Liquids. Ludwig Dienes (*Biochem. Zeitsch.*, 1911, **33**, 222—224).—In experiments with von Liebermann's modification of Coulomb's apparatus (this vol., ii, 585), it was noticed that the logarithmic decrement of the vibration amplitudes increases as the vibrating disc is sunk in the liquids in the case of non-colloidal substances, whereas in the case of colloids it is greatest near the surface. The author offers explanations of the phenomena. S. B. S.

Mode of Dissolution of Colloidal Substances. Paul Bary (*Compt. rend.*, 1911, **152**, 1386—1387).—The author regards a colloidal solution as containing solid–liquid particles in suspension, such that the attraction between the liquid and solid is in equilibrium with the sum of the elastic tension of the particles and the surface tension. The particles may be considered as spongy cells into which liquid has penetrated by osmosis. Coagulation in such solutions is brought about by the influence of soluble salts in effecting local alterations in osmotic pressure. W. O. W.

Ultra-microscopic Investigation of Certain Colloids Coagulated by Electrolytes. GEORG WIEGNER (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 227—232).—Ultra-microscopic observations of the process of coagulation in cow's milk and in colloidal solutions of gold indicate that the nature of the process is such that the smaller colloidal particles attach themselves to larger particles, and that there is little tendency for particles of the same size to cohere. The larger ultra-microscopic particles seem to act, therefore, as coagulation nuclei for the smaller particles.

The slight differences observed in the coagulation processes in milk and in colloidal gold solutions are probably due to differences in the size of the particles which may act as coagulation nuclei in the two cases. H. M. D.

The Coagulum from Gelatin-Gum Arabic Sols, and its Analogy to Casein. F. W. TIEBACKX (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 238—239. Compare this vol., ii, 378).—The swelling properties of the coagulation product obtained from solutions containing gelatin and gum arabic are described, and reference made to the similarity between these and the colloido-chemical properties of casein. H. M. D.

Distribution of Ammonia between Water and Chloroform. JAMES M. BELL and ALEXANDER L. FEILD (*J. Amer. Chem. Soc.*, 1911, 33, 940—943).—The distribution of ammonia between water and chloroform has been determined at 25°, and over a much wider range of concentrations than has been studied previously. The results show that the distribution ratio varies with the concentration from about 24 in very dilute solutions to about 10 in concentrated solutions, and that it is only very slightly affected by the presence of ammonium chloride. E. G.

Influence of Dissolved Salts on the Distribution of a Substance between Two Solvents. NICOLAS DE KOLOSSOVSKY (*Bull. Soc. chim. Belg.*, 1911, 25, 183—210*).—The distribution of acetic acid between water and ethyl ether has been measured for different concentrations up to the point at which the two liquids become identical. The relationship between the ratio of distribution between water and ether (C) and the quantity of acetic acid (p) contained in 100 c.c. of the aqueous layer is given by $C = 2{\cdot}066 - 0{\cdot}0667p + 0{\cdot}00106p^2$ at 18°.

In general, the presence of salts lowers the ratio of distribution, and for salts of different metals the lowering produced increases in the series: potassium, sodium, barium, magnesium. On the other hand, the acetates of the alkali and alkaline-earth metals raise the distribution ratio, and this is attributed to the formation of acid salts. H. M. D.

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* and *Bull. Soc. chim.*, 1911, [iv], 9, 632—637.

Solubility Equilibria between Iodine and Organic Substances. F. OLIVARI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 470—474).—The author has investigated the complete solubility diagrams of iodine and various organic compounds in order to ascertain whether complete or incomplete miscibility, solubility in the solid state, etc., exist between the compounds, and whether any possible complex compounds are capable of crystallising or of revealing their existence by the form of the equilibrium curves.

The solubility curves of iodine in proximity to the point of fusion of this element practically coincide for iodoform, azobenzene, *p*-dibromobenzene and *p*-dinitrobenzene, and deviate somewhat for benzoic anhydride and acid, the behaviour of these two compounds being due to their molecular polymerisation (compare Abstr., 1910, ii, 18).

The curves of solubility of iodine in *p*-dibromobenzene, *p*-dinitrobenzene, benzoic anhydride and benzoic acid exhibit an extended horizontal branch corresponding with the formation of two liquid strata; fused iodine is hence not completely miscible with these organic compounds.

The solubility diagrams for *p*-dibromobenzene and azobenzene show changes of curvature at concentrations of about 70% and 60% respectively, the adjacent solutions probably passing in the neighbourhood of the critical state.

The presence of the eutectic even in dilute solutions (5—6%) excludes the possibility of isomorphism between the components beyond this limit.

Thus, the curves furnish no indication of the crystallisation of iodine complexes, and, since there are reasons (such as the red or reddish-brown colour of the liquid phase) for believing that they exist in solution, the conclusion must not be drawn that their saturation temperatures in the mixtures are below the eutectic temperatures.

T. H. P.

Equilibrium in the System: Water, Sodium Sulphate, Sodium Chloride, Copper Sulphate, Cupric Chloride. FRANS A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1163—1177. Compare this vol., ii, 381).—Solubility data are recorded showing the composition of the solutions saturated respectively with one, two, and three solid phases at 15°, 25°, and 35°. Within this range of temperature, the quaternary system gives rise to only one double salt, $Na_6SO_4,CuSO_4,2H_2O$. By means of a spacial model, in which the solubility data are incorporated, the solid phases capable of co-existence at the different temperatures in contact with aqueous solution are clearly exhibited. H. M. D.

Equilibrium in the System: Water, Ethyl Alcohol, and Ethyl Ether. SHINKICHI HORIBA (*Mem. Coll. Sci. Eng.*, 1911, **3**, 63—78).—The equilibrium in the ternary system water– ethyl alcohol– ethyl ether has been determined at 25° by shaking the components together in varying proportions and finding the composition of the upper and lower layers after complete separation has taken place. The analysis of the layers was effected indirectly by means of data for the

specific gravity, index of refraction, and specific viscosity of homogeneous mixtures of the three components, which are given in tabular form. From these results and direct determinations of the binodal curve for the upper layer, the curve and tie lines representing the composition of the conjugate mixtures have been completely determined, and are represented graphically. At the critical point, the mixture contains 40% water, 28·4% alcohol, and 31·6% ether.
J. D. K.

The So-called Nucleus and Convergence Points of the "Crystalline-liquid Phase" of *p*-Azoxyphenetole. GEORG WULFF (*Ann. Physik*, 1911, [iv], 35, 182—184).—The peculiar structure which is exhibited by the crystalline-liquid form of *p*-azoxyphenetole when examined under the microscope can be explained on the assumption that the anisotropic phase is a colloidal solution. The nucleus points are the result of the primary coagulation, which then proceeds under the influence of the strain set up by the surface-tension, and thus leads to the production of the convergence points. H. M. D.

The Number of Electrons in the Atom. HAROLD A. WILSON (*Phil. Mag.*, 1911, [vi], 21, 718—722).—Assuming the atoms to be constituted, according to Sir J. J. Thomson's theory, of spheres of positive electricity containing freely moving negative electrons, the deduction is made that the constitution of an atom containing n-electrons in the positive sphere will be such that the positive sphere is divided into n equal volumes, as nearly spherical as possible, each containing a central negative electron. The electrons will thus arrange themselves on nearly spherical concentric surfaces, the distances between which are equal. Assuming that in a series of similar elements each is derived from the one preceding by the addition of one such spherical layer of electrons, and that the number of electrons is proportional to the atomic weight, the number of electrons per atom is deduced to be eight times the atomic weight of the element. The cube-root of the atomic weights plotted against the order of the element in the series fall nearly on straight lines for each series, the lines for different series being nearly parallel. F. S.

Classification of the Elements. TORIBIO CÁCERES (*Anal. Fis. Quim.*, 1911, 9, 82, 121—124).—The author proposes a periodic arrangement in which the elements of the rare earths lying between lanthanum and tantalum are made part of the fifth period, which thus extends from xenon to bismuth. The suggested arrangement is not essentially different from that brought forward by Werner (compare Abstr., 1905, ii, 308, 514). G. D. L.

Modification of the Periodic Table. ELLIOT QUINCY ADAMS (*J. Amer. Chem. Soc.*, 1911, 33, 684—688).—The elements are arranged in six horizontal rows or periods. The first period consists of hydrogen and helium. The second contains eight elements, beginning with lithium and ending with neon. The third also contains eight elements, beginning with sodium and ending with argon. The fourth and fifth periods each contain sixteen elements, the fourth extending from potassium to krypton, and the fifth from rubidium to xenon. The sixth period contains thirty-two elements, beginning with cæsium and ending with an unknown element. Each period contains homologues of all the elements of the preceding period. Several new families of elements appear in alternate periods. The rare earths proper and the radioactive elements are not homologous to any previous elements, but are two groups of families which enter into the sixth period. Apart from the rare earth and radioactive elements, seven elements await discovery. E. G.

Position of the Most Important Elements in the Periodic System. K. Scheringa (*Chem. Weekblad*, 1911, 8, 389—390).—The most important elements in each horizontal series of the periodic system lie on the same line, as is best illustrated by mapping out the whole system on a cylinder. A. J. W.

Molecular Magnitudes. Jean Perrin (*Compt. rend.*, 1911, **152**, 1380—1382. Compare Abstr., 1908, ii, 927; 1910, ii, 493; this vol., ii, 480).—An emulsion of resin with water and alcohol was submitted to fractional centrifugation during four months to obtain grains of uniform density. The grains had D 1·1942 and their mean radius, a, obtained by counting the particles in a definite volume, was 0·3667μ. The radius calculated by an application of Stokes' law was 0·368μ. Their concentration at different levels in the liquid was determined by a photographic method of counting. Avogadro's constant, N, the number of molecules in a gram-molecule, was thus found to be $68·3 \times 10^{22}$, whence the value for e, the charge on an electron, is $4·25 \times 10^{-10}$.

The displacement of a grain, ξ, in the fluid of viscosity, ζ, during time τ was measured microscopically. Einstein's formula, $\xi^2 = \tau(RT/N)(1/3\pi a\zeta)$, then gave $4·21 \times 10^{-10}$ as the value for e. This is practically identical with the number calculated from the electrification of solid spheres. W. O. W.

Regulator for Diminished Pressure with Periodic Alterations. Antoine Villiers (*Chem. Zentr.*, 1911, i, 857—858; from *Bull. Sci. Pharmacol.*, 1911, **18**, 7—11).—A full description is given of an apparatus by means of which the air or gas pressure in a vessel can be varied periodically from the normal pressure down to a pressure limited only by the capabilities of the air-pump used. T. S. P.

Luminosity of Phosphorus: Lecture Experiments. Luigi Marino and C. Porlezza (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 442—446).—By the following method the phosphorescence of phosphorus vapour may be rendered apparent to a large audience without the latter being inconvenienced by the fumes and without a specially darkened room. A current of carbon dioxide is passed through a saturated solution of sodium hydrogen carbonate, then dried by means of a tower containing calcium chloride, and finally passed over red phosphorus contained in a hard glass tube. The latter is first heated at its extremity, while the gas is passing slowly, until all moisture has been eliminated. A delivery tube reaching to the bottom of a flask of about 2 litres capacity is then attached, and the gas current reduced to a minimum. When drops of white phosphorus begin to deposit on the cooler parts of the delivery tube, the flask is placed under the latter, and a strong intermittent current of carbon dioxide passed. The phosphorus vapour, coming into contact with the air of the flask diluted with carbon dioxide, generates a green flame, and the whole of the bottom of the flask appears phosphorescent.

By suitably modifying this apparatus and by employing a mixture of carbon dioxide with 10% of air, a stable, lemon-yellow substance is deposited, which is found to have the composition P_4O (compare Michaelis and Pitsch, Abstr., 1899, ii, 285).

The authors draw the conclusion that, in the oxidation of phosphorus, three different stages are reached, according to the conditions employed: (1) formation of P_2O_5 when phosphorus vapour burns completely in excess of oxygen; (2) formation of P_2O_3 and P_4O when phosphorus is burnt in a current of air; (3) formation of a lower oxide, probably P_4O, when phosphorus is oxidised with highly diluted oxygen under the conditions of the authors' experiments. T. H. P.

Inorganic Chemistry.

Constitution of Water. Jacques Duclaux (*Compt. rend.*, 1911, **152**, 1387—1390).—Regarding water as a solution of ice, $(H_2O)_n$, in hydrol. H_2O, and supposing the ice to retain its normal density, the author attempts to find the value of n in the foregoing formula. When deduced from the variation of the coefficient of expansion of water with pressure, n is 9—12. The limits are 6—23 when derived from the variation of the coefficient of compressibility with temperature, whilst when calculated from the specific heat and expansion, $n = 12$.

If, as Sutherland has supposed, the density of ice in solution is lower than when in the solid state, the molecular weight is possibly not higher than that corresponding with the formula $(H_2O)_6$.

W. O. W.

Solubility of Water in Benzene, Petroleum, and Paraffin Oil. Erich Groschuff (*Zeitsch. Elektrochem.*, 1911, **17**, 348—354).—Benzene is dried by keeping over sodium and then by distillation over the liquid alloy of potassium and sodium. The high boiling petroleum and paraffin oil are first heated at 120° for some time, and finally distilled over fused sodium. The solubility is determined by sealing up the dry solvent with a known quantity of water, accurately measured by a capillary pipette, in a glass bulb, and heating until the water is dissolved ; by slight supercooling a cloud is then formed, which disappears again at a slightly higher temperature. The solubility of water in 100 grams of benzene is 0·030 gram at 3°; 0·061 at 23°; 0·114 at 40°; 0·184 at 55°; 0·255 at 66°, and 0·337 at 77°. In purified American petroleum, boiling between 190° and 250°, the solubility is much smaller, increasing from 0·0012 gram per 100 at −2° to 0·097 at 94°, whilst in the paraffin oil (distilling between 200° and 300° at 10 mm. pressure) it was 0·003 at 16° and 0·055 at 94°. The bearing of the results on the behaviour of oils when used as electrical insulators is discussed. T. E.

Distribution of Hydrogen Sulphide in a Large Laboratory and the Use of Aluminium Stopcocks. Edward D. Campbell (*J. Amer. Chem. Soc.*, 1911, **33**, 947—948).—An account is given of the system of supplying hydrogen sulphide in the laboratory of the University of Michigan, which has been found to be very satisfactory. Generators of the form described by Browne and Mehling (Abstr., 1906, ii, 609) are placed in the attic in a small room, which is provided with an exhaust fan operated by an independent motor. The waste pipe for carrying away the spent liquor is connected directly with the main sewer outside the building. Two generators have been installed, so that when one is being cleaned or re-charged, the other can be brought into use. The hydrogen sulphide for the generator is passed through a wash-bottle containing water and through a tower of calcium chloride, and is distributed by means of a system of ordinary gas pipes. The delivery ends of the pipes are fitted with aluminium stopcocks, which resemble ordinary laboratory gas taps, except that the hole in the tip is only about 0·5—1 mm. in diameter, so as to prevent excessive loss of the gas if the stopcock is left open. These aluminium stopcocks are not affected by dry hydrogen sulphide, and give no trouble if they are occasionally lubricated. E. G.

A Modification of Raschig's Theory of the Lead-Chamber Process. Edward Divers (*J. Soc. Chem. Ind.*, 1911, **30**, 594—603. Compare this vol., ii, 272).—What goes on in the lead-chambers is largely a matter of inference, but it may be inferred with certainty that, before sulphuric acid can be produced in the process, there must be combination between sulphur dioxide and nitrous acid or its equivalent. When the process is working normally, the single substance formed by the combination must decompose as fast as it is formed. The presence in the chamber of this intermediate substance will therefore be unrecognisable.

Nitrososulphuric acid (nitrosyl sulphate), $HNSO_5$, is not qualified to play the part of the intermediate substance, for it is no more than a compound of nitrous anhydride with sulphuric acid, the mixed hemianhydride of the two acids, into which it decomposes again when hydrated. It is not a sulphonic compound. Raschig's nitrosulphonic acid, $HNSO_4$, has probably no existence, and the evidence is all against the existence of his nitrosisulphonic acid, H_2NSO_5.

The intermediate combination will be a substance necessarily equal in composition to that of the substances formulated on either side of the summary equation of the chamber-process. The double equation will therefore be $2HNO_2 + SO_2 = H_2N_2SO_6 = 2NO + H_2SO_4$. Nitroxysulphuric acid, $OH\cdot N<^{O}_{O}>N\cdot SO_3H$, are the name and constitution given to this intermediate substance, in accordance with nitroxysulphurous acid, $HN<^{O}_{O}>N\cdot SO_3H$, given to the acid of Pelouze's potassium salt, to which it is allied, supposing it to be the same as the coloured substance studied by Sabatier and by Raschig, and seen occasionally in the acid of the Gay-Lussac tower The acid $H_2N_2O_3$, salts of which were discovered by Thum and by Angeli, appears to be the substance of which nitroxysulphuric acid is the sulphonic derivative. Instead of calling it azohydroxyl (Thum) or nitrohydroxamic acid (Angeli), the author suggests nitroxous acid and $HN<^{O}_{O}>N\cdot OH$ as being the suitable name and constitution for it.

It is no longer necessary to assume that nitric oxide unites with only enough oxygen to form nitrous anhydride, N_2O_3, although much more is present in the chambers. For, by applying the experimental knowledge gained by Raschig, it becomes evident that the nitric oxide does combine with enough oxygen to form a substance of the composition N_2O_4, which, although it soon becomes ordinary nitric peroxide, behaves for a time as the peroxide of nitrous acid, $ONO\cdot ONO$, yielding, in its interactions, nitrous acid and free oxygen. Thus, the nitric oxide oxidises, as it should, to (*iso*)N_2O_4, but the product behaves as nitrous acid.

The mist in the chambers consists, with continual resolution into drops and continual renewal, of minute particles of liquid sulphuric acid, each surrounded with its atmosphere of undiluted nitric oxide, the particle and its atmosphere being joint products of the decomposition of nitroxysulphuric acid. The nitric oxide then becomes nitrous peroxide, nitrous acid, and, completing the cycle, nitroxysulphuric acid again.

An important feature of the above theory is that only one intermediate substance, nitroxysulphuric acid, is assumed. T. S. P.

New Methods of Preparing Colloidal Selenium Solutions.

ALFREDO POCHETTINO (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 428—433).—Colloidal selenium solutions have been prepared previously by reduction methods or electrical means. The method now described by the author admits of the preparation of colloidal suspensions of selenium in the most varied indifferent solvents, either solid or liquid, those employed being retene, fluorene, phenanthrene, anthracene, naphthalene, α-naphthol, α-naphthylamine, diphenylmethane, diphenylamine, triphenylamine, phenol, thymol, and paraffin. The solvent is heated to about its boiling point (above the melting point of selenium) in presence of selenium, the liquid assuming an increasingly dark red coloration. When solidified, the solution appears red by reflected, and blue by transmitted, light, this double coloration being characteristic of colloidal suspensions of selenium with large particles. These solutions can be repeatedly solidified and liquefied without alteration of their properties. Even when the solid suspension in anthracene or phthalic acid is melted, the selenium does not pass into the grey crystalline condition, although the points of fusion of these solvents are higher than the transformation temperature. The higher the temperature reached in the preparation of these solutions and the slower the cooling, the smaller are the selenium granules.

When these solutions are dissolved in other solvents, the selenium passes into the new solvent liquid in a condition of marked dispersion. All the suspensions thus prepared show the double coloration, and the magnitude of the particles depends on the natures of the two solvents.

If platinum electrodes, placed in such a colloidal suspension, are connected to the poles of a Wimshurst machine, the selenium is deposited in a highly adherent, compact layer on the electrode joined to the positive pole. In some cases, however, the solvent employed may influence this phenomenon. Thus, with solutions made in the first place with phenanthrene, that in benzene always gives a deposit at the positive and that in carbon disulphide at the negative pole.

When heated the particles of disperse selenium become decomposed, the resultant particles diminishing in size as the temperature rises.

Characteristic for these solutions is the behaviour of their electrical resistance, which remains constant for a 1% solution, but gradually increases for a 0·3% or more dilute solution. T. H. P.

Tellurium. I. Action of Sulphuryl and Thionyl Chlorides on Tellurium. BÉLA VON HORVÁTH (*Zeitsch. anorg. Chem.*, 1911, **70**, 408—413).—Tellurium, prepared by the repeated reduction of purified telluric acid in hydrogen, reacts with sulphuryl chloride at the ordinary temperature. In an atmosphere of carbon dioxide at a red heat, tellurium tetrachloride and sulphur dioxide are formed. The same products, together with sulphur, are obtained from thionyl chloride and tellurium. C. H. D.

Production of Ammonia and the Economy of Nitrogen with Peat. HERMAN CHARLES WOLTERECK (*Compt. rend.*, 1911, **152**, 1245—1247. Compare Abstr., 1908, ii, 174, 400).—It has been suggested that the author's synthesis of ammonia from water and atmospheric nitrogen by passing these through peat depends solely on the action of water on the peat. It is now stated, however, that in the absence of free nitrogen less than one-third the amount of ammonia is formed than under similar conditions when it is present. W. O. W.

Electrolysis of Aqueous Ammonia. FRIEDRICH C. G. MÜLLER (*Chem. Zentr.*, 1911, i, 626; from *Zeitsch. physik.-chem. Unterr.*, 1911, **23**, 355—356).—Several irregularities occurring in the electrolysis of aqueous solutions of ammonia are noted. At an iron anode, oxygen, and not nitrogen, is evolved. Small quantities of ammonium nitrate may be produced during the electrolysis, which then play a considerable part in the conduction of the current. T. S. P.

The Preparation and Estimation of Nitric Oxide and its Behaviour towards Water. L. MOSER (*Zeitsch. anal. Chem*, 1911, **50**, 401—433).—An investigation of the various methods for the preparation of nitric oxide leads the author to the conclusion that the pure gas is best obtained either by the reduction with mercury of nitrous acid dissolved in sulphuric acid, or by the interaction of hydriodic acid and nitrous acid. The nitric oxide so obtained cannot be preserved unchanged over water; chemical reactions take place which are due, in part, to the oxygen dissolved in the water, and in part to the hydrions contained in the water. Nitrous and hyponitrous acids are formed, probably according to the equation: $4NO + 2H_2O \rightleftarrows 2HNO_2 + H_2N_2O_2$ (compare Zimmermann, Abstr., 1906, ii, 82), which then decompose, the latter acid giving, not only nitrous oxide, but also ammonium nitrite ($3H_2N_2O_2 = 2N_2O_3 + 2NH_3$: compare Hantzsch and Kaufmann, Abstr., 1897, ii, 25), which breaks down with the liberation of nitrogen. The quantity of nitrogen increases the longer the nitric oxide is preserved over water. Nitric oxide, whether moist or dry, can be preserved over mercury at room temperature for any length of time without undergoing a change.

Pure nitric oxide is completely absorbed by a solution of ferrous sulphate, but the results are inaccurate in the presence of nitrous oxide. Ferrous sulphate cannot be advantageously replaced by a slightly alkaline solution of sodium sulphide (compare Divers, Trans., 1899, **75**, 82), since the reaction is much slower, and the absorption is complete only after long shaking.

The volumetric determination of nitric oxide by means of permanganate, as carried out according to Lunge (*Zeitsch. angew. Chem.*, 1890, 567), generally gives too low results; small quantities of nitric oxide cannot be determined at all. The author modifies the method in such a way that the gas to be analysed is passed into an absorption vessel previously full of standard permanganate solution; after shaking well to complete the reaction, the diminution in the strength of the permanganate is measured. All errors caused by using a current of indifferent gas to sweep the nitric oxide through the permanganate solution are thus avoided. The same apparatus may be used with hydrogen peroxide in place of permanganate, the nitric acid formed by the oxidation of the nitric oxide being determined by titration with standard alkali. The method gives good results as long as the presence of acid vapours or gases is avoided.

The method of combustion after mixing with hydrogen gives inconstant results, owing partly to the formation of ammonia as a by-product, and partly to the permeability towards gases of platinum heated to a red heat. T. S. P.

Formation of Nitrosyl Chloride at Low Temperatures by Gay Lussac's Reaction. Liquidus Curve of the System Nitrosyl Chloride-Chlorine. N. Boubnoff and Philippe A. Guye (*J. Chim. Phys.*, 1911, **9**, 290—313).—The formation of nitrosyl chloride at low temperatures by direct interaction of chlorine and excess of nitric oxide was studied quantitatively with a view to estimating the atomic weight of chlorine by this method. The excess of nitric oxide having been removed by distillation at the temperature of liquid pentane (−160° to −150°), the nitrosyl chloride was found to contain 3 to 4% of chlorine more than the formula

NOCl indicates. When excess of chlorine is used for the synthesis, the same product is obtained. The excess of chlorine is readily removed by fractional distillation at higher temperatures than −80°, but is retained at −150°.

The existence of higher nitrosyl chlorides, such as $NOCl_2$, having been discredited by Tilden and others, it must be supposed that a highly dissociated additive compound of nitrosyl chloride and chlorine is formed. The liquidus curve of the mixed gases was determined, the liquids being distilled from weighed glass bombs into a special cryoscopic tube. The mixtures were agitated by a glass stirrer operated magnetically by an iron core fused into the upper part. All joints in the apparatus were made with ground glass flanges well greased and held together with screw clips. The mercury in the manometers was protected by a layer of syrupy phosphoric acid. The liquidus curve exhibits no maxima, but there is also no sharp minimum at the eutectic point, about −109°. The curve is well rounded here, indicating the presence of a compound of approximate composition $NOCl,Cl_2$, which is highly dissociated even at −107°.

It is suggested that the presence of excess of chlorine in the authors' synthetic nitrosyl chloride is due to the incompleteness of the reaction at the low temperatures employed. R. J. C.

Preparation of Certain Nitrides by Reduction of Alkaline Cyanides. ALEXANDER C. VOURNASOS (*Bull. Soc. chim.*, 1911, [iv], 9, 506—512).—A résumé of methods for the preparation of metallic nitrides is first given, and it is then pointed out that certain elements, such as boron and aluminium, decompose cyanogen or hydrocyanic acid at 750°, forming nitrides. The corresponding nitride is produced when boron, aluminium, cerium, or lanthanum in a finely divided state is added to fused potassium cyanide.

The potassium cyanide is first melted in a porcelain crucible at 650° in the absence of air, and poured out on a marble slab. It is then re-melted in a clay or porcelain crucible, and the dry, finely-powdered element added in portions, the mixture being agitated from time to time, and the heating continued for fifteen minutes after the final addition. The cooled black mass is placed in warm water, and the insoluble residue of nitride and amorphous carbon is carefully and gently ignited in air to removed the carbon.

Boron nitride, BN, so prepared, is a white powder, which is attacked with difficulty by warm water. Cold water slowly becomes alkaline in contact with the nitride, due to the formation of ammonia. Aluminium nitride, Al_2N_2, is an amorphous, yellow powder. Cerium nitride, CeN, is readily oxidised, and consequently the carbon produced along with it cannot be removed by ignition in air. Lanthanum nitride resembles the cerium compound. Both are readily decomposed by warm water, yielding ammonia. T. A. H.

Amorphous States of Silicon. LIVIO CAMBI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 440—442).—The amorphous silicon obtained by the author from the black sulphide (see following abstract) is distinguished from those previously described in possessing a paler reddish-yellow colour, different from the greyish-yellow tint sometimes assumed by crystalline silicon. The product containing 96% Si has D 2·08 (compare Vigouroux, Abstr., 1895, ii, 222, 263; Wilke-Dörfurt, Abstr., 1910, ii, 204). When heated, the properties, such as colour and specific gravity, of the author's product approach those of Vigouroux's silicon.

These amorphous silicons must be regarded, not as clearly defined allotropic forms, but as masses of forms possibly possessing different molecular structures. T. H. P.

Silicon Sulphides. II. Livio Cambi (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 433—440).—The author has studied the hydrolysis of the black and yellow silicon sulphides previously obtained (Abstr., 1910, ii, 952).

The yellow sulphide yields silicoformic anhydride, $(SiHO)_2O$, the corresponding acid being probably formed first: $SiS + 2H_2O = SiHO{\cdot}OH + H_2S$. The silicon in the sulphide hence acts as a bivalent element. The formation of silicoformic acid is analogous to that of formic acid, which can be obtained from chloroform, carbon monoxide, or compounds containing bivalent carbon, such as the carbylamine derivatives, $C{:}NR$; this analogy can be extended to the corresponding germanium compounds. The action of dry hydrogen chloride on the yellow sulphide yields hydrogen sulphide and silicochloroform. The properties of this sulphide fall into line with those of the sulphides of the other elements of the second half of the fourth group; for example, the orange-yellow colour of the silicon compound becomes reddish-brown for germanium, dark brown for tin, and black for lead.

The vitreous, black silicon sulphide (*loc. cit.*) undergoes dissociation: $2SiS \longrightarrow Si + SiS_2$, which may be more or less complete, the presence of unaltered monosulphide and possibly, also, of intermediate labile compounds similar to P_4S_3, not being excluded. On hydrolysis it yields soluble silica and amorphous silicon (see preceding abstract). T. H. P.

The Electrical Conductivity and Behaviour of Diamond at High Temperatures. Cornelio Doelter (*Monatsh.*, 1911, 32, 275—298).—The electrical conductivity of diamond has been measured at temperatures between 880° and 1290° in an atmosphere of nitrogen or hydrogen. For a plate 1 square cm. in area and 1 mm. thick, the resistance falls from 58800 ohms at 950° to 370 ohms at 1220°, then increases to 930 ohms at 1260°, and again falls to 590 ohms at 1290°. This behaviour is somewhat similar to that exhibited by quartz.

The reputed conversion of diamond into graphite at high temperatures is discussed, and the microscopic appearance of the diamonds used in some earlier experiments is described. These observations afford no evidence of the formation of graphite. New experiments, in which diamonds were heated in carbon dioxide at 1350°, in hydrogen at 1300° to 1550°, in nitrogen at 1300°, and in chlorine at 1200°, have also failed to give evidence of conversion into graphite. At these temperatures the diamonds acquire a brownish-black colour in certain cases, but this appears to be due to amorphous carbon. The effect is probably one of corrosion, and if sufficiently protected it seems likely that the diamond remains unchanged at temperatures of 2000—2500°.

H. M. D.

Action of Carbonyl Chloride on Natural and Artificial Sulphides.

ÉDOUARD CHAUVENET (*Compt. rend.*, 1911, **152**, 1250—1252. Compare Abstr., 1909, ii, 53; this vol. ii, 109).—Carbonyl chloride attacks metallic sulphides between 300° and 450° in accordance with the equation $MS + COCl_2 = MCl_2 + COS$. The ease with which sulphides are thus converted into anhydrous chlorides furnishes a useful method for the treatment of minerals in analysis. The process is also suitable for preparing carbonyl sulphide.

W. O. W.

Ratio of Argon to Nitrogen in Natural Gaseous Mixtures and its Significance.

CHARLES MOUREU and ADOLPHE LEPAPE (*Compt rend.*, 1911, **152**, 1533—1535. Compare this vol., ii, 392, 439).—The ratio of argon to nitrogen in natural gaseous mixtures from fifty-two mineral springs was determined and found to be fairly constant. In thirty-six springs $100A/N = 1{\cdot}0 - 1{\cdot}29$; the same ratio for air is 1·18. Geologically nitrogen behaves as an inert gas, and adopting the view expressed in a previous communication it would appear that the greater part of the gas has existed in the free state from the origin of the earth. W. O. W.

Luminescent Tubes of Neon.

GEORGES CLAUDE (*Compt. rend.*, 1911, **152**, 1377—1379).—The luminescence of tubes containing neon traversed by an alternating current gradually diminishes, owing to absorption of gas. It has been found that copper electrodes of small size become red hot, the metal rapidly volatilising and becoming deposited on the sides of the tube. The deposit produced in this way yields a gas when dissolved in nitric acid; in one experiment, 1·6 grams gave 2·5 c.c. of gas, whilst the same weight of unvolatilised electrode gave only 0·3 c.c. The latter contained a little neon, but no helium, whilst the gas from the deposit showed an intense spectrum of neon and helium. The two gases appeared to be present in about equal amounts, although the neon with which the tube was filled contained originally only a trace of helium.

The suggestion is offered that helium results from the dissociation of neon, or else that the greater part of the neon absorbed by copper is not liberated when the metal is dissolved in nitric acid.

By increasing the surface of the electrodes, absorption of gas is considerably diminished. Thus a tube 35 metres long and 45 mm. diam., with electrodes of area 3 sq. cm. per ampere, remained luminous for 210 hours, when an accident terminated the experiment.

W. O. W.

Preparation of Alkali Metals.

LOUIS HACKSPILL (*Bull. Soc. chim.*, 1911, [iv], **9**, 446—451).—Detailed descriptions of the apparatus and method of working are given for the reduction of alkali chlorides by means of metallic calcium as already described (Abstr., 1905, ii, 585). The prepared mixture of calcium and the alkali chloride is placed in an iron tube lying in a glass tube, which can be rendered vacuous. The glass tube is heated to the required temperature in a simple electric furnace of special form. Potassium, cæsium, and rubidium have been prepared in this way. Attempts to prepare lithium were unsuccessful, but by using a modified form of Guntz's apparatus, an alloy of lithium with 3 or 4% of calcium was obtained.

T. A. H.

Solubility of Sodium Carbonate. C. H. Ketner (*Chem. Weekblad,* 1911, **8**, 391—393. Compare Abstr., 1902, ii, 308.).—The author calls attention to his work on equilibrium in the system sodium carbonate, alcohol, water—which seems to have been overlooked.

A. J. W.

Hydrates of Rubidium and Cæsium Fluorides. Robert de Forcrand (*Compt. rend.*, 1911, **152**, 1208—1211. Compare this vol., ii, 488).—A saturated solution of rubidium fluoride deposits crystals of a hydrate, $2RbF,3H_2O$, m. p. 36°; the heat of dissolution at 15° is $-0·62$ Cal. When dried over phosphoric oxide, it forms the hygroscopic compound, $3RbF,H_2O$, having a heat of dissolution 3·76 Cal. at 15°.

Cæsium fluoride forms two hydrates, $2CsF,3H_2O$, heat of dissolution 0·99 Cal., and $3CsF,2H_2O$, heat of dissolution 4·23 Cal.; there is no compound intermediate between the two.

The general conclusion drawn from these observations and those previously published is that in respect to the hydration of its salts rubidium does not stand invariably intermediate between potassium and cæsium, but resembles sometimes one and sometimes the other in its properties.

When estimating rubidium and cæsium by conversion into their sulphates, it is necessary that the temperature of ignition should not exceed 1000°, otherwise volatilisation occurs. Cæsium sulphate is appreciably volatile at the temperature of the blowpipe. W. O. W.

Specific Gravity of Ammonium Sulphate Solutions. M. C. Dekhuyzen (*Zeitsch. physiol. Chem.*, 1911, **72**, 167—168).—The expression $^{\circ}P_{\circ b}$ is used to denote the number of grams of a substance dissolved in 100 grams of solvent, and $^{\circ}P_{\circ s}$ the number of grams of solute in 100 grams of solution. If p = the first quantity and p_1 the second, then $100p/100+p=p_1$. The expression $^{\circ}V_{\circ s}$ expresses the number of grams of solute in 100 c.c. of solution, and if represented by p_2 and density of solution by D, then $p_2=p_1D$. Wiener (this vol., ii, 394) has confused the expression $^{\circ}P_{\circ s}$ and $^{\circ}V_{\circ s}$. J. J. S.

Preparation of Ammonium Selenate: a New Method. Frank C. Mathers and Roy S. Bonsib (*J. Amer. Chem. Soc.*, 1910, **33**, 703—708).—The only method described hitherto for the preparation of ammonium selenate is by the action of ammonia on selenic acid, but this is unsatisfactory on account of the difficulty of preparing pure selenic acid. It has now been found that the salt can be readily prepared by treating barium or lead selenate with ammonium carbonate, and the best conditions have been determined in each case.

The barium or lead selenate is placed in a beaker with water and powdered ammonium carbonate. If barium selenate is used, for each gram of the salt 2·8 grams of ammonium carbonate (equivalent to 5 mols.) and 10 c.c. of water are employed. The mixture is left for thirty hours with occasional shaking, a yield of about 96—97% being thus obtained. In the case of lead selenate (1 gram), 0·55 gram of ammonium carbonate (equivalent to 1·2 mols.) and 5 c.c. of water are added, and the mixture left for one to two hours, when a yield of about 95—96% is obtained. Good yields can be obtained, however, in fifteen to thirty minutes. Lead selenate is therefore preferable to the barium salt for the purpose. The yield is not increased by heating the mixture or by agitating it by means of a current of air or carbon dioxide. E. G.

Fusion Experiments with Some Metasilicates. PETER LEBEDEFF (*Zeitsch. anorg. Chem.*, 1911, **70**, 301—324).—Mixtures of calcium metasilicate and calcium sulphide solidify to form solid solutions. It has not been found possible to investigate mixtures containing more than 50% of calcium sulphide on account of their corrosive action. Calcium sulphide is infusible in a kryptol furnace. The solid solutions undergo a transformation at temperatures below their freezing point, the transformation curve having a maximum at about 1300° and 20 mol. % of calcium sulphide. Rapidly cooled mixtures disintegrate completely when cold, whilst slowly cooled mixtures show, when examined microscopically, separate crystals of the pseudo-hexagonal modification of wollastonite and of calcium sulphide, identical with the oldhamite found in meteorites.

Magnesium and manganese metasilicates form two series of solid solutions, with a break in the freezing-point curve at 1328° and 50 mol. % $MgSiO_3$. The melting point of magnesium metasilicate is 1535°, and of manganese metasilicate 1210°. The optical examination shows that the crystals at the magnesium end of the series have the properties of enstatite, and those at the manganese end the properties of rhodonite, confirming the representation of the system as one of two series of solid solutions.

Calcium metasilicate, m. p. 1512°, and barium metasilicate, m. p. 1438°, form an isomorphous series, with a continuous freezing-point curve, having a minimum at about 35 mol. % $BaSiO_3$ and 1000°. A glass is obtained on cooling rapidly, whilst slowly cooled mixtures solidify to a homogeneous series of monoclinic solid solutions, which do not disintegrate or undergo further change. Barium and manganese metasilicates are isomorphous, and the freezing-point curve has a minimum, but its exact determination is impracticable, owing to the readiness with which a glass is formed.

Experiments with mixtures of manganese metasilicates with strontium and sodium metasilicates, as well as with those already mentioned, show that glass is formed when several silicates are melted together, even when the components crystallise well, and that the tendency to the formation of glass is greatest in eutectic mixtures and in solid solutions near to a minimum point. Mixtures having such compositions are highly viscous in the neighbourhood of the melting point. This confirms Vogt's views on the formation of glasses. C. H. D.

The Causes of the Variation in the Velocity of Hydration of Cement. Paul Rohland (*Zeitsch. Chem. Ind. Kolloide,* 1911, 8, 251—253).—Measurements of the rate of hydration of cement in contact with aqueous solutions show that sodium carbonate, aluminium chloride, and potassium sulphide accelerate the hydration process, whereas potassium dichromate, sodium borate and sulphates (with the exception of aluminium sulphate and the alums) retard it. The setting of the cement is not, however, solely determined by the velocity of hydration, but is influenced by the rate at which coagulation of the hydrolytically separated hydroxides of aluminium, iron, and silicon takes place. This process is also affected by the nature of the electrolytes present and by the temperature. H. M. D.

Barium Sulphate a Plastic Substance. Albert Atterberg (*Zeitsch. angew. Chem.*, 1911, **24**, 928—929).—The author defines a substance as plastic when its mixture with water can be rolled out into wire, the quantity of water not exceeding that which it is necessary to add to the substance in order to make it flow.

The "flow-limit" for ordinary precipitated barium sulphate is 22 parts of water to 100 parts of sulphate, whilst the "rolling-out limit" is 14 parts of water to 100 of sulphate. Barium sulphate is thus a plastic substance (plasticity = 8).

Further experiments have shown that minerals, such as kaolinite, potassium and magnesium micas, talc, etc., are strongly plastic when they are ground so finely that the size of their particles does not exceed 0·002 mm.; under the same conditions, minerals, such as quartz, felspar, and calcspar, show no plasticity. It is, therefore, the presence of fine particles of minerals which occur in laminated or shaly forms which confer plasticity on clay. T. S. P.

Crystallographic Examination of Fluorides Obtained by Moissan and Pupils. August de Schultén (*Compt. rend.*, 1911, **152**, 1261—1263. Compare this vol., ii, 486).—The results of crystallographic measurements are given for the fluorides of barium, strontium, manganese, nickel, cobalt, iron, and chromium; also for the double fluorides of nickel, cobalt, zinc, and calcium of the type $MF_2,2KF_2$, and for the compound $Cr_2F_6,6KF$. W. O. W.

Presence of Zinc Nitride in Zinc Powder and Commercial Zincs. Camille Matignon (*Compt. rend.*, 1911, **152**, 1309—1312).—A number of specimens of zinc dust were distilled with aqueous potassium hydroxide and the liberated ammonia determined. The amount of nitrogen found corresponded with about 0·4% of zinc nitride, Zn_3N_2. The latter was present to the extent of 1·2% in a dust prepared in such a way as to favour the formation of nitride. Commercial fused zincs were found to contain only traces of nitride, whilst this was absent from zinc oxide prepared by burning the metal in air. W. O. W.

Thermal Analysis of Mixtures of Cuprous Chloride with Chlorides of Univalent Elements. C. SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 457—464).—The author has studied the melting-point diagrams of mixtures of cuprous chloride with silver, sodium, potassium, or thallous chloride, the solidification temperatures for these salts being found from the cooling curves to be 422°, 455°, 806°, 776°, and 429° respectively.

The results show that cuprous chloride forms solid solutions, in limited degree, with the chlorides of the metals of the second half of the first group, homologous with copper, sodium, and silver. Double salts of the type CuCl,2MCl are formed with potassium and thallous chlorides, whilst mixed crystals are formed, within very restricted limits, between cuprous and thallous chlorides. T. H. P.

Binary Systems of the Chlorides of Certain Univalent Metals. G. POMA and G. GABBI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 464—470).—The authors have studied the cooling curves of the systems CuCl–KCl and CuCl–AgCl (compare Sandonnini, preceding abstract), the fusions being effected in an atmosphere of nitrogen, owing to the extreme oxidisability of cuprous chloride. The values found for the m. p.'s are: CuCl, 415°; AgCl, 451°; and KCl, 759°.

In the liquid state, cuprous and silver chlorides are completely miscible, but in the solid state there is a very wide gap in the solubility. From the fused mixtures, no compound of the two components separates on cooling.

In the case of cuprous and potassium chlorides, the fusion curve exhibits two arrests (142° and 236°), and has the form characteristic for binary systems, in which the two components form a compound which dissociates at a high temperature. The compound formed has probably the formula $K_2[CuCl_3]$. T. H. P.

The Binary Systems, CuCl–AgCl, CuCl–NaCl, CuCl–KCl. PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 597—599).—The author's investigation of the melting-point curve of the system CuCl–AgCl gives results in good agreement with those obtained by Sandonnini and by Poma and Gabbi (preceding abstracts).

The results for CuCl–NaCl give a curve very similar to that obtained by Sandonnini (*loc. cit.*), but differing from it in certain details.

For the system CuCl–KCl the author's results confirm Sandonnini's conclusion that these salts form the compound CuCl,2KCl.

T. H. P.

Catalytic Action of Copper Oxide. JAMES STRACHAN (*Chem. News*, 1911, 103, 241. Compare Sabatier, Abstr., 1909, i, 546).—Over a year ago the author noticed a similar action in the case of a Barthel spirit bunsen to that recently observed by Meunier (this vol., ii, 205) with an ordinary bunsen. The efficiency of such a burner becomes impaired in time by surface-combustion on the partly oxidised brass gauze, necessitating replacement of the latter. On extinguishing the burner, the gauze continues to glow so long as methylated spirit-vapour and air impinge on it. That surface-combustion commences at a low temperature may be shown by interrupting the stream of spirit-vapour for a few seconds. The combustion re-commences on the most oxidised portions of the gauze, proceeding rapidly over its whole surface. A strong odour of aldehyde is produced.

Various lecture experiments with asbestos fibre, alternately dipped in copper sulphate solution and ignited, are described. Asbestos so treated will ignite an explosive mixture of hydrogen and oxygen if fairly hot.

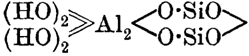
Other metallic oxides show like properties, and the experiments may be repeated, replacing copper sulphate by ferric chloride, but the ferric oxide so produced does not seem quite so active as copper oxide. It is pointed out that this catalytic action of ferric oxide may prove a source of danger with miners' safety lamps, in most of which iron gauze is used.

The author states that the mutual catalytic action of cellulose and copper oxide is one factor in the formation of dendritic growths of the latter on paper. J. D. K.

Elements in Thulium. CARL AUER VON WELSBACH (*Monatsh.*, 1911, 32, 373—375).—Spectroscopic examination indicates that thulium consists essentially of three elements. Of these three, thulium I. and thulium III. cannot be isolated by the present methods of purification. The salts of the former absorb rays in the extreme red down to λ 700, and show characteristic lines (quoted) between 2700 and 3270 (spark spectrum). Thulium III. exhibits a characteristic spark spectrum between 2800 and 3260.

The author hopes to isolate pure thulium II. in the near future. It forms an almost white sesquioxide. Its salts are pale yellowish-green in daylight and emerald-green in artificial light, and exhibit the absorption spectrum hitherto ascribed to thulium. The oxides of those fractions which are richest in thulium II. and aldebaranium exhibit a characteristic phenomenon in the flame; before becoming actually incandescent the oxides give out a purple light for a short time. The spark spectrum shows many strong lines (quoted) between 3400 and 3800. C. S.

The Chemical Constitution of the Kaolinite Molecule. JOSEPH W. MELLOR and A. D. HOLDCROFT (*Trans. Eng. Ceramic Soc.*, 1911, 10, 94—120).—Contrary to what is generally accepted, there is no definite temperature above which it can be said that kaolinite decomposes, and below which kaolinite does not decompose. The effect of raising the temperature is to accelerate the speed of decomposition, a result which can also be obtained by working under diminished pressure. The speed of decomposition at 500° is sufficiently rapid at atmospheric pressure to decompose an appreciable quantity of kaolinite in an hour.

The heating curve of kaolinite shows that an endothermic reaction occurs in the vicinity of 500°, and an exothermic reaction just above 800°; the curve shows no sign of the dehydration taking place in stages, such as might occur if the elements of the "combined water" were placed unsymmetrically in the molecule. In the absence of other evidence, and since solubility determinations show no sign of unsymmetrical aluminium groups, it is assumed that the hydroxyl and aluminium groups are symmetrically placed in the molecule, and the formula  $\begin{matrix}(HO)_2\\(HO)_2\end{matrix}\!>Al_2<\!\begin{matrix}O\cdot SiO\\O\cdot SiO\end{matrix}\!>O$ is suggested for kaolinite.

The solubility in acids, the hygroscopicity, and the density of kaolinite calcined at different temperatures, show that there is a certain parallelism in the properties of alumina and calcined kaolinite. The exothermal change indicated by the heating curve of kaolinite corresponds with that furnished by alumina derived from aluminium nitrate. The endothermal change shown in the heating curve in the neighbourhood of 500° corresponds with a decomposition of kaolinite into free silica, free alumina, and water. The restoration of from 3—4% of water to calcined kaolinite, which can be accomplished by heating it under pressure in steam, corresponds with a re-hydration of silica or alumina.

When kaolinite is heated to over 1200°, sillimanite is formed by the re-combination of the free alumina with some of the free silica formed at about 500°. The exothermal change in the heating curve at 800° corresponds with a physical change of the free alumina, which becomes less soluble in acid, less hygroscopic, and more dense.

Kaolinite may be represented as one member of a series of aluminodisilicic acids, and these in turn form one group of a large number of alumino-silicates, comprising alumino-mono-, -di-, -tri-, -tetra-, -penta-, and hexa-silicates; the different classes of which may be represented, for example, by allophane, kaolinite, natrolite, pyrophyllite, chabazite, and orthoclase respectively. T. S. P.

The System Manganous Oxide–Silica. FRIEDRICH DOERINCKEL (*Metallurgie*, 1911, 8, 201—209).—Mixtures containing from 20 to 60 mol. % of silica may be prepared in a platinum crucible, embedded in magnesia. Mixtures containing more manganese attack the platinum, whilst those richer in silica require too high a temperature. It is necessary to melt the mixture a second time to obtain complete reaction. Three crystalline constituents are observed in the sections obtained, namely: manganosite, MnO; tephroite, Mn_2SiO_4; and rhodonite, $MnSiO_3$, identical with the naturally-occurring minerals. The thermal results indicate that tephroite is formed by a reaction at 1323° between some primary crystals and the liquid, and that, also, in mixtures containing 49—60 mol. % of silica, primary crystals rich in silica react with the liquid at 1215° to form rhodonite. The tephroite–rhodonite eutectic point is at 1190° and 45 mol. % SiO_2. C. H. D.

Existence of a New Type of Dioxides: Reaction between Selenious Acid and Manganese Dioxide. LUIGI MARINO and V. SQUINTANI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 447—452. Compare Marino, Abstr., 1908, ii, 106).—The authors find that the compound obtained by Laugier (Abstr., 1887, 775) by the action of selenious acid on manganese dioxide in a sealed tube at 140° is the selenite corresponding with the dioxide, $MnSe_2O_6$, the other products observed by Laugier being formed by the decomposition of this compound. This selenite, which is obtained as an orange-yellow, crystalline powder, liberates chlorine from dilute or concentrated hydrochloric acid, and iodine from potassium iodide solution containing acetic acid. With alkali hydroxides or carbonates, manganese dioxide is set free, whilst with oxalic acid solutions, carbon dioxide is liberated quantitatively. It oxidises mercurous to mercuric salts, cuprous salts to the cupric state, potassium ferrocyanide to ferricyanide, and arsenious to arsenic acid. In presence of a slight excess of alkali hydroxide, it decomposes quantitatively according to the equation: $MnSe_2O_6 = MnO_2 + 2SeO_2$. Attempts to prepare a selenium acid corresponding with dithionic acid were unsuccessful.

When heated, the selenite decomposes in the following manner· $MnSe_2O_6 = SeO_2 + MnSeO_4$. At a higher temperature and in a vacuum, however, the decomposition proceeds according to the equation: $5MnSe_2O_6 \rightleftarrows 8SeO_2 + 2MnSeO_4 + Mn_3O_4 + O_2$ T. H. P.

The Gas Contained in Steels. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1911, **152**, 1247—1250).—The amount of gas obtained by heating different varieties of steel at 950° in a vacuum has been determined, taking special precautions to prevent the access of water vapour. The disengagement of gas was continuous during five days, but tended towards a limit. Hard and soft steels showed the same critical points after treatment as before the removal of gas.

W. O. W.

Cementation of Nickel Steel. I. FEDERICO GIOLITTI and F. CARNEVALI (*Atti R. Accad. Sci. Torino*, 1911, **46**, 409—432).—The authors have applied the methods previously employed in the investigation of carbon steels (Abstr., 1909, ii, 240; 1910, ii, 507, 616, 780) to the study of steels containing from 2·03% to 29·8% of nickel, the gases employed for cementation being pure ethylene and carbon monoxide.

The results show that the maximum content of carbon in the cementation zone diminishes continuously as the proportion of nickel present increases, the diminution becoming very marked when the percentage of nickel exceeds 5. The variation of the concentration of carbon in the successive layers of the cementation zone is much more regular for nickel steels than for ordinary carbon steels. The phenomena observed during the slow cooling of nickel steels, cemented so as to exhibit a hypereutectic zone, are qualitatively analogous to those shown by carbon steels subjected to similar treatment, but differ quantitatively from these in two directions: (1) The entity of the liquation phenomena of the cementite is less marked in the case of the nickel steels, and (2) the transition from the hypereutectic to the hypoeutectic zone corresponds with a content of carbon (0·6—0·65%) lower than that (0·9%) of the similar zone for carbon steels.

T. H. P.

Iron-Chromium Alloys and their Resistance to Acids. PHILIPP MONNARTZ (*Metallurgie*, 1911, 8, 161—176, 193—201).—Alloys of iron and chromium, free from carbon, may be prepared from chromite by the aluminothermic method. An elaborate apparatus is described by means of which cooling curves of the alloys may be taken immediately the temperature has fallen to 1600°. The fusibility of the slag, and the temperature reached in the reaction, are regulated by the addition of varying quantities of fluorite.

The freezing-point curve has a maximum at about 66% of chromium, corresponding with a compound Cr_2Fe (compare Treitschke and Tammann, Abstr., 1907, ii, 958). The higher the original temperature of the mass, the coarser is the resulting crystalline structure. The alloys are softer than cast iron. Homogeneous castings may be obtained by a special apparatus.

The addition of chromium to iron in the absence of carbon increases the readiness of attack by hydrochloric and sulphuric acids. Concentrated nitric acid renders the alloys passive. The resistance to dilute nitric acid diminishes from 0 to 4% Cr, increases very rapidly from 4 to 14%, and slowly from 14 to 20%. Alloys containing from 40 to 100% Cr even resist prolonged heating with dilute nitric acid to which 5% of sodium chloride has been added. The maximum passivity occurs at 66% Cr. These alloys also remain perfectly bright in laboratory air and in water. The presence of combined carbon increases the resistance to acids very greatly, but at the same time renders the alloys excessively hard. The resistance to acids is also much increased by molybdenum, which improves the mechanical properties. Titanium, vanadium, and tungsten have a similar influence, whilst manganese hastens the attack by acids. C. H. D.

Colloidal Ferric Hydroxide. A. V. DUMANSKI (*Zeitsch. Chem. Ind. Kolloide*, 1911, 8, 232—233; *J. Russ. Phys. Chem. Soc.*, 1911, 43, 546—553).—A colloidal solution of ferric hydroxide, prepared by addition of ammonium carbonate to ferric chloride solution, and purified by dialysis, was kept for a year, and then filtered through a collodion membrane. The freezing point of the solution which did not pass through the membrane was found to be slightly lower than that of the filtrate, and from the difference it is calculated that the molecular weight of the colloid is 3120. From the density of the colloidal solution, the density of the colloidal particles was found to be 4·704 at 0°. H. M. D.

Preparation of Chromyl Compounds. HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1911, 33, 697—703).—This work was undertaken with the object of obtaining chromyl bromide and iodide. These salts cannot be prepared by the interaction of the halide and dichromate of a metal in presence of sulphuric acid, owing to the oxidation of the hydrobromic and hydriodic acids by the chromic and sulphuric acids.

When anhydrous potassium chromate is heated with acetyl chloride and a little glacial acetic acid in presence of carbon disulphide, the mixture becomes dark red. On filtering the product, the filtrate is found to contain a small quantity of chromyl chloride, whilst the residue consists almost entirely of potassium chromate coated with a brown substance, the formation of which prevents the reaction from proceeding to completion. This brown compound is *chromyl acetate*, $CrO_2(OAc)_2$, and when treated with water is hydrolysed into chromic and acetic acids. It is also produced when a solution of chromyl chloride in carbon tetrachloride is added to silver acetate, suspended in the same liquid, but cannot be separated from the silver chloride which accompanies it.

When dry, powdered chromium trioxide is treated with a solution of acetyl chloride in carbon tetrachloride, and a few drops of glacial acetic acid are added, chromyl chloride is obtained in a yield of 82·43% of the theoretical, together with small quantities of chromic acetate and chloride. The oxychloride cannot be separated from the carbon tetrachloride by fractional distillation.

If chromium trioxide is treated with acetyl bromide under similar conditions, an intense permanganate-red coloration is produced, which rapidly changes to reddish-brown. The latter colour is due to bromine, and the former to an unstable chromyl bromide. The production of the permanganate-red colour is recommended as a test for traces of chromium, and is capable of detecting 0·01 mg. per 1 c.c. of solvent.

On treating chromium trioxide with acetyl iodide, iodine is liberated, but direct evidence is not obtained of the formation of chromyl iodide.

If chromium trioxide is heated with acetic anhydride, and carbon tetrachloride is added to the reaction product, *chromyl acetate* is precipitated as a slightly deliquescent, pale green powder. E. G.

Chromotellurates. ARMAND BERG (*Compt. rend.*, 1911, **152**, 1587—1589; *Bull. Soc. chim.*, 1911, [iv], **9**, 583—585).—On spontaneous evaporation, an aqueous solution containing potassium dichromate (1 mol.), chromium trioxide (2 mols.), and telluric acid (1 mol.) deposits crusts of ill-defined crystals corresponding with the formula $2K_2O,4CrO_3,TeO_3$; *ammonium chromotellurate* closely resembles the *potassium* salt. The *sodium* salt is very soluble and was not obtained pure. The compounds may be regarded as salts of the hypothetical acid $TeO(OH)_4$, of the type $TeO(OCrO_2 \cdot OM)_4$.

W. O. W.

Alloys of Molybdenum with Nickel, of Manganese with Thallium, and of Calcium with Magnesium, Thallium, Lead, Copper, and Silver. N. BAAR (*Zeitsch. anorg. Chem.*, 1911, **70**, 352—394).—Alloys of nickel and molybdenum may be prepared by fusing the metals in hydrogen, in crucibles lined with magnesia. The thermal examination has only been carried as far as the alloy containing 70% of molybdenum, as the freezing point of the remaining alloys is above 1700°, that of molybdenum being above 2100°. A single compound is formed, having the composition MoNi, and melting with decomposition at 1340°. There is a eutectic point at 49·5% Mo and 1300°, and nickel holds up to 33% of molybdenum in solid solution. Microscopical examination confirms the thermal results.

Liquid manganese and thallium are practically immiscible at 1200°, but the freezing point of manganese is slightly lowered by the addition of thallium. Manganese is very viscous just above its melting point, and freezing takes place over an indefinite range of temperature.

Alloys of calcium with other metals may be investigated by the thermal method if heated rapidly in hydrogen. Only one cooling curve can be taken with each alloy. The freezing-point curve of mixtures of calcium and magnesium has a simple form, the single compound, Ca_3Mg_4, being indicated by a maximum at 715°, whilst there are eutectic points at 514° and 446°, and 18·7 and 78·7% Ca respectively. Solid solutions are not formed to any appreciable extent. The compound, Ca_3Mg_4, is brittle, silvery in appearance, stable in air, and only slowly acted on by water.

Calcium and thallium form three compounds, of which only one, CaTl, is indicated by a maximum on the freezing-point curve, at 969°. A compound, Ca_3Tl_4, is formed at 555°, and another, $CaTl_3$, at 524°. There is a eutectic point at 692° and 38% Ca, and solid solutions are formed to a limited extent, so that the transformation point of thallium is raised by the addition of calcium.

Lead and calcium react together violently in the molten state. The freezing point has maxima at 649° and 1105°, corresponding with the compounds $CaPb_3$ and Ca_2Pb respectively. Another compound, CaPb, is formed at 950°, and there are eutectic points at 625° and 10% Ca, and at 701° and 58% Ca. All the alloys fall to a black powder in air.

Copper and calcium form only a single compound, $CaCu_4$, melting at 933°, with eutectic points at 5·7% Ca and 910°, and at 38% Ca and 560°. A thermal change, unaccompanied by change of structure, occurs at 480° in all alloys containing the compound $CaCu_4$. These alloys are white, and unstable in air.

Silver and calcium form a complicated system, the compounds Ag_3Ca_2 and AgCa being marked by maxima in the freezing-point curve at 726° and 665° respectively, whilst the compounds Ag_4Ca, Ag_2Ca, and $AgCa_2$ (?) are formed at 683°, 595°, and 555° respectively. Solid solutions containing AgCa and $AgCa_2$ undergo a transformation at a lower temperature. All the alloys containing more than 11% Ca decompose water.

The results with alloys of calcium differ in many respects from those of Donsky (Abstr., 1908, ii, 278). C. H. D.

Iso- and Hetero-poly-acids. IV. The Constitution of Metatungstates and Borotungstates. ARTHUR ROSENHEIM (*Zeitsch. anorg. Chem.*, 1911, 70, 418—424. Compare Rosenheim and Kohn, this vol., ii, 116; Copaux, *ibid.*, 402).—The uncertainty of determinations of constitution by dehydration experiments at 100—120° is admitted, but the composition of barium metatungstate,

$$BaW_4O_{13},9H_2O,$$

is considered to be well established. Copaux's views on the borotungstates are also criticised. C. H. D.

Definite Compounds of Arsenic and Tin. PIERRE JOLIBOIS and EUGÈNE L. DUPUY (*Compt. rend.*, 1911, 152, 1312—1314).—Metallographic evidence has been obtained for the existence of two definite compounds, Sn_4As_3 and SnAs. The former is deposited in crystals, D 6·31, when an alloy containing 7% of arsenic is employed as anode in the electrolysis of ferrous chloride. Both compounds are attacked by hydrochloric, nitric, and sulphuric acids, and by aqueous solutions of alkalis. W. O. W.

Arsenides of Tin. NICOLA PARRAVANO and PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 593—596).—Investigation of the melting-point diagram of the system arsenic–tin indicates the existence of the compounds Sn_3As_2 and SnAs. T. H. P.

Auric Hydroxide Formed on a Gold Anode. Deportment of Auric Hydroxide when Heated. WILLIAM G MIXTER (*J. Amer. Chem. Soc.*, 1911, 33, 688—697).—The compound formed on a gold anode consists of auric hydroxide with 3 mols. or less of water. When potassium sulphate is used as the electrolyte, the deposit contains potassium, probably present as a potassium hydrogen aurate. If sulphuric acid is employed as the electrolyte, the product contains a little basic auric sulphate which is not removed by cold water. The auric hydroxide deposit is translucent, ruby-red, and appears to be partly crystalline.

When either auric hydroxide from the anode, or the amorphous form obtained by the hydrolysis of auric nitrate or sulphate, is heated, it gradually loses water up to 172°, but does not become anhydrous at 200—210°. At temperatures above 172°, the compound slowly gives off oxygen, but does not yield aurosoauric oxide, Au_2O_2, as stated by Krüss (Abstr., 1887, 15) or auric oxide, Au_2O_3, as indicated by Schottländer (Abstr., 1883, 853).

When auric hydroxide is treated with hydrogen peroxide or a solution of sodium peroxide, it is reduced to the metal.

The deposit formed on a gold anode in presence of ammonium carbonate contains a fulminate. E. G.

Mineralogical Chemistry.

Composition and Occurrence of Rinneite. FRITZ RINNE and R. KOLB (*Centr. Min.*, 1911, 337—342).—The formula given by H. E. Boeke (Abstr., 1909, ii, 153) for the original rinneite from Wolkramshausen was $FeCl_2,3KCl,NaCl$, but a later analysis by O. Schneider (*Centr. Min.*, 1909, 503) of material from Hildesia, near Hildesheim, showed an excess of sodium chloride; this was, however, explained by the presence of mechanically admixed halite. A new analysis of carefully selected material from Hildesia gave:

Fe.	K.	Na.	Cl.	Mg.	SO_4.	H_2O.
13·57	28·99	5·69	52·02	0·03	0·12	0·02

agreeing with the formula $FeCl_2,3KCl,NaCl$ (the small amounts of magnesium sulphate and water are present as kieserite). Analysis of artificially prepared rhombohedral crystals also lead to the same formula. Rinneite is therefore a triple salt, and not an isomorphous mixture, as would be expressed by the formula $FeCl_2,4(K,Na)Cl$. The rhombohedral double salts CdK_4Cl_6, etc., MnK_4Cl_6 (chlormanganokalite, Abstr., 1908, ii, 395) are very similar crystallographically to rinneite, but they are regarded as isotypes (of Rinne).

At Wolkramshausen, near Nordhausen in the Harz, rinneite occurs as large, lenticular masses in beds of rock-salt, sylvite, and anhydrite, whilst at Hildesheim, Salzdetfurth, and Riedel, in Hanover, it forms a kieserite-rinneite rock.

L. J. S.

New Occurrence of Pearceite. Frank R. Van Horn and C. W. Cook (*Amer. J. Sci.*, 1911, [iv], **31**, 518—524).—The mineral was found in some abundance in a silver-copper vein in the Veta Rica mine at Sierra Mojada, Coahuila, Mexico; associated minerals are native silver, argentite, proustite, and barytes. It forms aggregates of platy crystals, with a black colour and brilliant metallic lustre; the crystals are twinned, the twin-plane being probably (702). The following analysis agrees with the formula $8(Ag,Cu)_2S,As_2S_3$, rather than with $9(Ag,Cu)_2S,As_2S_3$ (Abstr., 1896, ii, 658):

S.	As.	Sb.	Ag.	Cu.	Total.	Sp. gr.
17·46	7·56	nil	59·22	15·65	99·89	6·07

L. J. S.

Mexican Minerals. Henri Ungemach (*Bull. Soc. franç Min.*, 1910, **33**, 375—409).—Detailed crystallographic descriptions are given of several species, and analyses of the following. Polybasite from I. Las Chiapas, Sonora, and II, from Sonora:

	Ag.	Cu.	Fe.	Zn.	Sb.	As.	S.	Total.
I.	64·49	9·70	0·41	0·34	8·08	1·78	15·10	99·90
II.	68·90	5·21	0·09	—	8·85	1·07	15·33	99·45

Pyromorphite from Cusihuiriachic; crystals, associated with dolomite and hemimorphite, gave:

PbO.	P_2O_5.	As_2O_5.	CaO.	MgO.	CO_2.	Cl.	Total.
80·85	15·01	1·11	0·58	0·22	not det.	2·57	100·34

L. J. S.

Parisite, etc., from Granite-pegmatite at Quincy, Massachusetts. Charles Palache and Charles H. Warren (*Amer. J. Sci.*, 1911, [iv], **31**, 533—557).—The crystallised minerals described are found in the central cavity of pegmatite pipes intersecting the Quincy granite.

Parisite occurs as small, clear yellow or amber-coloured crystals of rhombohedral habit ($c = 1·9368$); several new crystal-forms are noted. Determinations of the refractive indices by the immersion method gave $\epsilon = 1·757$, $\omega = 1·676$ (similar values were obtained for the Colombian parisite, so that the older determinations of Senarmont appear to be incorrect). Analysis I agrees with the usual formula $(R'''F)_2Ca(CO_3)_3$. The synchysite from Greenland (Flink, Abstr., 1901, ii, 663) does not differ essentially in its physical characters from parisite, and it is suggested that the excess of calcium carbonate in Flink's formula, $(R'''F)_2Ca_2(CO_3)_4$, may be due to the presence of admixed calcite. In both minerals the perfect basal cleavage is only seen in altered specimens, the fresh crystals breaking with a conchoidal fracture:

	CO_2.	F.	Ce_2O_3.	$(La,Di)_2O_3$.	Fe_2O_3.	CaO.	Na_2O.	K_2O.	Gangue.	Total (less O for F).	Sp. gr.
I.*	24·16	6·56	30·94	27·31	0·32	11·40	0·30	0·20	1·02	99·35	4·320

* Also traces of Yt_2O_3, SrO, H_2O.

Riebeckite occurs as black, prismatic crystals several cm. in length. The angle between the prism cleavages is 55°5′; the acute negative bisectrix is inclined at 4—5° to c', and the plane of the optic axes is perpendicular to (010). The pleochroism is intense. The mineral is always to a greater or less extent intergrown in parallel position with aegirite. Analysis II gives 0·582 $Na_2Fe_2'''Si_4O_{12}$, 0·834 $R_4Si_4O_{12}$, with a slight excess (0·058) of silica. Containing only 42% of the molecule $Na_2Fe_2Si_4O_{12}$, this riebeckite resembles that from Colorado and New Hampshire much more closely than the original riebeckite from Socotra (which contains 68—69%):

	SiO_2.	TiO_2*.	Al_2O_3	Fe_2O_3	FeO.	MnO.	CaO.	MgO.	Na_2O.	K_2O.	F.	H_2O.	Total (less O for F).	Sp. gr.
II.	51·79	1·28	0·68	14·51	21·43	1·15	1·28	0·10	6·16	1·10	0·20	1·30	101·17	3·391
III.	51·73	0·64	1·91	31·86	0·87	0·60	0·87	0·14	11·43	0·40	nil.	0·20	100·65	8·499

* Present as ilmenite and anatase.

Aegirite forms blackish-green crystals $[a:b:c=1·1044:1:0·6043;\ \beta=73°27']$. The extinction angle $\mathfrak{a}:c'=6°$. Analysis III agrees closely with the formula $(R_2',R'')Fe_2Si_4O_{12}$, and approximates more closely to the theoretical compound $Na_2Fe_2Si_4O_{12}$ than any previous analysis of aegirite.

Crystallographic notes are also given of microcline, ilmenite, anatase, fluorite, and wulfenite. L. J. S.

Crystallographic Constants of Some Artificial Apatites.

AUGUST DE SCHULTEN (*Compt. rend.*, 1911, **152**, 1404—1406).—Crystallographic details are given of the artificial apatities prepared by fusing a tribasic arsenate or phosphate with calcium, strontium, barium or cadmium chloride, or with cadmium bromide. The axis *c* diminishes with the atomic weight of the metal in the calcium, strontium, barium, and lead compounds, or on substituting the halogen for one of higher atomic weight, as in the replacement of fluorine in natural apatite by chlorine. The axis also diminishes when arsenic is replaced by phosphorus. W. O. W.

Thomsonite in New Jersey.

FREDERICK A. CANFIELD (*School Mines Quart., New York*, 1911, **32**, 215—216).—White spherical masses with a radially-fibrous internal structure and blades forming sheaf-like aggregates, found associated with the several zeolites of Bergen Hill, have been previously thought to be epistilbite. The following analysis proves, however, that this material is thomsonite:

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.	Total.	Sp. gr.
37·90	31·40	12·80	4·53	13·05	99·68	2·35

L. J. S.

The Olivine Group. Helge Backlund (*Trav. Museé Géol. Pierre le Grand. Acad. Sci. St. Pétersbourg*, 1909, **3**, 77—105).—The refractive indices and chemical composition of 18 samples of minerals of the olivine group are tabulated, and curves are drawn. Some of these are quoted from other authors, but many of the refractive indices have been newly determined; the following new analyses are given: I, olivine from Windisch-Matrey, Tyrol: asparagus-green, transparent. II, from Kammerbühl, Eger, Bohemia: yellowish to brownish. III, from Vesuvius: dark variety. IV, "glinkite" from Itkul, Urals: large brownish-yellow nodule from talc-schist:

	SiO_2.	MgO.	FeO.	MnO.	Al_2O_3.	Total.	α.	β.	γ (Na).
I.	41·63	51·44	7·36	—	—	100·43	1·6507	1·6669	1·6856
II.	40·09	45·06	14·58	0·21	0·35	100·34	1·6649	1·6830	1·7015
III.	40·35	43·37	16·28	—	0·14	100·14	1·6674	1·6862	1·7053
IV.	38·97	42·29	18·07	0·32	—	99·83*	1·6694	1·6878	1·7067

* Ni(Co)O, 0·18%.

It is seen that the refractive indices increase progressively with the percentage of iron in the series $(Mg,Fe)_2SiO_4$. Forsterite from the Urals with 0·22% FeO gave $\alpha = 1·6361$, $\beta = 1·65185$, $\gamma = 1·66975$ (Na); and fayalite from Rockport, Massachusetts, with 68·12% FeO has $\alpha = 1·8236$, $\beta = 1·8642$, $\gamma = 1·8736$ (Na) (Penfield and Forbes, Abstr., 1896, ii, 373). The determination of the refractive indices of olivines in rock-sections can thus be used as a criterion of the chemical composition, but the determinations of the birefringence and optic axial angle are of no help in this direction. L. J. S.

The Dokáchi Meteoric Stone. Herbert E. Clarke and Herbert L. Bowman (*Min. Mag.*, 1911, **16**, 35—46).—In the neighbourhood of the village of Dokáchi, in the Decca district of Bengal, there fell on October 22, 1903, a shower of some hundred meteoric stones, the largest of which weighed 1570·99 grams. Examination of a stone, weighing 17·79 grams, which fell in the village of Rána, showed it to consist of a rather finely granular mixture of olivine and bronzite, with irregular grains of nickel-iron and traces of troilite; some chondrules are present, and the stone is referable to the group of intermediate chrondites (Ci) of Tschermak. Analysis by the methods previously described (Abstr., 1910, ii, 783) gave:

					Silicates.		
Nickel-iron.	Magnetite.	Troilite.	Schreibersite.	Chromite.	Attacked by HCl.	Unattacked by HCl.	Total.
18·66	1·11	4·10	0 17	0·05	37·71	37·93	99·73

The composition of the nickel-iron alloy is:

Fe.	Ni.	Co.	Cu, Mn, Zn.	Total.
93·5	5·5	1·0	traces	100·0

The silicates attacked by hydrochloric acid gave the results under I, and the unattacked silicates, II :—

	SiO_2.	FeO.	CaO.	MgO.	Al_2O_3.	Cr_2O_3.	NiO.	Na_2O.	K_2O.	Total.
I.	35·49	37·72	1·48	23·10	0·67	nil	0·26	0·99	0·16	99·87
II.	57·60	14·87	3·51	21·68	0·51	—	0·22	1·23	0·31	99·93

L. J. S.

"Bad Reinerz" in Silesia and its New Medicinal Springs. Rudolf Woy (*Zeitsch. öffentl. Chem.*, 1911, **17**, 181—192).—Exhaustive analyses are given of the water of four new medicinal springs in Reinerz, Silesia. Besides the chemical analyses, the specific conductivities and the lowering of the freezing points have been determined.

The radioactivity of the samples has also been investigated by means of a Mache-Meyer's fontaktometer. As the activity sank to about one-half when the waters were kept for four days in a closed vessel, it is inferred that the radioactivity is due to the presence of radium. L. de K.

Physiological Chemistry.

Excitability of the Respiratory Centre. J. LINDHARD (*J. Physiol.*, 1911, **42**, 337—358).—Carbon dioxide is the adequate stimulus for the respiratory centre as pointed out by Haldane; but the excitability of the centre is governed by the tension of the oxygen present, and by a number of different physico-chemical factors. The excitability of the centre, moreover, has for different individuals quite a different value. W. D. H.

The Effects of Asphyxia on Medullary Centres. I. The Vaso-motor Centre. G. C. MATHISON (*J. Physiol.*, 1911, **42**, 283—300).—Lack of oxygen, small doses of carbon dioxide, and intravascular injection of weak organic acids stimulate the vaso-motor centre. In asphyxia, both lack of oxygen and increase of carbon dioxide are factors. Prolonged lack of oxygen, larger doses of carbon dioxide, and repeated injections of acids produce narcosis. Traube waves are seen in lack of oxygen, and administration of carbon dioxide. The results suggest the existence of a common factor, probably the hydrogen ion content of the blood underlying all these actions on nerve-centres. W. D. H.

Viscosity of Body Fluids. CHARLES D. SNYDER and MARTILLUS H. TODD (*Amer. J. Physiol.*, 1911, **28**, 161—166).—The viscosity of blood sera and plasmata increases with fall of temperature, so resembling what is seen with water and other fluids of known composition. The temperature-coefficients are greater for the lower ranges of temperature. This variation is in the same direction and of the same character as the variation of the temperature-coefficient of velocities of chemical reactions and of physiological actions.

W. D. H.

The Meaning of Variation in the Magnitude of Temperature-coefficients of Physiological Processes. CHARLES D. SNYDER (*Amer. J. Physiol.*, 1911, **28**, 167—175).—Variations in the magnitude of temperature-coefficients at various ranges of temperature have been regarded by some writers on physiological processes as being evidence that the phenomena in question cannot be chemical. This assumption is incorrect. Such variations are always seen in all chemical processes.

W. D. H.

Positive and Negative Phases of Blood-coagulation in Man. D. A. WELSH (*J. Path. Bact.*, 1911, **15**, 467—474).—The positive and negative phases of blood-coagulation are found in certain diseases, associated with cellular disintegration and abnormal increases in leucocytes. They are probably due to liberation of thrombokinase. Thrombi in the heart and pulmonary artery are formed while the blood is in motion; they represent the positive phase, and lead to death. They are analogous to the coagulation produced by injection of nucleo-protein (thrombokinase).

W. D. H.

Chemical Dynamics of Serum Reactions. A. G. MCKENDRICK (*Proc. Roy. Soc.*, 1911, *B*, **83**, 493—512).—It is shown that amboceptor and complement are opposed in their action on the cell; in addition, however, the amboceptor acts as a catalyst for the complement. On this basis the expression $dz/dt = y[(x/cz) - z]/c - [(y/c) - z]^2$ is deduced, where y = per cent. of amboceptor, x = per cent. of complement, c is a constant of dilution, z is a complex quantity denoting effect (from a chemical point of view, the amounts of x and y which have been transformed), and t is the time. $(y/c) - z$ denotes the concentration of *free* amboceptor, $(x/cz) - z$ the concentration of *free* complement, and the equation, which was deduced experimentally, indicates that amboceptoral action is bimolecular, complement action unimolecular, and that the former also exerts a catalytic effect. When the substance acted on is present in sufficient quantity, the above equation is applicable to all serum reactions.

It is considered that toxins are of a compound nature, consisting of amboceptor and complement. The action of complement is lytic (hæmolytic, bacteriolytic, etc.), that of the amboceptor primarily polymerising or agglutinative.

Owing to the complicated part which amboceptor and complement play in serum reactions, the present system of bacteriolytic and opsonic indices, based on experiments with only one dilution of the serum, is liable to error.

G. S.

The Mechanism of the Complement Deviation in the Case of Antiprotein Sera. EDMUND WEIL and WILHELM SPÄT (*Biochem. Zeitsch.*, 1911, **33**, 63—72).—The authors draw the conclusion that there is no anchoring between the antigen and precipitin. The complement-deviation method was employed, and the influence of the antigen-precipitin mixture on the deviation of the complement was compared, when the former substances had been treated with a non-specific adsorbent (coagulated serum-albumin), and when they had not so been treated. It was found that the albumin could adsorb the precipitin both in presence and absence of the antigen, which fact is in contradiction of the Ehrlich theory of a maximal chemical relationship between antigen and precipitin. S. B. S.

Anti-agglutination by Extracts of Bacteria. EDMUND WEIL (*Biochem. Zeitsch.*, 1911, **33**, 56—62).—Quantitative investigation of the anti-agglutinating action of bacterial extracts on different immune sera shows that this action is not specific. S. B. S.

The Sugar of Plasma and Blood-corpuscles. RAPHAEL LÉPINE and RAYMOND BOULUD (*Biochem. Zeitsch.* 1911, **32**, 287—289). —The authors quote some of their previous publications showing that before Michaelis and Rona and Rona and Döblin (this vol., ii, 302) they had determined the sugar content of blood corpuscles and plasma. They also point out that they had noticed a possible error in determination owing to the setting free of sugar from corpuscles during centrifugalisation of the blood, so that the sum of the sugar in the blood plus the sugar of the plasma is always slightly greater than the sugar of the total blood. S. B. S.

Glycolysis. II. PETER RONA and A. DOBLIN (*Biochem. Zeitsch.* 1911, **32**, 489—508).—Glycolysis (sugar destruction) takes place in the blood when the corpuscles are not hæmolysed, hæmolysis almost entirely destroying the glycolytic capacity. The greater the ratio of the amount of corpuscles in the amount of sugar, the greater the glycolysis. Experiments carried out in the presence of oxygen, carbon dioxide, and hydrogen showed that even in hydrogen a certain amount of destruction of sugar takes place, and the process does not appear therefore to be, at any rate in the early stages, an oxidative process. In certain cases glycolysis was hastened by the presence of phosphates. When kept the blood loses its glycolytic power; this is also injured by antiseptics. The experiments were carried out with human blood, collected under aseptic precautions. S. B. S.

The Maltase of Blood-serum and Liver. LEONIDAS DOXIADES (*Biochem. Zeitsch.*, 1911, **32**, 410—416).—The serum and liver of different animals contain different quantities of maltase. The action can be increased if the serum or liver extract containing the maltase be neutralised with acid before being allowed to act on maltose. The action is diminished if the liquids containing maltase be warmed to 50° first, but is very appreciably increased, even beyond the action of the simply neutralised preparation, if they are warmed to 50° after neutralisation. It is suggested that this result is due to the acid setting free a weakly-basic substance which is in combination with the maltase.

It was also found that if the maltase preparation is allowed to act on glucose solutions (20—30%), there is a continued increase in the polarisation, suggesting the presence of a synthetic enzyme.

S. B. S.

Oxydase Properties of Oxyhaemoglobin. ÉLOI DE STŒCKLIN (*Compt. rend.*, 1911, **152**, 1516—1518).—Lumière and Chevrotier's experiments (Abstr., 1905, ii, 642) on the oxydase properties of protoplasmic extracts of blood-corpuscles have been repeated and confirmed. These properties appear to be localised in the basic constituents of the extract.

W. O. W.

Physiology of Lymph. XVI. Local Hæmodynamic Action of Tissue Metabolites. ANTON J. CARLSON, A. WOELFEL, and H. W. POWELL (*Amer. J. Physiol.*, 1911, **28**, 176—189).—Extracts of most fresh organs made with Ringer's solution cause vaso-dilatation and fall of arterial blood-pressure. This effect is more marked if the organs used form an external watery secretion. As such organs require more water for their functions, they produce a greater amount of metabolites or hormones, which act as depressor substances. The action decreases with fatigue of the organs (salivary glands); the depressor substance passes in traces into the saliva. The depressor substances are thermostable, and are probably relatively simple materials, such as choline or proteose. They are not acid. The probable mode of action of their metabolites on the blood capillaries is discussed.

W. D. H.

The Influence of Loss of Blood on Digestive Processes. N. A. DOBROWOLSKAJA (*Biochem. Zeitsch.*, 1911, **33**, 73—104, 105—152).—The experiments were carried out on several dogs with fistulæ in different parts of the digestive tract, made by Pawloff's method, and analyses of the secretions through these fistulæ were made when the animals received different diets, control experiments being carried out both before and after the removal of the blood from the body. In the latter case one-third to one-half of the total blood was removed. The amounts of the various digestion products and of the enzymes were estimated in the secretions. It was found that the removal of blood caused considerable disturbances both in the secretory and motor functions and in the digestive and absorptive processes. In the secretory and motor functions two stages could be observed, namely, a stage of depression of the secretion, and of the rate of movement of the food; this was followed by a second stage of increased secretion and increased rate of movement of the foodstuffs down the alimentary tract. The secretions in the first stage contained a higher percentage of solid matter. A diminution of the digestive and absorptive functions was noted chiefly in the second stage of the secretory and motor processes. The absence of a diminution in the first stage may be ascribed to the higher concentration of the solids in the secreted juices, and the prolongation of their time of action on the food, owing to the depression of the motor functions. The digestive and absorptive functions are more efficient immediately after the blood-letting if the foodstuff contains larger quantities of water. Repeated blood-letting causes disturbances of the same character, but more pronounced. An intravenous infusion of physiological saline diminishes somewhat the immediate effect of the blood-letting, but does not exert any marked influence on the subsequent stages of restitution. The effect of the disturbance on the different varieties of foodstuffs (fats, carbohydrates, and proteins) is similar. The restitution of functions after blood-letting takes place at different rates in different parts of the alimentary tract.

S. B. S.

The Rennet Zymogen of the Calf's Stomach SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1911, **72**, 187—214).—An infusion of the calf's stomach as nearly neutral as possible contains not only the zymogen of rennin, but also active rennin, which differs somewhat in its properties from rennet obtained by making an extract with hydrochloric acid, the principal difference being that it does not obey the time law of enzymic action. An extract of the zymogen made with dilute ammonia and then neutralised, loses its rennetic power and inhibits the activity of rennet added to it. The inhibitory power resembles that which is exercised by serum. The inhibition disappears and rennetic activity returns when hydrochloric acid is added. The conclusion drawn is that the zymogen consists of rennet in combination with an inhibitory substance; ammonia liberates the latter and destroys the rennet; hydrochloric acid liberates the rennet and destroys the inhibitory substance. W. D. H.

Antipepsin. I. SERAFINO DEZANI (*Atti R. Accad. Sci. Torino*, 1911, **46**, 371—380. Compare Schwarz, Abstr., 1905, ii, 731).—The author describes experiments on the conditions of action of antipepsin.

Gastric mucus of a freshly-killed pig was well stirred up for ten minutes with an equal weight of 0·35% hydrochloric acid, then left to digest for fifty minutes at 50—60°, and filtered. In this way a yellow liquid, D^{15} 1·010—1·016, was obtained, which gave 1·926—2·360% of solid residue and 0·25—0·32% of ash. It showed the biuret and Millon's reactions, but in most cases it possessed no proteolytic properties. This liquid, which contains no free hydrochloric acid, arrests digestion completely, its antipeptic properties being somewhat diminished by the addition of hydrochloric acid in the proportion present in normal digestive fluids.

About one-fourth part of the ash of the extract consists of calcium phosphate, which exerts a function analogous to that of the co-enzymes, since the dialysed extract exhibits no antiproteolytic properties and regains these partly on addition of the phosphate. But, since the existence of an enzyme which resists boiling cannot be admitted, antipepsin must be regarded as a substance capable of forming, with calcium phosphate, a labile compound which is dissociated on dialysis and re-formed on addition of the original proportion of the salt.

T. H. P.

The Increase of Metabolism Due to the Work of Typewriting. THORNE M. CARPENTER (*J. Biol. Chem.*, 1911, **9**, 231—265). From observations on five subjects, it was found that typewriting at the rate of 57—115 words per minute increases the pulse rate from

90—120, and the respiration rate from 19 to 30 per minute. There is a rise of body temperature, and an average rise of 50% in total metabolism. The work done is calculated as 145 kilogram-metres per 1000 strokes of type-writing. W. D. H.

Action of Colloidal Sulphur on Sulphur Metabolism. Sulphoconjugation. LOUIS C. MAILLARD (*Compt. rend.*, 1911, **152**, 1583—1586).—Colloidal sulphur, prepared by the interaction of hydrogen sulphide and sulphur dioxide, is completely and rapidly absorbed by rabbits when introduced into the oesophagus. Within twenty-four hours somewhat less than half is eliminated in the urine as mineral sulphates, and a portion in the form of organic sulphates. The normal amount of the latter is increased by 5—13% after the ingestion of sulphur, but the proportion falls below normal when this is withdrawn from the diet. About half of the sulphur is excreted in an incompletely oxidised condition, probably in organic combination, since no sulphur, hydrogen sulphide, or sulphur dioxide is formed on treating the urine with acid. It may be supposed that substances are formed by the conjugation of compounds of the type $R\cdot SO_2\cdot OH$ with phenols, and that more highly oxidised compounds escape combination in this way. W. O. W.

Calcium Metabolism. II. The Calcium Content of Human Blood After Oral Administration of Large Doses of Calcium. N. VOORHOEVE (*Biochem. Zeitsch.*, 1911, **32**, 394—409).—The method of estimation employed was that devised by the author. It was found that by the daily administration of 2727 mg. of calcium oxide *per os*, either in the form of lactate or chloride, the calcium content of the blood can be increased in the adult or nearly adult man on a calcium rich diet. Under the same conditions, 545 mg. of calcium oxide caused no very appreciable increase. The increase in the calcium content of the blood can be continued for weeks, without any deleterious effects, and continues even for a period after cessation of medication. No decrease of the calcium content could be detected after administration of extra quantities of calcium salts. S. B. S.

Biochemical Study of Manganese. I. Metabolism of Manganese and the Law of Minimum Regarding Manganese and Iron. GUIDO M. PICCININI (*Arch. Farm. sperim. Sci.*, 1910, **9**, Reprint 20 pp. Compare following abstract).—Manganese occurs in varying quantities in the different tissues of the animal and human organism. It is obtained from the food, but does not disappear when a diet which does not contain it is administered. The addition of manganese to the ordinary diet causes an increase in the iron of the blood, and of the liver and spleen, and in fact the absorption of iron (and probably also its assimilation) is regulated by the quantity of manganese available in the body (law of minimum). R. V. S.

Biochemical Study of Manganese. II. GUIDO M. PICCININI (*Biochim. Terap. sperim.*, 1910, **2**, Reprint 10 pp. Compare preceding abstract).—Colloidal manganese augments *in vitro* the available oxygen of blood, and maintains this increase for some time. It seems also to have the same action *in vivo*. Colloidal manganese retards the death of guinea pigs injected with the minimum lethal dose of diphtheritic toxin. R. V. S.

Fat Metabolism in the Absence of the Pancreatic Juice in the Intestine. B. C. P. JANSEN (*Zeitsch. physiol. Chem.*, 1911, **72**, 158—166).—Fat absorption goes on to a relatively high degree if the pancreatic juice is absent, provided that the pancreas or a part of it is still in the body. If this organ is extirpated, the loss of fat in the fæces is greatly increased. Such animals, however, are in a marasmic state. W. D. H.

Formic Acid as an Intermediary Substance in the Catabolism of Fatty Acids and Other Substances. HENRY D. DAKIN and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1911, **9**, 329—330). —Formic acid is a small constituent of normal urine. Since this acid is readily oxidisable, it is fair to conclude that the quantity actually formed in metabolism must exceed that which finally passes out of the body. It was found that the administration to cats of the sodium salts of acetic, propionic, and butyric and other fatty acids leads to a ten to thirty fold increase in the amount of formic acid in the urine. It is thus probable that formic acid is a stage in the catabolism of fatty acids from acetic acid upwards. The relation of carbohydrates and amino-acids to formic acid formation is under investigation. W. D. H.

The Esterification Method and its Use in Experiments on Metabolism. BRUNO O. PRIBRAM (*Zeitsch. physiol. Chem.*, 1911, **71**, 472—478).—Fischer's esterification method is used, not only for determining and separating the amino-acids formed by the hydrolysis of complex proteins, but also for determining whether amino-acids are formed in the stomach and its ducts. For this purpose the product is evaporated under reduced pressure, and then treated with alcohol and hydrogen chloride as recommended by Fischer. It is pointed out that the results thus obtained may frequently lead to wrong conclusions, as proteins, when suspended in absolute alcohol and treated with hydrogen chloride, are decomposed and esters formed. The decomposition is not a process of alcoholysis, but of hydrolysis and subsequent esterification, the hydrolysis being due to the minute traces of water in the alcohol.

In certain experiments on the hydrolysis of gelatin, glycine could not be isolated as its ester, although proline, alanine, phenylalanine, etc., were readily isolated. This was shown to be due to the fact that the glycine was present as its hydrochloride, and had either not been esterified or the ester formed had been subsequently hydrolysed. J. J. S.

Relation between the Digestibility and the Retention of Ingested Proteins. DONALD D. VAN SLYKE and GEORGE F. WHITE (*J. Biol. Chem.*, 1911, **9**, 219—229).—A dog was fed once a day and the urine collected at intervals afterwards; the rate of nitrogen excretion is taken as an index of the rate of intestinal absorption. Addition of starch to the diet decreased the rate of nitrogen metabolism, but had no effect on the completeness of absorption. Nitrogen excretion followed most rapidly after ingestion of cod; then followed beef, tautog (*Tautoga onitis*), eel, weakfish (*Cynascion regalis*), mussel, salt cod, and periwinkle. Some of the results noted indicate incomplete absorption. The lowest cleavage products appear to be less capable of maintaining nitrogenous equilibrium than the higher cleavage products. There doubtless is an optimum rate of digestion.

W. D. H.

Digestion of Protein in the Stomach and Intestine of the Dog-fish. DONALD D. VAN SLYKE and GEORGE F. WHITE (*J. Biol. Chem.*, 1911, **9**, 209—217).—The most noticeable difference in digestion between the warm-blooded and cold-blooded carnivora is the time occupied. Meat in the dog is completely digested and absorbed in twelve hours; about six times as long is required in the dog-fish. The stomach in the dog is empty in about five hours; in the dog-fish it is not entirely empty after forty-eight hours. The slowness is related to the lower temperature of the dog-fish. Protein in the dog-fish is only partly peptonised in the stomach; in the intestine cleavage proceeds probably as far as in the dog. Lipolysis occurs rapidly. The presence of large amounts of urea in the bile, as in the blood, appears peculiar to the shark family. W. D. H.

Muscular Work and Protein Metabolism. ANGELO PUGLIESE (*Biochem. Zeitsch.*, 1911, **33**, 16—29).—The experiments were carried out on large dogs, in which one leg was tetanised (sometimes with the attachment of a weight to the muscle), and the other remained at rest. Analyses were carried out of the muscular substance, the plasma of the arterial and venous bloods of the two limbs, the samples employed for analysis corresponding as nearly as possible. The samples were taken from the resting limb before tetanisation of the other. Only a very small diminution (0·02 to 0·06%) was found in the total nitrogen of the tetanised limb. A small, but constant, increase of the uncoagulable nitrogen was found both in the arterial and venous plasma; this increase was more marked in the venous plasma. A small, but constant, increase of albumin was found in the arterial plasma, and a diminution in the venous. On the other hand, a small, but constant, decrease of globulin was found in the arterial plasma and an increase in the venous. The increase of the incoagulable and albumin nitrogen and the decrease of the globulin nitrogen in the arterial plasma, on the one hand, and the increase of the coagulable nitrogen and globulin nitrogen and decrease of the albumin nitrogen in the venous plasma on the other, almost compensated one another, that is to say, there is no appreciable change in the total nitrogen of the arterial and venous bloods together owing to tetanisation. The author draws the conclusion that during tetanisation the chief nitrogenous change is the conversion of albumin into globulin, and that the protein does not serve as the main source of energy. S. B. S.

Purine Metabolism. VII. Purine Metabolism during Starvation. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1911, **33**, 153—166).—In animals with synthetic uric acid formation (ducks), the uric acid forms the chief product of metabolism (42—53% of the total nitrogen), and its variations, during starvation or under-nutrition, run more or less parallel with those of the total nitrogen, in which respect it is similar to the urea excretion of mammals. The relationship of total nitrogen to uric acid nitrogen does, however, vary to some extent with the conditions of experiment, being 2·27 under normal conditions and 1·89—1·97 during starvation. In the case of animals, in which the uric acid formation is an oxidative process (dogs), the changes of uric acid secretion caused by starvation are small when the animal has been kept for some time before on a purine-free diet. There is, however, a fall of the uric acid during starvation, which does not appear to have any definite relationship to the changes in the total nitrogen. S. B. S.

Purine Metabolism. VIII. The Content in Purine Bases of Various Kinds of Muscular Tissue. VITTORIO SCAFFIDI (*Biochem. Zeitsch.*, 1911, **33**, 247—251).—The different kinds of muscular tissue of one and the same animal do not possess the same purine content. The heart muscle contains the greatest quantity, then come the ordinary striped muscle fibre, and lastly the plain muscular tissue, which contains only about half of that of the other muscles. The heart is richest in the free purine bases (as contrasted with the combined), then come the plain muscles; ordinary striped muscular tissue contains least. The amounts of purine bases are not proportional to the total nitrogen content. In no case was uric acid found. S. B. S.

Rice as a Foodstuff. The Nitrogen and Phosphoric Acid Metabolism with Rice and other Vegetable Foodstuffs as the Chief Source of Nutrition. HANS ARON and FELIX HOCSON (*Biochem. Zeitsch.*, 1911, **32**, 189—203).—The authors give a series of analyses of unmilled rice and milled rice of various grades, and show that unmilled rice contains 0·7—0·8% P_2O_5, whereas "under-milled" rice contains 0·4—0·6, and over-milled rice 0·15—0·4%. They carried out a series of metabolism experiments on several individuals with rice as the chief article of diet, with the addition of fish, white bread, etc., and determined the nitrogen and phosphoric acid balances. They showed that with rice as the chief article of diet, nitrogen equilibrium could be attained with a nitrogen intake of about 8 grams per 50 kilo. of body-weight, but that not much more than about 30% of the rice nitrogen was absorbed. Somewhat more than 1·65 grams of P_2O_5 per 50 kilo. of body-weight are necessary under the same conditions for phosphoric acid equilibrium. The authors discuss in conclusion the economic food-value of rice in the tropics. S. B. S.

The Regeneration of Proteins in the Mucous Membrane of the Stomach. P. GLAGOLEFF (*Biochem. Zeit.*, 1911, **32**, 222—230).—The experimental methods employed were similar to those used by the earlier workers on this subject (Glaessner, etc.). It is found that in the symmetrical halves of the mucous membrane of the dog's stomach the albumose and the nitrogenous substances not precipitable by zinc sulphate are symmetrically distributed. The content in these nitrogenous substances, whether from a fasting or a fed dog, is not constant, and is not, therefore, a function of the state of nutrition of the animal. The origin of these nitrogenous substances is therefore, for the present, unknown, and no conclusions as to the question of protein formation in the mucous membrane can be drawn from the quantitative estimation of them. Furthermore, the mucous membrane during incubation, as in Glaessner's experiments, undergoes autolysis. S. B. S.

Histo-chemistry of Spermatozoa. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1911, **72**, 305—312).—The isolated heads of the spermatozoa of the salmon after extraction with alcohol and ether consist of protamine nucleate (nucleic acid, 60·5, and protamine, 35·56%). Very similar figures have been obtained by others in the case of other fish-sperm. Nucleic acid was isolated by Neumann's method; it contained in different preparations 20·71% to 20·87% nitrogen and 6·21 to 6·78% phosphorus. These figures are not very different from those of Miescher and of Mathews, except that the phosphorus is somewhat higher than in their experiments. The figures do not, however, come anywhere near what is required for the author's formula for nucleic acid; the possible sources of error are discussed. W. D. H.

Notes. I. Presence of Dextrose and Creatinine in Hen's Egg. II. Contents of a Dermoid Cyst. III. Some Properties of Hæmatin. IV. Estimation of Peptone in the Presence of Albumoses. V. The Estimation of Sulphur in Urine and the Significance of Neutral Sulphur. Ernst Salkowski (*Biochem. Zeitsch.*, 1911, **32**, 335—361).—I. The author refers to statements of Diamare that egg-white contains dextrose which can be separated by dialysis, and that the egg-white after dialysis and hydrolysis yields another sugar. The former statement is confirmed. The other sugar referred to is glucosamine. An investigation of the egg-yolk also revealed the presence of dextrose (in contradiction to another conclusion of Diamare's), and, in addition, a substance which reduced Fehling's solution even after removal of the glucose by fermentation. Further examination of the aqueous extract of egg-yolk revealed the presence of creatinine, and also possibly that of a further unknown substance.

II. The author gives a preliminary account of a non-saponifiable substance obtained from the cyst, as to the nature of which no definite conclusions could be drawn, owing to lack of material.

III. In addition to the hæmase of Senter, which is contained in the blood; another substance, namely, hæmatin, exists, which can decompose hydrogen peroxide. In the experiments described the hæmatin was prepared by the peptic digestion of blood. The iron obtained from hæmatin by decomposition with hydrogen peroxide is in the form of a ferrous salt.

IV. The author gives some details for manipulating when the acid zinc sulphate method is employed for separating peptone from albumoses.

V. Controversial. S. B. S.

The Relationship between the Higher Fatty Acids and Unsaponifiable Substances during Different Stages in the Development of the Organism. A. COSTANTINO (*Biochem. Zeitsch.*, 1911, **32**, 473—481).—In four experiments on fœtuses of dogs it was found that the ratio of fatty acids to unsaponifiable substances was approximately constant. In a fifth case, when the embryos were in an early stage of development, there was a marked deviation from this constant. The iodine number of the fatty acids from embryos was high. Newly-born offspring from the same mother killed at intervals of twelve days after birth showed a greater increase in the fatty acids than in the unsaponifiable substances; the iodine numbers also showed a decrease with advancing age. S. B. S.

Hydrolysis of Esters in the Tissues. PETER RONA (*Biochem. Zeitsch.*, 1911, **32**, 482—488).—The experiments were carried out on mono- and tri-butyrin by measuring the diminution of the surface-tension of the mixtures by the method already described by the author and Michaelis. The maximum hydrolysis is in the kidney tissue, then follow liver and the mucous membrane of the intestine, and then spleen and lungs. The muscles and brain were inactive in the time intervals occupied by the experiments (generally two hours). S. B. S.

Soluble Ferments of the Brain. AUGUSTIN WROBLEWSKI (*Compt. rend.*, 1911, **152**, 1334—1337).—The brains of vertebrates contain a catalase, peroxydase, lipase, and amylase and enzymes capable of hydrolysing arbutin and salol. Negative results were obtained in a search for invertase, inulase, and proteolytic enzymes. W. O. W.

Influence of Various Substances on the Gaseous Interchange of Surviving Frog's Muscle. X. TORSTEN THUNBERG (*Skand. Arch. physiol.*, 1911, **25**, 37—54).—Battelli and Stern found that the gaseous exchange in tissues is lessened by previous extraction with water, and this is restored by again adding the aqueous extract. The substance responsible for this they named *pnein*. It is now shown that treatment with 1·5% dipotassium hydrogen phosphate solution also causes an increase in the exchange in extracted tissue. Various neutral salts of organic acids (succinic, oxalic, malonic, citric, malic, etc.) elevate the exchange, especially as regards the carbon dioxide given out; their action occurs whether the muscles have been previously extracted or not. Dextrose, sodium acetate, and salts of maleic acid produce no restitution effect on extracted muscles. W. D. H.

Muscular Work and its Relation to Ketone Formation. Luigi Preti (*Biochem. Zeitsch.*, 1911, 32, 231—234).—Both in dog and man an increase in the output of acetone substances in the urine was observed after muscular work. S. B. S.

Rôle of Potassium Salts in Frog's Muscles. W. Burridge (*J. Physiol.*, 1911, 42, 359—382).—Shortening of frog's muscle produced by lactic acid occurs in two stages: (1) a surface shortening, and (2) a deep shortening. Other acids, alcohol, chloroform, nicotine, and bile act similarly with minor differences in some cases. The action of acids is regarded as a direct one on the contractile substance. The shortening produced by potassium salts is probably produced indirectly. Muscles rendered inexcitable by tetanisation or by alcohol still shorten with appropriate concentrations of potassium salts and lactic acid. Persistent contraction is also produced in cardiac muscle by high concentrations of potassium salts. The action on muscle of widely differing substances is explained by assuming that they affect the mobilisation of the potassium salts in muscle. W. D. H.

Action of Acids on Skeletal Muscle. Dorothy Dale and George R. Mines (*Proc. physiol. Soc.*, 1911, xxix—xxx; *J. Physiol.*, 42).—Experiments with various acids on frog's muscles indicate that the effects are mainly due to hydrogen ion concentration.
W. D. H.

Action of Salts on the Neural and Non-neural Regions of Muscles. John Newport Langley (*Proc. physiol. Soc.*, 1911, xxiv—xxv; *J. Physiol.*, 42).—Nicotine causes a transient contraction in certain frog-muscles which is confined to the neural region, and this is antagonised by curare. Potassium salts cause a contraction which is not abolished by curare. The "receptive substance" acted on by nicotine and curare is not specially stimulated by salts. Different muscles exhibit such effects in varying degrees.
W. D. H.

Intravital Inhibition of Oxidation in the Liver by Narcotics. Georg Joannovics and Ernst P. Pick (*Pflüger's Archiv*, 1911, 140, 327—353).—Recent researches have shown the importance of oxidation in the liver, especially in reference to fat metabolism. The question here investigated is whether such oxidations are influenced by such narcotics as ether and chloroform. Dogs were fed on cod liver oil, with and without narcosis, killed later, and their livers examined chemically for fats and lipoids. In every case without narcosis evidence of intense oxidative activity was found in the liver during the course of fat-digestion. Under the influence of ether or chloroform narcosis, this was only present to a small degree, and this condition lasts some time. The amount of lipoids remains constant if the narcotic is given shortly after the meal, and diminishes only after a long interval; thus the fatty acid component of lipoids behaves like that of ordinary fat. W. D. H.

Biological Properties of Glycuronic Acid. I. Amount of Glycuronic Acid Contained in the Organism. CESARE PADERI (*Arch. Farm. sperim. Sci.*, 1911, **11**, Reprint 24 pp.).—Neither blood nor pancreatic extract has any action on glycuronic acid, but an infusion of liver decomposes it in the course of twelve hours at 38°. When injected intravenously or subcutaneously into rabbits, glycuronic acid is rapidly and almost completely excreted unchanged in the urine. The organism will support large amounts when administered by the mouth, especially if the doses are small. The substance does not cause the appearance of acetone or of formic acid in the urine, but the oxalic acid there is increased. The urine also contains possibly saccharic acid, and a reducing substance which, it is suggested, may be gulose. The administration of glycuronic acid, together with toxic doses of camphor or chloral, does not diminish the toxicity of the latter, so that it is improbable that the combined glycuronic acid occurring in urine is preformed. R. V. S.

The Degradation of Carbohydrates in the Liver. JOSEPH WIRTH (*Biochem. Zeitsch.*, 1911, **33**, 49—55).—According to earlier investigations of the author and Embden, those substances which are readily oxidised inhibit the formation of the acetone substances from ketogenic compounds when perfused with them through the liver. Gluconic acid and saccharic acid, when perfused with *iso*valeric and hexoic acids, which are ketogenic, did not diminish the amount of acetone that is formed by the latter acids alone; on the contrary, the amount of acetone was high. It was found that when gluconic acid and saccharic acid alone were perfused through the liver, acetone was formed in appreciable quantities. These acids are therefore ketogenic. Similar results were obtained with mucic acid. The results obtained were not, however, very constant, and the author suggests there may be alternative methods of degradation of these acids in the body.
S. B. S.

Relationship between Urea and Ammonium Salts. ALFRED J. WAKEMAN and HENRY D. DAKIN (*J. Biol. Chem.*, 1911, **9**, 327—328). —Many simple chemical reactions in the body are reversible. The liver, as is well known, makes urea from ammonium carbonate or carbamate. Dog's livers were perfused with urea dissolved in a mixture of blood and saline solution. The concentration of urea was varied, but in every case no increase of ammonia at the expense of the urea was found. W. D. H.

Formation of Bile-pigment from the Blood. II. THEODOR BRUGSCH and S. YOSHIMOTO (*Chem. Zentr.*, 1911, i, 994; from *Zeitsch. expt. Path. Ther.*, 1911, **8**, 639—644).—The bile-pigment excreted was determined in the urine, fæces, and bile in animals with an artificial biliary fistula and ligatured bile-duct before and after the injection of hæmin. The increase of biliverdin excreted during the period of injection corresponded very nearly with the amount of hæmin injected, and only small amounts of the latter substance were discovered in the urine. The change of the injected blood-pigment may be represented by the equation: $C_{32}H_{32}O_4N_4Fe + 2H_2O - Fe = C_{32}H_{36}O_6N_4$. The details of the experimental methods are given, the urobilin solutions obtained by the different analytical processes being examined spectrophotometrically. S. B. S.

The Influence of Hæmatoporphyrin, Hæmin, and Urobilin on the Formation of Bile-pigments. III. THEODOR BRUGSCH and K. KAWASHIMA (*Chem. Zentr.*, 1911, i, 995; from *Zeitsch. expt. Path. Ther.*, 1911, **8**, 645—648).—The influence of hæmatoporphyrin, and then successively of hæmin and urobilin on the excretion of biliverdin, was determined by the same method as that employed in the previous investigation. It was found that hæmatoporphyrin is not entirely converted into bile-pigment, as part escapes unchanged in the bile. It is questionable whether it is converted into urobilin at all. Both hæmin and urobilin are oxidised to bilirubin and biliverdin. S. B. S.

Some Constituents of Suprarenal, Thyroid, and Testis. ALFRED LOHMANN (*Zeitsch. Biol.*, 1911, **56**, 1—31).—In addition to adrenaline, choline is obtainable from the suprarenal body. Choline, prepared from this organ and from the thyroid and testis, and made synthetically, was purified by Modrakowski's method, and was found to produce a fall of blood-pressure, as originally stated by Halliburton and Mott, and confirmed by numerous other observers since, Modrakowski and his colleagues excepted. Large doses of choline exacerbate respiration, and still larger doses stop it. The suprarenal extract also yields neurine, leucine, tyrosine, and certain bases grouped together as the "histidine fraction." From thyroid extract, choline, a "histidine fraction," and a substance not identified were obtained; the last substance yields a crystalline gold compound, and it may be *d*-aminovaleric acid. W. D. H.

Proteins and Protein Cleavage Products in Egyptian Mummies. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1911, **72**, 15—23).—In previous work it was shown that the muscles of mummies yield amino-acids on hydrolysis. It is now found that aqueous extracts of the same material without hydrolysis contain glycine, alanine, valine, leucine, aspartic acid, glutamic acid, phenylalanine, and proline. Other acids, including diamino-acids, were found after hydrolysis. The aqueous extract without hydrolysis gives the biuret reaction. The fat of the mummies had undergone cleavage. W. D. H.

The Precipitation of Proteins. ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1911, **25**, 166—173).—The author gives numerical results of the fractional precipitation of proteins of milk, colostrum, ox- and horse-serum, and eggs by various methods, both when fresh and after antiseptic preservation. He gives tables showing the changes they have undergone when kept under these conditions. S. B. S.

Original Acidity of Milk. Fréd. Bordas and F. Touplain (*Compt. rend.*, 1911, **152**, 1274—1276; *Ann. Falsif.*, 1911, **4**, 297—301).—By treating milk with an alcoholic solution of acetic acid (Abstr., 1905, ii, 49), and determining the acidity of the serum, the coagulum, the casein with associated insoluble salts, and the pure casein, it has been found that the original acidity of milk is identical with, and therefore probably due to, the acidity of the free casein. It follows then that fresh milk cannot contain lactic or tartaric acid. The serum which has been filtered through a Berkefeld filter, and is optically transparent is not acid, whilst if it contains particles visible under the ultra-microscope it is found to be acid towards phenolphthalein. W. O. W.

Excretion of the Alkali Metals in Purine Diuresis. Johannes Bock (*Skand. Arch. Physiol.*, 1911, **25**, 239—246).—From experiments on rabbits treated with theophylline, the author finds that in purine diuresis the amount of sodium and potassium excreted increases, but not necessarily *pari passu*. In a case of very strong diuresis the sodium in the urine corresponded almost with the proportion in serum, but the amount of potassium was much greater than in serum. These observations cannot be explained on the hypothesis that the diuresis is due to an increased filtration and diminished resorption. R. V. S.

The Excretion of Ingested Amino-acids in Liver Diseases, and Diseases Involving Disturbed Metabolism. Niro Masuda (*Chem. Zentr.*, 1911, **1**, 999; from *Zeitsch. expt. Path. Ther.*, 1911, **8**, 629—638).—The Sörensen-Henriques method was employed. When no amino-acids are ingested, the amount of amino-acids excreted depends on the total nitrogen metabolism, and is higher (4—5% of the total nitrogen excreted) with meat diets than on meat-free diets (1—3%). In normal cases, glycine and alanine are excreted to the extent of 25—30% as amino-acids, but higher numbers are obtained in pathological cases, such as in malignant tumours, especially such as implicate the liver (40—50%), and also in non-malignant diseases of the liver (cirrhosis, etc.). High values were also obtained in diseases of metabolism, such as diabetes and gout, although in the latter case they were but little above the normal. S. B. S.

The Pressor Bases of the Urine. III. William Bain (*Lancet*, 1911, i, 1409—1411. Compare Abstr., 1910, ii, 528).—The pressor bases are absent from the urine of children, and begin to be excreted about the age of fourteen. A vegetable diet considerably reduces the amount formed. Eggs and fish reduce the quantity to some extent, but if chicken is taken the amount is but little less than is obtained on an ordinary mixed diet containing butcher's meat. The bases are either absent or much reduced in amount in cases of high blood pressure. This is only partly explained by the low dietary which many such patients take; the main explanation is that the bases are retained in the system and produce the rise of arterial pressure. In gouty people with normal blood pressure, the pressor bases are excreted in normal amounts. W. D. H.

Colloids in the Urine. III. Quantity and Conditions of Solubility of the Urinary Colloids in Healthy and Pathological Kidneys. L. Lichtwitz (*Zeitsch. physiol. Chem.*, 1911, **72**, 215—225).—The urinary colloid (non-protein) occurs in the form of a sol, a gel (reversible by heat), and an irreversible precipitate. Diuretin and theocin increase the precipitation, but other circumstances leading to change in solubility are still not clear. Urinary protein is in a coarser form of division than that in the blood-serum. The amount of urinary colloid is independent of the quantity of water. The non-protein colloid is increased in certain pathological conditions of the kidney, and in many cases runs parallel with the amount of protein. In one case of nephritis, the urine contained more protein than the blood-serum. W. D. H.

Pathogenesis of Hereditary Haemophilia. Thomas Addis (*J. Path. Bact.*, 1911, **15**, 427—452).—The blood in "bleeders" is not deficient in fibrinogen; it yields the normal amount of thrombin and thrombokinase, and contains anti-thrombin, prothrombin, and calcium in normal quantities. The defect is that the change of prothrombin into thrombin occupies so long a time, hence blood coagulation is slow. W. D. H.

The Esterase and Nuclease Content of Serum in Different Forms of Insanity. Giacomo Pighini (*Biochem. Zeitsch.*, 1911, **33**, 190—217).—Chiefly of clinical interest. S. B. S.

Nature of Parathyroid Tetany. Anton Carlson and Clara Jacobson (*Amer. J. Physiol.*, 1911, **28**, 133—160).—The amount of ammonia in the blood of dogs in parathyroid tetany falls within physiological limits. Injections of calcium salts in amounts sufficient to suppress the tetany do not alter the ammonia concentration of the blood. In ammonia tetany, calcium salts have much less inhibiting action. Parathyroid tetany is also arrested by strontium salts, and except in extreme cases by injection of pituitary extract, hypertonic sugar solution, proteoses, and amyl nitrite, by section of the vagi, and by stimulation of the afferent fibres of the vagus. All such measures are temporary palliatives only. Parathyroid transplantation is alone an effective cure. The other methods merely decrease the excitability of nervous tissues, directly or indirectly, by causing partial cerebral anæmia. W. D. H.

The Action of Antimony on Experimental Trypanosome Infection. Julius Morgenroth and Rosenthal (*Chem. Zentr.*, 1911, i, 834—835; from *Berlin klin. Woch.*, 1911, **48**, No. 2).—The action of tartar emetic on trypanosomes is more rapid and powerful than any other preparation yet tried, as 0·2 c.c. of a solution of 1 in 1000 causes a disappearance of this organism. The acquisition of a noticeable resistance to the drug by repeated treatment was not observed. The authors, with Halberstädter, succeed in getting an antimony-resistant strain, however, by previous treatment with arsacetin. Potassium hexatantalate had no influence on the trypanosome infection, and exerted no prophylactic action; on the other hand, it protects the organisms against the action of arsacetin and antimony. A secondary action of the tantalum preparation was also noticed. S. B. S.

Accumulation of Iodine in the Tissues of Tumours.

M. TAKEMURA (*Zeitsch. physiol. Chem.*, 1911, **72**, 78—92).—After the subcutaneous administration of alkali iodides, the partition of iodine in the organism of the rat and mouse agrees with what O. Loeb (*Arch. expt. Path. Pharm.*, 1907, **56**, 320) found in the rabbit. The iodine content of malignant tumours in the mouse and rat is relatively higher. In mouse carcinoma the tumour approaches in this particular the tissues which are richest in iodine (blood and skin), whereas in rat sarcoma the quantity is not so great. W. D. H.

Action of Tervalent Ions on Living Cells and on Colloidal Systems. II. Simple and Complex Cations.

GEORGE R. MINES (*J. Physiol.*, 1911, **42**, 309—331).—Eleven simple tervalent cations (from rare earths) produce diastolic arrest of the frog's heart at a concentration of 0·00001*M*. Five complex tervalent cations tested scarcely affect the heart in concentrations one hundred times greater. It is not possible to ascribe the physiological action of ions to any one factor (solution-tension, valency, or ionic velocity); one and the same ion may act differently on different tissues by virtue of different characters or groups of characters. Further, two ions which from the point of view of one tissue exhibit constellations of properties which are alike, may present wholly dissimilar aspects toward another tissue. In certain cases, described in full, these actions are closely paralleled in the relations of ions to various colloidal systems. W. D. H.

Sodium and Potassium Chlorides.

E BIERNACKI (*Chem. Zentr.*, 1911, i, 995; from *Zeitsch. expt. Path. Ther.*, 1911, **8**, 685—694).—Dogs were fed with a daily diet of rice and horse-meat which contained 0·4—0·6 gram of K_2O, to which were added varying quantities of sodium chloride (1—8 grams). In addition to a certain influence on the nitrogen metabolism, it was noticed that the ingestion of the sodium chloride caused a loss of potassium by the organism. The sodium salt appears therefore to play a rôle in regulating the potassium metabolism, and replacing an excess of potassium. On the other hand, with a diet poor in potassium a large amount of sodium chloride is not permissible, in that it causes a loss of potassium from the organism itself. S. B. S.

Pharmacological Action of Uranium.

DENNIS E. JACKSON and FRANK C. MANN (*Indiana University Studies*, 1911, **8**, 2—15).—Intravenous injections of a solution of sodium uranyl tartrate into dogs did not produce any marked increase in the rate of lymph flow from the thoracic duct. The action of this salt differs from that of the cyanides in that it produces a more pronounced and prolonged rise in blood pressure, and a much smaller action on the respiration. The method by which uranium prevents coagulation of blood appears to be different from that exercised by most other substances, and probably consists in the formation of a combination between the metal and those proteins of the blood which are essential for the process of coagulation. The addition of thrombokinase, fibrin ferment, or calcium chloride to blood previously treated with sodium uranyl tartrate does not cause clotting to occur. Nor is it possible to bring about coagulation in such blood by precipitating the uranium with sodium phosphate.

Sodium uranyl tartrate differs further in its action from the cyanides, in that it does not form chemical combinations with hæmoglobin and methæmoglobin, whilst it does not produce a similar inhibition of the decomposition of hydrogen peroxide by blood, or of the oxidation of guaiacum tincture by potato extract. W. J. Y.

The Influence of the Chlorinated Hydrocarbons of the Fatty Series on the Organism. KARL B. LEHMANN, VAL. BEHR, LEONHARD QUADFLIEG, MARGARETE FRANZ, GEORG HERRMANN, ADOLF [? HEINRICH] KNOBLAUCH, KARL GUNDERMANN, and WÜRTH (*Arch. Hygiene*, 1911, **74**, 1—60).—The toxic effects of air mixed with various vapours was investigated by the methods repeatedly employed by Lehmann and his pupils. The toxicity of the chloro-derivatives may be represented as the result of a large number of comparable experiments on cats by the following numbers: Tetrachloromethane 1, perchloroethylene 1·6, trichloroethylene 1·7, dichloroethylene 1·7, chloroform 2·2, pentachloroethane 6·2, tetrachloroethane 9·1. The methane derivatives are more toxic than the ethane derivative; the ethylene derivatives are intermediate in their action between the two. In the three series of hydrocarbons investigated, it was found that the increase in the chlorine substitution caused a decrease in the toxicity. S. B. S.

The Value of Individual Amino-acids in the Dog's Organism under Various Conditions. EMIL ABDERHALDEN and JOSEPH MARKWALDER (*Zeitsch. physiol. Chem.*, 1911, **72**, 63—77).—It is found that glycine and *d*-alanine behave differently in the dog's organism. If glycine is added to non-nitrogenous material (sucrose, lard), the amount of amino-acids in the urine falls off markedly. The effect of *d*-alanine in this direction is not so great. The administration of *d*-alanine in general leads to less amino-acid in the urine than does that of glycine. W. D. H.

The Fate of Non-nitrogenous Components of Aromatic Amino-acids in the Normal Body. AKIKAZU SUWA (*Zeitsch. physiol. Chem.*, 1911, **72**, 113—130).—In alcaptonuria the view is held that the aromatic amino-acids (tyrosine and phenylalanine), which are converted into homogentisic acid, lose ammonia, and so are first converted into the corresponding hydroxy-acids; phenylalanine will thus yield phenyl-α-lactic acid, and tyrosine will yield *p*-hydroxyphenyl-lactic acid, as intermediate products; the latter, however, does not yield alcapton, but the ketonic acid (hydroxyphenylpyruvic acid) may possibly do so. It is now shown by experiments on rabbits and men that this ketonic acid is in health better burnt in the body than the hydroxy-acid, and this is regarded as additional evidence that the ketonic acid is the intermediate substance both in alcaptonuria and in experiments with perfused livers. W. D. H.

Glycogenic Property of Dihydroxyacetone. St. Mostowski (*Compt. rend.*, 1911, **152**, 1276—1278).—Thirty to sixty grams of dihydroxyacetone were administered to fowls during four or five days, and the amount of glycogen in the liver and muscles determined after killing the animals. Although the muscles contained only traces of glycogen, a considerable quantity had accumulated in the liver; thus, in three cases, 0·98, 2·14, and 3·14 grams were found, whilst the control livers gave only 0·013, 0·043, and 0·297 gram. Practically all the dihydroxyacetone was assimilated; in one experiment only traces of a reducing substance could be detected in the fæces and intestinal contents after the ingestion of 50 grams of the compound. Külz and others have shown that glycogen may be synthesised from glycerol in the organism, and Lüthje has demonstrated the production of dextrose from the same substance (*Archiv Klin. Med.*, **80**, 151). It appears probable from the present experiments that trioses are formed as intermediate compounds in this transformation. W. O. W.

The Fate of Subcutaneously Administered Sucrose in the Animal Body, and its Effects on Protein and Fat Metabolism. Ernst Heilner (*Zeitsch. Biol.*, 1911, **56**, 75—86).—If large quantities of an aqueous solution of sucrose are given subcutaneously, a small fraction is not excreted, but burnt in the body. The cleavage of the disaccharide is brought about by an enzyme formed *ad hoc*; such enzymes may be termed protective or immunising.

These large doses of sugar produce nephritis and albuminuria. The injection in fasting animals diminishes protein catabolism, not because it "spares" protein, but because the strong solution interferes with the osmotic processes in the body-cells. Fat metabolism, on the other hand, is increased. W. D. H.

Chemico-Toxicological Study of Adrenaline. Giuseppe Venturoli and Guido Tartarini Gallerani (*Giorn. Farm. Chim.*, 1911, **60**, 97—105).—Adrenaline, when kept in air, is converted into oxyadrenaline, and this is also the only transformation product of adrenaline which the authors could discover in animals poisoned with adrenaline.

The reactions of adrenaline are not given by oxyadrenaline, with the exception of those of Brouardel and Boutmny (blue coloration with ferricyanide and ferric salt) and Jungmann (blue coloration with phosphomolybdic acid and ammonia).

In the systematic examination for alkaloids, the oxyadrenaline accompanies morphine and narceine in the amyl-alcoholic extract of the ammoniacal solution. If the solution of all three is treated with chloroform, these bases are removed, and oxyadrenaline can then be extracted with amyl alcohol. R. V. S.

Di-iodotyrosine and its Possible Application in Therapeutics. Albert Berthelot (*Compt. rend.*, 1911, **152**, 1323—1325. Compare Oswald, this vol., i, 203, 372).—Animals support the intravenous injection of 3 : 5-di-iodotyrosine without ill effects. Rabbits tolerate doses of 0·4 gram per kilo. of body-weight, and 2·0 grams has been administered in twenty-four hours by intramuscular injection to a human syphilitic without symptoms of iodism becoming manifest.

W. O. W.

Pilocarpine. II. N. Waterman (*Zeitsch. physiol. Chem.*, 1911, **72**, 131—139).—Repeated injections of pilocarpine produce diuresis and glycosuria. An injection of 10—15 mg. in rabbits raises the percentage of sugar of the blood for the first two hours; it then falls. The glycosuria is due to increased permeability of the kidney to sugar during the diuresis. The prevention of adrenaline-glycosuria by pilocarpine (Falta, Rudinger, and Epstein) may be due to the lessening of diuresis which occurs during the first hour after pilocarpine injection.

W. D. H.

Artificial Pyrexia Produced by Tetrahydro-β-naphthylamine Hydrochloride. Adam Black (*Proc. Roy. Soc. Edin.*, 1911, **31**, 333—341).—This drug induces a high temperature in rabbits and dogs by acting on the nervous system; its action is antagonised by ether. The rise of temperature is probably due to decreased heat-elimination. The change in nitrogenous metabolism is very small compared with that produced by diphtheria-toxin. It is probably the action of toxins on the tissues, and not the high temperature which modifies protein metabolism. W. D. H.

Physiological Action of *d*- and *l*-Tetrahydroquinaldine. Dorothy Dale and George R. Mines (*Proc. physiol. Soc.*, 1911, xxxi—xxxii; *J. Physiol.*, **42**).—In producing diastolic arrest of the frog's heart, no difference could be detected in the *d*- and *l*-compounds, but on skeletal muscle shortening and gradual loss of irritability is more rapidly produced by the *l*-compound. As Cushny first pointed out one tissue may differentiate between a pair of optical isomerides, whilst another tissue cannot do so. W. D. H.

Atoxyl. V. Ferdinand Blumenthal and Emanuel Navassart (*Biochem. Zeitsch.*, 1911, **32**, 380—393).—Experiments on rats showed that after administration of bromine and iodine atoxyl compounds, considerable quantities of arsenic can be detected in the liver, which is not the case after administration of atoxyl itself. Experiments were also carried out on rabbits to determine the rate of excretion of arsenic in the urine after administration of various organic arsenic compounds. It was excreted most rapidly after hectine, which only contains 17% arsenic; the next most rapid excretion followed after administration of atoxyl; the rate of excretion was about the same after the calcium salt. In the case of the bromine and iodine compounds the excretion is relatively slow. It is also relatively slow after the administration of insoluble compounds (silver or mercury salts).

In the case of soluble compounds the more toxic they are the more slowly is arsenic eliminated. Experiments on the distribution of arsenic in the various organs after injection of soluble compounds did not reveal any great differences, except in the case of the bromine and iodine compounds already referred to. Tumours (rat sarcomas) exhibited a certain slight affinity for arsenic after injection of certain preparations. S. B. S.

Biochemical Investigations with Aromatic Mercury Compounds. Walther Schrauth and Walter Schoeller (*Biochem. Zeitsch.*, 1911, **32**, 509—511).—The authors call attention to certain investigations with various organic compounds of mercury which were not quoted by Blumenthal (this vol., ii, 517), especially their own on "Asurol," and those of E. Fischer and von Mering on β-mercuridipropionic acid. They doubt the spirillocidal action of mercury compounds of this character. S. B. S.

The Inefficiency of the Suprarenals in Cases of Phosphorus Poisoning. Ernst Neubauer and Otto Porges (*Biochem. Zeitsch.*, 1911, **32**, 290—307).—It has been observed that in diseases of the suprarenals (Addison's disease), the glycogen is absent in the liver. This happens also in phosphorus poisoning. It seemed possible, therefore, that the failure of glycogen in the liver in cases of phosphorus poisoning is due to the injury to the suprarenals. Histological examination of these glands after phosphorus poisoning (of rabbits) was undertaken, and it was found that, in contrast to normal animals, they had lost their capacity of being stained by chromium; adrenaline was also absent in the glands of the poisoned animals. Adrenaline was then administered to animals before the phosphorus poisoning, and in several of the experiments it was found that the liver of these animals contained glycogen, whereas in the case of those animals which had been poisoned without previous administration of adrenaline, glycogen was absent. The authors explain why, in certain cases, after administration of adrenaline and poisoning, glycogen was also absent. S. B. S.

The Antagonistic Action of the Salts of Calcium and Other Alkaline Earths to Potassium Poisoning. Jacques Loeb and Hardolph Wasteneys (*Biochem. Zeitsch.*, 1911, **32**, 308—322).—Whereas the toxic action of potassium chloride is antagonised by sodium chloride when 15—17 molecules of the latter salt are present to one of the former, 1/30th of a molecule of calcium chloride only is necessary to produce the same effect, and partial antagonism is effected even by 1/300th of a molecule. The limiting concentration for antagonism is not, however, very sharp. Magnesium chloride is capable of acting antagonistically only to a limited extent, and for a short period; strontium chloride acts like calcium chloride, as does to some extent barium chloride, but in this case the salt itself is toxic. The action of the calcium salt is assumed to be due to the fact that it forms an insoluble calcium compound on the surface of the fish, whereas the corresponding potassium and sodium salts are soluble; hence, a small quantity of calcium can replace relatively much larger quantities of potassium than can sodium. The highest concentration of potassium chloride that can be antagonised by calcium salts is the same as that which can be antagonised by sodium salts, namely, 6·6 c.c. *m*/2-potassium chloride in 100 c.c. of the solution. As in previous investigations, *Fundulus* was the animal employed. S. B. S.

Lactones as Fish Poisons. HANS PRIESS (*Ber. Deut. pharm. Ges.*, 1911, 21, 267—270).—A résumé of recent work on the method of action of fish poisons, including that of Kobert (Abstr., 1904, i, 1905), Herzog (Abstr., 1910, i, 124), Fickendey (*Zeit. angew. Chem.*, 1910, 2166), Overton (Abstr., 1897, ii, 337), Ellinger (Abstr., 1908, ii, 1060), and Hanriot (Abstr., 1907, ii, 292, 386). Xanthotoxin (this vol., ii, 646) produces narcosis in carp in solutions containing one part in 100,000, but the fish recover when placed in clean water.
T. A. H.

The Combination of Tetanus Toxin with Other Substances. SIEGFRIED LOEWE (*Biochem. Zeitsch.*, 1911, **33**, 225—246).—The capacity of the tetanus toxin to combine with other substances is not confined to brain tissue, but can also take place with red blood-corpuscles and bone-marrow. Combining capacity for brain substance is to a great extent lost by heating the latter. It depends to a great extent on the lipoid substances, and can be demonstrated with the lipoid-containing extracts of the brain. The binding capacity of the grey substance is greater than that of the white, and that of the basal ganglia greater than that of the cortex. In the grey substance are substances of great combining capacity which are different from the cerebrosides, and can be extracted by light petroleum. Numerous fatty substances also show a combining capacity for tetanus toxin, especially the higher fatty acids and their salts with the alkali metals.
S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Relations between the Sugar-Content of Nutrient Media and Nitrogen Metabolism by Bacteria. KARL ERNEST BOEHNCKE (*Arch. Hygiene*, 1911, 74, 81—109).—The rapidity of decomposition of various nitrogenous substances (peptone, asparagine, etc.) is regulated largely by the presence or absence of other compounds capable of serving as a source of energy. This is especially the case where the amount of nitrogenous substance is small, as in bouillon; dextrose then serves as the chief source of energy, and leads to an economy of nitrogen for metabolic processes.

Specific differences exist in the behaviour of the bacteria tested; such organisms as *Bacillus proteus* and *B. Friedländer* utilise the sugar less than *B. mesentericus*, *B. alcaligenes*, and *Vibrio Metschnikoff* as a source of energy, and therefore lead to a more vigorous decomposition of the nitrogenous compounds. These differences were more marked in peptone than in asparagine cultures. H. B. H.

Lipase Produced by Bacteria. N. L. SÖHNGEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1200—1210. Compare this vol., ii, 319).—The nature of the source of carbon and nitrogen is of no importance for the formation of lipase by micro-organisms. For the former, glycerol, dextrose, calcium lactate, or sodium malate may be used, and for the latter, peptone, asparagine, ammonium chloride, or potassium nitrate. The addition of dextrose to cultures inhibits the hydrolysis of fat only when the organisms concerned are able to produce acids therefrom. It was found that the decomposition of fat decreases as the amount of acid rises, and that it ceases entirely when the culture liquid is about *N*/50 acid. This acid limit is the same for the enzymes of *B. Stutzeri*, *B. lipolyticum-α*, *B. lipolyticum-β*, and of *Oidium lactis*. Mineral acids are more potent than organic acids. The conclusion is drawn that rancidity of dairy products can only take place when, owing to the action of alkali-producing bacteria and moulds, the acidity of these products falls below the above limit. The effect of the presence of various compounds on the rapidity of change induced by bacterio-lipase was investigated, and it was found that calcium and magnesium salts, sodium glycocholate, and trimethylamine favour the change; sodium and potassium hydroxide, ferric and manganese salts are less active, univalent alcohols retard the process, whilst sugars and glycerol are without effect.

Oxygen and light favour the decomposition of fats by lipase. Fats may be prepared synthetically by the action of bacterio-lipase on oleic acid and glycerol, but the monoglyceride chiefly results.

H. B. H.

Purification of Sewage by the Soil and by Bacterial Beds. ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1911, **152**, 1204—1208. Compare this vol., ii, 421).—It has been shown by experiments in which large quantities of earth were treated with sewage, that destruction of organic matter by oxidation with loss of gaseous nitrogen takes place to a much smaller extent in the soil than when sewage is purified by bacterial beds. Nitrification in the former case, however, is increased. The loss of nitrogen from the sewage under the conditions employed was 16·36% during purification by soil and 60% after treatment in the septic tanks. W. O. W.

Variation and Carbohydrate Metabolism of Bacilli of the Proteus Group. T. H. GLENN (*Centr. Bakt. Par.*, 1911, i, **58**, 481—495).—An account of experiments designed to lead to the production of strains of organisms of the *Proteus* group, which would possess distinctive powers of acid production from dextrose. No essential variations in the acid-producing power of the organisms resulted. It was found that, although *P. vulgaris* does not ferment lactose under aerobic conditions, it was possible by means of cultivations under anaerobic conditions to induce and increase this power. Further investigations showed that the production of indole by *P. vulgaris* and *Bacillus coli* occurs in the presence of peptone solution alone, or with the addition of glycerol, lactose, and starch; dextrose and sucrose inhibit its production. This inhibitive effect only takes place where the organisms are able to ferment the carbohydrate with production of acid. The addition of more than 0·5% lactic acid to the culture medium had a similar effect.

The acid formed by the fermentation of carbohydrates also leads to an inhibition of gelatin liquefaction by members of the *Proteus* group. The liquefaction of gelatin by *B. cloacae* is not affected by the presence of sucrose and dextrose; this is suggestive of the formation of a peptic ferment by *B. cloacae*, and a tryptic ferment by *Proteus vulgaris*.

P. mirabilis appears to be an intermediate form between *P. vulgaris* and *P. Zopfii*, and *P. Zenkeri*, and differs only in the intensity, but not in the quality, of its biochemical reactions. H. B. H.

The Juice of Beer Yeast. E. KAYSER (*Compt. rend.*, 1911, **152**, 1279—1280. Compare this vol., ii, 421; Lebedeff, *ibid.*, i, 248; ii, 519).—The most active zymase preparations have been obtained by allowing beer yeast to remain for thirty-five to forty hours at 25° before macerating with water according to Lebedeff's process. The ferment prepared in this way is activated by salts of manganese in the same way as yeast itself. W. O. W.

Fermentation with Yeast. HANS EULER and GUNNAR LUNDEQVIST (*Zeitsch. physiol. Chem.*, 1911, **72**, 97—112).—The yeast employed was poor in maltase; nevertheless, it fermented maltose as rapidly as dextrose. The fermentation of dextrose was greatly accelerated by neutralised or by pure monosodium phosphate; that of mannose was not affected. Previous treatment of yeasts with sugar, phosphate, or mixtures of the two substances does not affect their fermenting power. In other yeasts where such treatment has an effect, it is probably not the zymase, but the auxiliary substances which are affected. Those yeasts which do not respond to previous treatment with phosphate contain a high percentage of phosphoric acid. W. D. H.

Influence of Antiseptics on Yeast Autolysis. E. NAVASSART (*Zeitsch. physiol. Chem.*, 1911, **72**, 151—157).—The influence of various antiseptics on the autolysis of yeast was investigated on the lines of Salkowski's previous work on liver autolysis. Certain differences are stated in detail between the effect of various antiseptics in the two kinds of autolysis and in the enzymes (nuclease, proteolytic enzyme, etc.) concerned. W. D. H.

The Degradation of Nitrogenous Substances by Yeast. OSWALD SCHWARZ (*Biochem. Zeitsch.*, 1911, **33**, 30—31).—The evolution of carbon dioxide when glycogen, starch, alanine, caseinogen, etc., were treated with yeast took place in the presence of adrenaline. The latter, however, only acted when added in the form of the tartrate, and not in the form of hydrochloride. The tartaric acid must therefore be regarded as the source of the fermentative energy.

S. B. S.

Influence of Enzymes on the Respiration of Plants. S. D. LWOFF (*Bull. Acad. Sci. St. Pêtersbourg*, 1911, [vi], 655—678).—Unboiled taka-diastase exerts a marked retarding influence on alcoholic fermentation by hefanol or zymin, but, after boiling, the enzyme stimulates the action of the zymase. On the respiration of the higher plants, either living or dead (*Vicia faba*, wheat seeds), taka-diastase exerts a stimulating action; this action is especially marked with living objects (*Vicia faba*), where anaerobiosis, according to Palladin, initially takes the form of alcoholic fermentation. Thus, it seems that where alcoholic fermentation proceeds alone and is not complicated by oxidation processes, taka-diastase exhibits its maximum destructive activity, whilst, where the fermentation is only the initial phase, and is connected biologically with subsequent oxidation charges, the taka-diastase possesses its maximum stimulating action. Merck's diastase, boiled or unboiled, produces effects opposite to, and of less magnitude than, those of taka-diastase.

Emulsin, which produces the same effects in the boiled as in the unboiled condition, exerts a marked retarding action on alcoholic fermentation brought about by hefanol, and so proceeding apart from respiration. On the respiration occurring in dead organisms, and hence under abnormal conditions, emulsin exhibits a stimulating influence; but on the normal respiration of living higher plants (*Vicia faba*), emulsin has no action.

T. H. P.

Variations in the Amounts of Single Phosphoric Acid Compounds in Seeds Depending on Conditions of Vegetation. Mlle. S. LEWONIEWSKI (*Bull. Acad. Sci. Cracow*, 1911, 85—96).—The amounts of total nitrogen, protein nitrogen, total phosphorus, and phosphorus as lecithins, phytin, in proteins, and in inorganic forms were estimated in different varieties of barley grain obtained with different manures. The results show that the variations in the amounts of nitrogen and phosphorus depend chiefly on the conditions of growth. The amount of phosphoric acid in the same variety of barley grown in different places varied from 0·562 to 0·782%, whilst two different varieties grown in the same place contained respectively 0·957 and 0·937%.

The amounts of phosphoric acid in the proteins vary only slightly; the differences in total phosphorus are due mainly to variations in inorganic phosphorus and phytin. With deficient phosphatic manure the phosphorus is chiefly utilised for the production of nucleo-compounds; production of phytin and accumulation of inorganic phosphorus only occur when the plants have abundance of phosphatic manure. The relations of total phosphorus and of phosphorus soluble in 1% acetic acetic acid to total nitrogen vary widely; the former varied between 100 : 50 and 100 : 32, and the latter between 100 : 20 and 100 : 6.

It is probable that the estimation of phosphorus soluble in 1% acetic acid (inorganic phosphorus + phytin) will afford indications of the amount of available phosphorus in the soil as good or better than those obtained by estimating the relation P_2O_5/N in the grain.

N. H. J. M.

Origin of Carbon Assimilated by Plants.

LOUIS CAILLETET (*Compt. rend.*, 1911, **152**, 1215—1217).—Experiments on plants, such as ferns, which flourish in the absence of much light show that these organisms obtain the carbon requisite for development principally from the organic matter of the soil, and to a much smaller extent from carbon dioxide in the atmosphere.

W. O. W.

Phenomena of Fermentation are Actions of Digestion. Study of Denitrification in the Vegetable Kingdom.

PIERRE MAZÉ (*Ann. Inst. Pasteur*, 1911, **25**, 369—391. Compare this vol., ii, 518).—The experiments, previously referred to, on the reduction of nitrates by seedlings and on the assimilation of nitrites by plants are described.

Peas and maize seeds all germinated in solutions containing 0·5% of sodium nitrite, and most of them in presence of 1%. In stronger solutions peas failed to germinate, whilst some of the maize seeds germinated in presence of 2% of sodium nitrite.

Culture experiments in which maize was grown in presence of 0·05% of sodium nitrite and the usual minerals, gave very unsatisfactory results until the roots reached the calcareous deposit at the bottom of the bottles. The plants then recovered and grew quite normally.

N. H. J. M.

Function of Hormones in Regulating Metabolism.

HENRY E. ARMSTRONG and E. FRANKLAND ARMSTRONG (*Annals of Botany*, 1911, **25**, 507—519. Compare Abstr., 1910, ii, 883).—When exposed to the action of hormones the leaf of *Aucuba japonica* becomes a rich chocolate-brown black, and ultimately black. In the case of both *Aucuba* and laurel leaves weak solutions of mineral acids, sodium hydroxide and carbonate, and most metallic salts were without action; those substances able to penetrate the leaf membrane were mercuric chloride (but not nitrate or sulphate), cadmium iodide (but not chloride), sodium and potassium fluorides; further, iodine, carbon dioxide, hydrogen sulphide, and ammonia. Acids of the acetic series are more active as their molecular weight increases; the same applies to the corresponding alcohols. Lactic, benzoic and salicylic acids penetrate the leaf. Volatile organic vapours, especially toluene, chloroform, ether, acetone, piperidine, etc., are all very active excitants.

The action of the excitant is to liberate the enzymes of the cell, the amount of reducing sugar is increased, glucosides are hydrolysed, and oxydases rendered active. The interpretation of the action of hormones previously given is extended to the explanation of a variety of manifestations in vegetable and agricultural chemistry; it is supposed that growth will be stimulated in those cases where hormones are present in the soil.

The physiological significance of glucosides is discussed, and it is suggested that the compound associated with the dextrose may in some cases act simply as a hormone. In cases where a cyanogenetic glucoside disappears as the seed ripens, as in *Linum*, the hydrogen cyanide may hasten ripening. Glucosides in seeds may furnish hormones on germination which stimulate further growth. The explanation is extended to the attack of plants by fungoid growths which secrete hormones.

The primary effect of the hormone is to condition the separation from each other of the successive layers constituting the protoplasmic complex. E. F. A.

Formation of Nitrous Acid in the Living Cell. PIERRE MAZÉ (*Compt. rend.*, 1911, **152**, 1624—1627).—The property shown by plant extracts of developing substances capable of liberating iodine from hydrogen iodide is shared by certain micro-organisms which have been isolated from such extracts. Six species, including sarcinæ, cocci, and aerobic and anaerobic bacilli were found to produce nitrous acid in cultures in ordinary media, but not in those containing reducing substances, such as milk. The reaction is not due to autolysis, or to the presence of a peroxydase. It appears to take place more rapidly in well aerated cultures than in those deprived of air, although the total amount of nitrous acid obtained in the former case is less, owing to further oxidation. W. O. W.

Physiological Importance of Manganese and Aluminium in the Vegetable Cell. JULIUS STOKLASA (*Compt. rend.*, 1911, **152**, 1340—1342).—An account of experiments confirming Bertrand's observations on the beneficial effect of manganese on plant development. Nutrient solutions containing 1/1000 of the gram-atomic weight of manganese or aluminium per litre increase the yield of the plant, but if both are present in these proportions, a toxic effect is exerted. The best results were given by solutions containing half the above quantities. W. O. W.

Behaviour of Benzyl Alcohol in Plants. GIACOMO L. CIAMICIAN and CIRO RAVENNA (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 392—394. Compare Abstr., 1909, ii, 604).—When maize plants are watered with a solution of benzyl alcohol, mixed with dextrose in order to render the introduction of the alcohol into the plant more active, part of the alcohol is converted into a glucoside-like compound, which has not been obtained crystalline, but is possibly identical with Fischer's benzylglucoside (Abstr., 1894, i, 4). T. H. P.

The Function of the Plant Catalases. W. ZALESKI and ANNA ROSENBERG (*Biochem. Zeitsch.*, 1911, **33**, 1—15).—The catalase action under varying conditions was determined by measuring the increase of pressure in a closed apparatus, when the catalase is allowed to act on a given quantity of hydrogen peroxide. More catalase was found in fresh than in dried plants. Extraction with ether and acetone diminished the catalase content slightly, extraction with ethyl alcohol very considerably, and with methyl alcohol completely. Acids and acid salts inhibited catalase action, either partly or completely, whereas alkalis or alkaline salts increased the action. Various neutral substances, such as arbutin, pyrogallol, resorcinol, and aloin inhibited the action. The amount of catalase during various stages of germination was also determined; in the case of wheat embryos the amount increased to a maximum and then diminished. The exact determination of the amount is difficult, owing to the presence in the seeds of substances which act deleteriously on the catalase. There appears to be some connexion between the catalase content and the respiratory energy, as determined by estimating the catalase content in different plants by the above-mentioned method, and the amount of carbon dioxide evolved per unit of weight of plant per hour. The majority of experiments carried out up to the present indicate that the catalase plays some part in the oxidation processes of the cell.

S. B. S.

Pentosans in Lower Fungi. Arthur W. Dox and Ray E. Neidig (*J. Biol. Chem.*, 1911, **9**, 267—269).—Various moulds of the *Aspergillus* and *Penicillium* groups were grown on a medium consisting of sucrose and inorganic salts. Pentosans and furfuraldehyde (derived from them) were subsequently obtained from the cultures. The percentage yield of pentosans varied from 0·86 to 1·17%. It therefore appears that fungus cells have the power of constructing pentosans out of hexoses or their decomposition products. The nature of the pentoses yielded by the pentosans was not determined.

W. D. H.

Influence of Zinc and Manganese on the Mineral Composition of "Aspergillus niger." Gabriel Bertrand and Maurice Javillier (*Compt. rend.*, 1911, **152**, 1337—1340. Compare Abstr., 1908, ii, 124; this vol., ii, 222).—Manganese accumulates to a greater extent in *Aspergillus niger* when zinc is present in the nutrient solution than when it is absent. Both zinc and manganese individually increase the total ash of the organism, but this is still more marked when both metals are present together. W. O. W.

Belladonna and Henbane Extracts. P. W. Danckwortt (*Arch. Pharm.*, 1911, **249**, 247—253).—The yields of extract obtainable by different methods from (1) the leaves, (2) the whole subaerial portion of belladonna and henbane and the alkaloidal content of these extracts have been determined.

As regards belladonna, it is shown that leaves yield extracts poorer in alkaloid than those from the whole herb, and that the best yield of extract from either source is obtained by extracting the dry material with alcohol, without removing chlorophyll, whilst extracts richest in alkaloids are obtained in like manner from the dry material, chlorophyll being removed in the process of manufacture.

Dry henbane leaves, by extraction with alcohol, yield about the same amount of extract as is obtained by evaporation of the expressed juice of the fresh green herb, but the former extract is much richer in alkaloids than the latter. The finished extracts should contain 15% of water. T. A. H.

Estimation of Pentosans and Methylpentosans in Cereals and in Wood Fungi. MIGAKU ISHIDA and BERNHARD TOLLENS (*J. Landw.*, 1911, **59**, 59—67).—The amounts of (*A*) pentosans and (*B*) methylpentosans of (1) maize, (2) wheat, (3) rye, (4) barley, (5) oats, (6) *Polyporus fomentarius*, (7) *P. pinicola*, (8) *P. hirsutus*, (9) *P. fulvus*, and (10) *Daedalia quercina*, were found to be as follows (% in dry matter) :—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
A	4·60	6·93	8·41	9·04	12·39	2·58	5·11	4·62	4·10	3·05
B	0·94	1·72	1·69	1·96	1·52	1·74	2·21	2·08	1·01	1·17

The estimations were made by Ellett's method, a special reflux apparatus, described with sketch, being employed for the alcohol extraction. The separation of the two phloroglucides is not absolute; the error is, however, only small, and is to some extent diminished by mutual compensation. N. H. J. M.

Cotton Wax. EDMUND KNECHT and JOHN ALLAN (*J. Soc. Dyers*, 1911, **27**, 142—146).—By extraction with benzene, Egyptian cotton yielded 0·47%, American cotton 0·55%, and East Indian cotton 0·38% of cotton-wax, which had m. p. 76°, and resembled beeswax in appearance. About 70% of the crude wax was soluble in light petroleum, and this portion (cotton-wax A), as obtained from "sliver" made from Egyptian cotton, had m. p. 66—67°, acid number 44·1, saponification number 84·3, iodine number 28·55, and was partly soluble in alcohol; it had a dull yellow colour, and resembled beeswax in texture and fracture. On saponification, it gave glycerol and 47·5% of "unsaponifiable" matter. The latter contained (1) hydrocarbons, possibly a mixture of $C_{31}H_{64}$ and $C_{32}H_{66}$ with unsaturated hydrocarbons; (2) a phytosterol, which furnished an acetyl derivative, m. p. 127·2°, and (3) colourless aliphatic alcohols. The soap formed from fraction A furnished on acidification stearic, palmitic, and cerotic (?) acids.

The portion (cotton-wax B) of the crude wax insoluble in light petroleum but soluble in benzene amounted to 30%, and was a dark green, granular, plastic mass, which had m. p. 68°, acid number 4·03, and saponification number 83·3. On saponification this portion furnished (1) a black, tarry material, soluble in hot benzene; (2) unsaponifiable matter composed of a phytosterol (acetyl derivative, m. p. 122·4°), viscous hydrocarbons, and a brown gummy substance, and (3) acids, including melissic acid (?) and a mixture of solid and liquid fatty acids. T. A. H.

Constituents of Derris Species. WILHELM LENZ (*Arch. Pharm.*, 1911, **249**, 298—305. Compare van Sillevoldt, Abstr., 1900, i, 109; Power, Abstr., 1903, ii, 323).—The root of *Derris elliptica* from New Guinea does not contain any alkaloid. It furnished the following percentages of extract to the solvents named when applied in the order given: light petroleum, 2·1; ether, 8·9; alcohol, 6·8; water, 4·8. The first of these consisted mainly of fat, and the second of fat with a crystalline substance, derrin. The alcoholic extract contained phlobaphens, resin, and a little tannin.

Derrin is best extracted from the roots by boiling benzene. It crystallises from alcohol or ether in small, colourless plates, and melts at 158°. It is toxic to fish, and to its action is probably due the use of this material as a fish poison.

Derris Stuhlmanni bark from German East Africa gave the following percentages of extract to the solvents named, applied in the order given: light petroleum, 3; ether, 5; alcohol, 2; water, 10·2. The first of these extracts was a colourless, semi-solid fat, and the second a colourless, wax-like mass, m. p. 89—90°, consisting mainly of a wax alcohol. The alcoholic extract contained more of the wax-like substance, but was chiefly resin. The aqueous extract was chiefly gum and sugar. No alkaloid was present. T. A. H.

Constituents of Fagara xanthoxyloides. Hans Priess (*Ber., Deut. pharm. Ges.*, 1911, **21**, 227—267).—The fruit-rind and root-bark of *Fagara xanthoxyloides*, Lam. (*Xanthoxylon senegalense*, D.C.), used in native medicine in the Cameroons have been examined; the first yields a volatile oil and a crystalline lactone, *xanthotoxin*, which is poisonous, whilst the second furnishes a crystalline phytosterol, fagarol (compare Giacosa and Monari, Abstr., 1888, 167; Giacosa and Soave, Abstr., 1890, 918).

The seeds of *F. xanthoxyloides* contain 31·9% of fixed oil having a pungent, rancid taste.

The rinds of the fruit gave 2·4% of bright yellow, volatile oil, which at $-5°$ deposited from 3—4% of crystalline matter, and after removal of this had D^{15} 0·9229, $[\alpha]_D^{15}$ $-1·20°$, acid number 2·19, and saponification number 60·7. It contained methyl nonyl ketone, and an unidentified aldehyde (possibly decoic aldehyde), decoic acid, linalool, dipentene, and an unidentified *sesquiterpene*, D^{14} 0·9214, $[\alpha]_D^{14}$ $+4°16'$, which yields a crystalline *hydrochloride*, and gives a greenish coloration with acetic anhydride and sulphuric acid. The oil on saponification yields acetic acid and a mixture of non-volatile, fatty acids; the linalool is partly present as linalyl acetate.

The crystalline substance, *xanthotoxin*, deposited by the oil was isolated in larger quantity along with resin by extracting the fruit rinds freed from volatile oil with alcohol. It crystallises in large, rhombic, biaxial needles, has the formula $C_{12}H_8O_4$, m. p. 145°, contains one methoxy-group, yields a *mononitro*-derivative, m. p. 230°, crystallising in yellow needles, a *dibromide*, m. p. 164°, separating from xylene in crystals, and behaves as a lactone with alkalis. This substance is being further examined by Thoms, who regards it as a coumarin derivative; it resembles picrotoxin in its toxic action on fish.

A benzene extract of the root-bark on treatment with light petroleum deposited *fagarol*, $C_{20}H_{18}O_6$, m. p. 127—128°, crystallising in colourless needles, and giving the reactions of phytosterol; it is probably identical with an unnamed substance isolated by Giacosa and Monari from the same source (*loc. cit.*), and by Eberhardt from *Fagara carolina.*

The paper concludes with an account of the pharmacognoscy of *Fagara* and *Xanthoxylon* species, and gives a tabular statement of the constituents of these so far as they are known. T. A. H.

Diastases of the Latex of the Japanese Mulberry Tree (Broussonetia papyrifera). C. Gerber (*Compt. rend.*, 1911, **152**, 1611—1614).—The sap of the Japanese mulberry tree contains three very active enzymes which are probably concerned in converting reserve materials of the organism into a form suitable for assimilation. Their activity is most marked at the commencement of inflorescence, after which it slowly diminishes until the leaves are fully developed, when it falls more rapidly. The enzymes are lypolytic, amylolytic, and proteolytic respectively. The last named is remarkably stable towards heat, and in experiments on milk had an optimum temperature at 75°; moreover, metallic salts which are toxic to similar ferments have little influence on this one, whilst other salts, normally retarding or indifferent, may even act as activating agents.

W. O. W.

Investigation of the "Urucuri" Fruit. I. Fritz Frank and Gnädinger (*Gummi Zeit.*, 1910, **24**, 1328—1329).—The kernels of "urucuri" fruit obtained from the palm *Attalea excelsa* when extracted with chloroform yielded a fat which on saponification furnished a small quantity of butyric acid, large amounts of decoic, octoic, and hexoic acids with traces of lauric and myristic acids; an *alkaloid*, forming glistening, pearly leaflets decomposing at 287° without fusion, and a *ketone* (probably of the terpene series), to which the characteristic odour of the kernel is due, were also isolated.

The woody portion of the fruit, on dry distillation, yielded a tar, which on fractionation furnished cœrulignol, a phenolic methyl ether, $C_9H_{12}O_2$, b. p. 240—241°, and creosol, b. p. 220°; a brown oil consisting principally of methylpyrogallol dimethyl ether was also obtained.

The more volatile products of distillation yielded formaldehyde, acetone, xanthogallol, a *compound*, $C_{18}H_4O_6Br_{14}$, m. p. 122° (obtained by treating the steam distillate with bromine water), catechol, pyrogallol dimethyl ether (m. p. 52°), with formic, acetic and propionic acids. Attention is drawn to the similarity of composition to beech wood tar. F. M. G. M.

A Colloidal Copper Soap as an Anticryptogamic Paste. V. Vermorel and E. Dantony (*Compt. rend.*, 1911, **152**, 1263—1265).—Copper is more effective as a fungicide when applied in the form of a colloidal solution than in the state of a powder as usually employed. Such a solution is prepared by adding a 1% solution of copper sulphate to an equal volume of a 4% soap solution free from alkali. The presence of much sodium stearate is a disadvantage. Addition of a stable colloid of the same electrical sign, such as gelatin, renders the solution more stable towards the action of electrolytes. W. O. W.

Manurial Experiments with Sugar Beet. J. GRAFTIAU (*Bied. Zentr.*, 1911, **40**, 300—302; from *Ann. Gembloux*, 1910, 65).—Experiments are described in which sugar-beet grown on plots, 2 × 1·25 m., was manured with sodium nitrate, ammonium sulphate (both alone and with lime), and cyanamide respectively. The greatest yield of roots (7·41 kilos.) was obtained with sodium nitrate, and the lowest yield (5·67 kilos.) with cyanamide. The yield of leaf and heads was also greatest with sodium nitrate (7·28 kilos.), and was lowest on the plot which received ammonium sulphate and lime. The latter plot, however, produced roots with the highest percentage of sugar (15·1) and the highest amount of sugar (108·42 grams). The results as regards sugar were very similar with sodium nitrate and with ammonium sulphate, whilst with cyanamide the percentage and yield of sugar were only 14·1 and 79·95 grams respectively.

N. H. J. M.

Manganese in Wine. ORESTE PRANDI and ANGELO CIVETTA (*Staz. sper. agrar. ital.*, 1911, **44**, 66—83).—All the wines examined (twenty-four) were found to contain manganese ($Mn = 0·53 - 1·65$ per million), the average amount being 0·82 per million. Usually the wines of better quality contain the highest amounts of manganese.

N. H. J. M.

A New Treatment of Wine. PHILIPPE MALVEZIN (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, **28**, 770—774).—When wine is left in an atmosphere of nitrogen, clarification rapidly takes place, and the wine takes on the clear limpid appearance associated with age. The author shows that, in absence of oxygen, the fermentation and other changes going on all come to an end, the organisms die, and rapidly settle to the bottom. It seems probable that this is the change normally taking place, the oxygen of the air being gradually absorbed, leaving only nitrogen; by this artificial means, however, the normal process can be much hastened. As nitrogen can be obtained commercially, the treatment is quite practicable on a large scale.

E. J. R.

Presence of Oxalic Acid in Certain Wines. L. MONNIER (*Ann. Chim. anal.*, 1911, **16**, 168—169).—The author calls attention to the presence of oxalic acid (also crystals of potassium and calcium oxalates) in a wine from a locality in the east of France. The reason of its occurrence seems somewhat doubtful. L. DE K.

The Greasiness ("Graisse") of Ciders. E. KAYSER (*Compt. rend.*, 1911, **152**, 1422—1424).—The disease affecting ciders is due to an anaerobic bacillus which is capable of fermenting sucrose with production of carbon dioxide, alcohol, lactic and acetic acids, mannitol, and lævulose. W. O. W.

Effect of Lime and Humus on the Mechanical and Physical Properties of Clay, Loam, and Sandy Soils. WILL THAER (*Gekrönt. Preisschr. Univ. Göttingen*, 1910, 145 pp.).—A study of five different soils showed that the calcium extracted by 4·26% hydrochloric acid is in combination with carbonic acid and colloidal acids, and, in humous sand, also in combination with strong mineral acids. The amount of colloidal calcium compounds is calculated from the difference in the amounts of lime as indicated by the amount of acid used and by the estimation of carbon dioxide.

Addition of lime to soils results in the precipitation of the colloids, and in increasing the permeability and water-holding power of the soil. In the case of humus soils, addition of lime is especially favourable to the activity of bacteria (nitrogen-fixing and nitrifying organisms); decomposition of the humus may become so rapid as to impoverish the soil.

The methods employed in investigating the soluble soil-colloids consist in extracting the soils with water, precipitating with alcohol, dialysis, and filtration. Partial analyses of the original extracts and of the alcohol precipitates, etc., were made. N. H. J. M.

Amount of Manganese in Some Italian Soils. A. CONTINO (*Staz. sper. agrar. ital.*, 1911, **44**, 51—55. Compare Leclerc, *Compt. rend.*, 1871, **75**, 1209).—Analyses of twenty-three soils of various kinds (sandy, volcanic, clay, and calcareous soils) showed that manganese was always present. One soil (calcareous clay) contained only a trace, whilst the amounts of manganese in the others varied from 0·03 to 0·48% (as Mn_3O_4). The average amount was 0·17%.

N. H. J. M.

Fixation of Phosphoric Acid by Organic Matter of the Soil. AUGUSTE PETIT (*Compt. rend.*, 1911, **152**, 1317—1319).—Phosphoric acid or soluble phosphates are fixed by the inorganic constituents of soil and not by the organic substances. When the latter are isolated, they are found to be incapable of removing phosphates from solution. An ordinary garden soil fixes much more phosphoric acid than a surface soil rich in humus, taken from a forest.

W. O. W.

Ammonia and Nitrate Formation in Soils. JACOB G. LIPMAN, PERCY E. BROWN, and IRVING L. OWEN (*Centr. Bakt. Par.*, 1911, **30**, 156—181. Compare Abstr., 1910, ii, 435).—The production of ammonia from dried blood in a heavy loam with which various amounts of sand were mixed decreased as the amount of sand increased; with large amounts of sand a good deal of ammonia escapes in the free state.

In mixtures of loam and sand (70 : 30), considerable amounts of ammonia were produced when only 8% of water was present; the maximum amount of ammonia was with 16% of water. Ammonia production was increased by addition of 0·05% of calcium carbonate, and still more by larger amounts up to 0·3%. With 0·5% there was a fall in the amount of ammonia. With calcium carbonate obtained as a by-product in a borax factory, the amount of ammonia produced was somewhat less, owing probably to the boron present. The same calcium carbonate (containing $B_2O_3 = 2\%$) was found to be injurious to barley and vetches.

Mono- and di-calcium phosphates were found to have about the same effect in increasing ammonia production from dried blood added to soil. Tricalcium phosphate was without effect. N. H. J. M.

Field Trials with Nitrogenous Manures from the Atmosphere. JAMES HENDRICK (*J. Soc. Chem. Ind.*, 1911, **30**, 522—524).—The results of field experiments showed that calcium nitrate and calcium cyanamide are quite comparable with sodium nitrate and ammonium sulphate in their effects on grain crops. On the whole, calcium nitrate gave the best results, probably owing to the soils being deficient in lime.

When calcium cyanamide is stored, the percentage of nitrogen diminishes. This is chiefly due to the increase in weight which the manure undergoes; there is, however, a slight loss of nitrogen as well. When the manure is mixed with superphosphate, the phosphate is, to a great extent, rendered insoluble; the reaction is accompanied by a considerable rise in temperature, but no loss of nitrogen was detected.

Calcium cyanamide may be mixed with basic slag, bone meal, steamed bone flour, and potassium manures without loss in manurial value. N. H. J. M.

Manurial Value of Calcium Nitrate and Calcium Cyanamide as Compared with Sodium Nitrate and Ammonium Sulphate. PAUL BAESSLER (*Bied. Zentr.*, 1911, **40**, 302—304; from *Jahresb. Versuchsstat. Köslin*, 1909, **23**).—Field experiments in which winter rye was grown in slightly peaty, loamy sand without manure and with the four nitrogenous manures. Phosphoric acid was applied in the forms of superphosphate and basic slag respectively, and all the plots received potassium salts.

Similar experiments were made with winter wheat (on heavy loam), barley (on a loam soil), oats, and carrots.

Sodium nitrate produced the highest yields in every case except oats, with which calcium cyanamide (33·8 kilos. of nitrogen per hectare) gave a somewhat better result. On the whole, calcium nitrate gave the next best results after sodium nitrate. With calcium cyanamide the manurial effect was very variable (40 to 103, as compared with sodium nitrate = 100). Ammonium sulphate varied from 74 to 99%.

N. H. J. M.

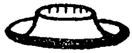
Analytical Chemistry.

The Simplest Arrangement for Reading Burettes. JULIUS F. SACHER (*Chem. Zeit.*, 1911, 35, 622—623. Compare this vol., ii, 432).—The author has used, for some years, an arrangement similar to that described by Goetze (this vol., ii, 531). A hair is fastened round a test-tube which will just slide over the burette, and the closed end of which has been cut off. The position of the meniscus is read off by means of the hair.

The simplest method of all is to put a small mirror at the back of the burette and make the reading when the meniscus coincides with its mirror image. Greater accuracy still can be obtained by making a horizontal mark with a diamond on the mirror; the reading is then taken when the lower edge of the meniscus, the mark on the mirror, and its mirror image are in a line. T. S. P.

A Re-fill Burette. RICHARD VON DER HEIDE (*Chem. Zeit.*, 1911, **35**, 568).—At the top of the burette is a two-way stopcock, the one way connecting with a soda-lime tube, and the other with a pear-shaped stoppered vessel fused on to the stopcock. The stock of standard solution is kept in the stoppered vessel, and may be run into the burette as required. The calibration of the burette commences at the two-way stopcock. T. S. P.

Improved Rapid Condenser and Extraction Apparatus. RICHARD VON DER HEIDE (*Chem. Zeit.*, 1911, **35**, 531). A double surface condenser is fitted into the Soxhlet apparatus by a ground-glass joint. In the top of the Soxhlet is a glass partition (annexed diagram), so arranged that the liquid used in the extraction drops from the condenser and is collected in the gutter of the partition, to overflow finally through a central hole into the Soxhlet.



If it is desired to collect the liquid coming from the condenser, it is usually necessary to go to some trouble in altering the position of the condenser. To obviate this, the ground-glass joint of the condenser is fitted with a hole which can be brought into direct connexion with a side-tube fused on to the top of the Soxhlet apparatus. When this connexion is made, the condensed liquid runs through the side-tube into a receiver instead of overflowing through the central hole in the partition.

The flask containing the extracting liquid is heated by means of an electric lamp. T. S. P.

Sedimentation Tube for Microscopic Analysis. EMIL SCHWABE (*Chem. Zeit.*, 1911, **35**, 577).—A thin glass tube is drawn out to a capillary at one end and sealed. The liquid containing the precipitate in suspension is put into the tube, and the precipitate allowed to settle into the capillary. The top of the tube is then closed with the finger, the tip of the capillary broken off, and the tube then used as a dropping pipette. With precipitates of varying densities, a rough quantitative separation can be carried out. T. S. P.

Burette for the Volumetric Estimation of Gaseous Mixtures, Especially of Furnace Gases. A. GAWALOWSKI (*Zeitsch. anal. Chem.*, 1911, **50**, 435—439).—A portable burette is described for use in gas analysis. It is somewhat similar in shape to the Lunge gas burette, but with the following alterations. The cup at the top of the burette is replaced by a stoppered U-tube, by means of which the various absorbents can be introduced into the burette. The stopper of the burette is so bored that the two limbs of the U-tube can be connected with each other, or each limb separately with the burette, or the burette with the gas reservoir containing the gas to be analysed. The burette has no tap at the bottom, but is cut off flush at the zero mark, the gas being confined in the burette by immersion in a cylinder containing brine. T. S. P.

Exact Gas Analysis. ARTHUR WILHELMI (*Zeitsch. angew. Chem.*, 1911, **24**, 870—874).—The author discusses the various methods for determining the constituents of a gaseous mixture, and also the errors which occur in the ordinary methods of taking samples. For the latter purpose it is recommended that a vacuum pipette be used, blank experiments being made to determine the amount of residual air in the exhausted pipette, so that an appropriate correction can be applied.

A full description is given of a new universal gas analysis apparatus, which is so arranged that the absorption and explosion pipettes, etc., are conveniently arranged round a burette, fitted with a specially-designed central tap by means of which rapid connexion can be made between the various parts. T. S. P.

Estimation of Chlorides, Chlorates, and Perchlorates in a Mixture of their Salts. MARQUEYROL (*Ann. Chim. anal.*, 1911, **16**, 167—168).—Chlorine present as chloride is estimated as usual. The total chlorine is estimated by fusing a portion of the salts with ten times the weight of a mixture of equal parts of sodium carbonate and potassium nitrate; thus converting the chlorate and perchlorate into chlorides.

For the estimation of the perchlorate alone, advantage is taken of the fact that both chloride and chlorate are converted into nitrate by evaporating twice with nitric acid (D 1 36) on the water-bath. The perchlorate remains unaffected, and is then converted as before into chloride by fusion. The chlorine as chlorate is obtained by difference. L. DE K.

Characteristic Reaction of Bromine. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1911, [iv], **9**, 542—544).—The author has shown that Malaquin's test for strychnine (Abstr., 1910, ii, 165) depends on the formation of a red or reddish-purple coloration when oxidising agents are added to the reduction products of strychnine (this vol., ii, 655, 672). He proposes to use a reduced strychnine solution as a reagent for bromine by means of the characteristic reddish-purple coloration which this halogen gives with reduced strychnine. The absorption spectrum of the colour given by bromine shows a band in the yellow, the more intense zone of which is in the neighbourhood of $\lambda = 550$. The red colours given by other oxidising agents, including chlorine, are characterised by two absorption bands in the green, the more intense having $\lambda = 510$ and the weaker $\lambda = 495$.

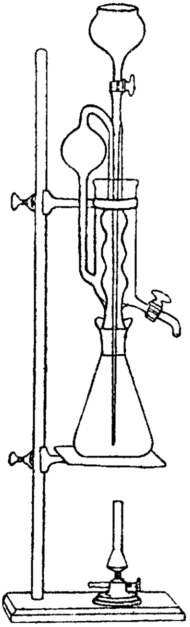
Reduced brucine gives an olive-green coloration with oxidising agents. T. A. H.

Extraction of Bromine and Iodine from Aqueous Solutions by means of Chloroform or Carbon Disulphide. A. LABAT (*Bull. Soc. chim.*, 1911, [iv], 9, 503—506).—Of the reagents employed in analysis for the liberation of iodine and bromine simultaneously from halogen salts of alkalis in aqueous solution, chlorine is objectionable, since it obscures the presence of iodine, and sodium nitrite is only useful for iodine. Bromides and iodides may occur in such proportions in a solution that one or both may be undiscoverable by the use of such reagents.

When bromine water is added to an aqueous solution of iodine a colourless or pale yellow solution is produced when the quantities of the two halogens present correspond to those required for the compound IBr_3, and this solution does not colour chloroform or carbon disulphide if either of these liquids is shaken with it. The detection of iodine in presence of bromine under these conditions is not facilitated by shaking the separated organic liquid with sodium hydrogen carbonate except by the method prescribed by Bourcet (*Thèse*, Paris, 1908), who used sodium nitrite and sulphuric acid for the liberation of the two halogens. In using sodium nitrite no action takes place with bromides unless sufficient sulphuric acid is present. Then nitrosyl bromide is formed, which colours carbon disulphide or chloroform brown. Nitrosyl bromide is destroyed by water or a solution of sodium hydrogen carbonate, and consequently on shaking the coloured organic liquid with either of these, the brown colour disappears and that of iodine becomes apparent if the latter is present. T. A. H.

Estimation of Total Respiratory Exchange in Man. C. GORDON DOUGLAS (*Proc. physiol. Soc.*, 1911, xvii—xviii; *J. Physiol.*, 42)—A light and portable apparatus is described, which can be carried on the back, and so expired air can be collected during exercise. W. D. H.

Apparatus for the Estimation of Sulphur [in Iron or Steel]. D. WENNMANN (*Chem. Zeit.*, 1911, 35, 596).—The apparatus dispenses with the use of rubber connexions and washbottle, and the absorption vessel also serves the purpose of a cooling arrangement. When the flask is removed, the upper part of the apparatus remains in its place.



Five grams of iron or steel borings are placed in the flask, the absorption vessel is filled with 60 c.c. of potassium hydroxide solution (100 grams per litre), and 100 c.c. of dilute hydrochloric acid (1 : 1) are introduced through the separating funnel, the tap of which is then again closed. The ascending hydrogen sulphide fumes are cooled in the bulbs, pass through the side bulb-tube, and then get absorbed in the alkali. Heat is applied until evolution of gas ceases and the absorption vessel becomes hot; in the case of steel, however, it is best to wait until it is completely dissolved. Finally, the tap of the separating funnel is turned on, and the alkaline liquid drawn off through the lower tap into a flask. The left side bulb prevents regurgitation of the liquid.

The alkaline solution is acidified with 50 c.c. of dilute sulphuric acid (1 : 3), and to the liquid is added 1 c.c. of starch solution (800 c.c. of water + 10 grams of starch + 200 c.c. of the above potassium hydroxide solution), and the hydrogen sulphide is then titrated with iodine solution (3·91 grams of iodine, 20 grams of potassium iodide + 1000 c.c. of water); 1 c.c. = 0·05% of sulphur. L. DE K.

Estimation of Sulphur in Steel and Iron. ÉMILE JABOULAY (*Rev. gen. chim. pure appl.*, 1910, **12**, 190—192).—The author confirms the researches of Corleis, Wolf, and Kinder, who have shown that in this estimation the metal should be rapidly attacked with concentrated hydrochloric acid (D 1·19), and that the evolution of sulphur compounds is largely due to the employment of dilute acid. The paper contains a sketch of apparatus, with detailed description of the author's procedure, in which the hydrogen sulphide evolved is absorbed in a solution of zinc acetate and titrated directly with iodine and thiosulphate. F. M. G. M.

The Estimation of Sulphides in Alkali Cyanide. EDMUND C. ROSSITER (*J. Soc. Chem. Ind.*, 1911, **30**, 583—588).—The author has examined the three methods in use for the estimation of sulphides in alkali cyanide, namely, those of Ewan (Abstr., 1909, ii, 263), Williams (*J. Chem. Metall. Soc. S. Africa,* 1905, **6**, 170), and the mercury method as used by the British Cyanides Co. The last method consists essentially in precipitating the sulphide with mercuric chloride solution and collecting and weighing the precipitate obtained, but it is now shown that it cannot be depended on for a greater degree of accuracy than 0·005% of sodium sulphide.

Williams' method may be trusted to within 0·0025% of sodium sulphide when care is taken to insure the formation of the lead sulphide in a colloidal form. Ewan's method is equally accurate when the "personal error" of the operator has been determined, but both these methods are influenced too much by external circumstances, such as the light in the laboratory, individuality of the operator, etc., to be recommended for standard use.

The author recommends the following "powdered lead nitrate method," which is accurate to 0·001% of the sulphide present. The sample of cyanide is tested by the Ewan method, and from the result obtained the quantity of lead nitrate required to precipitate the sulphide in 100 grams of the sample is calculated. One hundred grams of the sample are then treated with about 10% more powdered lead nitrate than is required to precipitate the sulphide and 200 c.c. of air-free water, the mixture being stirred and gently warmed until the solution of the cyanide is complete. A small quantity of the solution is filtered, and tested to prove the presence of excess of lead nitrate; if not present in excess, a fresh sample of cyanide must be treated with a larger quantity of lead nitrate. The excess is then estimated by adding standard sodium sulphide solution until a small sample of the solution, after filtration, no longer shows lead on testing with sodium sulphide.

If the cyanide contains only 0·015% of sodium sulphide, then 150—200 grams are taken for analysis. The lead nitrate used is finely powdered and dried in a desiccator over sulphuric acid; its purity must be determined before use. T. S. P.

Nitrogen Estimations by Kjeldahl's Method. A. C. ANDERSEN (*Chem. Zentr.*, 1911, i, 1442; from *Skand. Arch. Physiol.*, 1911, **25**, 96—104).—Potassium sulphate should not be added unless strictly necessary, as in the case of derivatives of pyridine, piperidine, lysine, etc.; the use of platinum chloride as a catalyst should be avoided, as it causes an appreciable loss in nitrogen. The estimation of the ammonia by formaldehyde titration instead of by distillation cannot be recommended. L. DE K.

Improvements in Kjeldahl's Nitrogen Apparatus. LEO VON LIEBERMANN (*Chem. Zeit.*, 1911, **35**, 549).—A small tube provided with a stopcock is fused into the lower end of the distillation tube, and serves to contain a dilute solution of the indicator used in titrating the ammonia. Towards the end of the distillation a few drops are allowed to flow into the tube to test whether the distillation is completed. E. F. A.

Estimation of Nitric Oxide. L. MOSER (*Zeitsch. anal. Chem.*, 1911, **50**, 401—433).—See this vol., ii, 598.

Detection of Nitrates and Nitrites in Water by means of Reduced Strychnine. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1911, [iv], **9**, 544—546).—This is a further application of a solution of the reduction products of strychnine, which as already indicated gives reddish colorations with oxidising agents (this vol., ii, 652, 672). The reagent used is made by adding 5 grams of zinc amalgam to a mixture of 5 c.c. of hydrochloric acid (D 1·18) with 5 c.c. of a 1% solution of strychnine sulphate. This mixture is boiled, cooled, and decanted. With 10 c.c. of water containing 0·0001 gram of nitrous acid per litre, 0·5 c.c. of the reagent gives a red coloration. A coloration is not given by nitrates, except in presence of sulphuric acid, and consequently it is possible to estimate the nitrites colorimetrically first, and then the nitrates, by means of the increase in colour after addition of 5 c.c. of sulphuric acid, comparison being made with that afforded by a nitrite solution of the same strength in nitrites as the water under examination. It is advisable, however, in some cases to eliminate nitrites before testing for nitrates by this reagent, and this may be done by adding to 10 c.c. of the water two drops of ammonia and three or four drops of acetic acid, and evaporating to dryness, the treatment being repeated if necessary.

T. A. H.

Modification of the Diphenylamine Test for Nitrous and Nitric Acids. W. A. Withers and B. J. Ray (*J. Amer. Chem. Soc.*, 1911, **33**, 708—711).—Various methods of preparing the diphenylamine reagent and of applying the test for nitrites and nitrates have been described previously. A study of these has led to a modification of the test which has proved to be very delicate.

The reagent is prepared by dissolving 0·7 gram of diphenylamine in 60 c.c. of concentrated sulphuric acid and 28·8 c.c. of water; after the solution has been well cooled, 11·3 c.c. of hydrochloric acid (D 1·19) are slowly added.

The test is applied as follows: One c.c. of the liquid under examination is placed in a test-tube, one drop of the reagent is added, and the tube is shaken. Concentrated sulphuric acid (2 c.c.) is poured down the side of the test-tube so as to form a layer at the bottom. The tube is now shaken gently in order to cause a slight admixture of the two liquids at the plane of contact, and is then heated at 40° for fifteen to twenty minutes. By this means one part of nitrous nitrogen can be detected in 25 million, or one part of nitric nitrogen in 35 million. By heating for an hour, instead of fifteen to twenty minutes, one part of nitrous nitrogen can be found in 32 million, or one part of nitric nitrogen in 44 million. E. G.

The Mechanism of the Partial Disappearance of Phosphorus in the Calcination of Organic Matters, and a Method for Estimating the Ash in those Substances. Émile Fleurent and and L. Levi (*Ann. Chim. anal.*, 1911, **16**, 125—132, 179—183; *Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 779—793).—The loss in phosphorus during the burning of animal and vegetable matters is due to the presence of fatty matter, also to the action of carbon and silica at a high temperature. No loss, however, occurs when operating as follows: After removing the fatty matter by suitable solvents, the mass is completely charred in a closed crucible. The char is then moistened with water containing in suspension a known amount of calcium hydroxide (about 0 04—0·15 gram for 10 grams of sample), and the whole is evaporated to dryness. The mass is then transferred to one or several platinum boats, and heated in a combustion tube, first in a current of carbon dioxide, and then in a slow current of oxygen. This way of working also prevents loss of chlorine. When the percentage of ash is required, allowance must be made for the calcium oxide introduced. L. de K.

Volumetric Estimation of Phosphoric Acid Soluble in 2% Citric Acid Solution. L. Wuyts (*Ann. Chim. anal.*, 1911, **16**, 134—137).—Ten c.c. of the citric acid extract (5 grams of the phosphate plus 500 c.c. of 2% citric acid) are mixed with a few drops of hydrochloric acid, and evaporated to dryness in a small, flat porcelain dish. The residue is taken up with 3 or 4 drops of nitric acid and a few c.c. of water, and transferred to a 150 c.c. beaker; 10 c.c. of nitric acid (D 1·4) and 15 c.c. of saturated ammonium nitrate are added, and the solution is heated to boiling. After cooling for two or three minutes, 25 c.c. of molybdate solution are added (90 grams of ammonium molybdate and a few drops of ammonium in 1 litre). After stirring and waiting for ten minutes, the liquid is decanted through a filter, and the free acid is removed by washing five or six times with cold water. The precipitate is then dissolved in a slight excess of standard potassium hydroxide (326·5 c.c. of *N*-potassium hydroxide to 1 litre), and, after adding 0·5 c.c. of 1% phenolphthalein solution, the excess of alkali is titrated with standard sulphuric acid (1 c.c. = 1 c.c. alkali); 1 c.c. of alkali = 0·001 gram of phosphoric oxide. L. DE K.

Physical Properties of Aqueous Solutions containing Ammonia and Citric Acid. ROBERT A. HALL and JAMES M. BELL (*J. Amer. Chem. Soc.*, 1911, 33, 711—718).—In estimating the "available" phosphoric acid in artificial manures, an "exactly neutral" solution of ammonium citrate is employed. The preparation of this solution is rendered very difficult, owing to the lack of sensitiveness of indicators. A study has therefore been made of some physical properties of mixtures of ammonia and citric acid with a view to applying them to the determination of the end-point, and the results are now given of measurements of conductivity and of density of solutions containing constant amounts of citric acid and varying amounts of ammonia. The curve obtained by plotting the conductivities against the number of c.c. of ammonia solution shows a sharp break at a certain point at which the reagents are present in the proportions required to form triammonium citrate. This indicates the applicability of the conductivity method for determining the point of neutrality. It is also shown that the neutral solution of triammonium citrate has the maximum density. The presence of an excess of ammonia in the ammonium citrate solution can be detected by shaking the solution with chloroform, which dissolves a portion of the excess of the base, but not the free acid or salt. E. G.

Detection of Boric Acid in Preservatives. THEODOR VON FELLENBERG (*Chem. Zentr.*, 1911, i, 1248; from *Mitt Lebens Mittel-unters. Hyg.* 1, 193—194).—One gram of the sample is dissolved in 2 c.c. of hot water, and 1—2 c.c. of strong hydrochloric acid are added. On cooling, boric acid and alkali chloride are deposited; if necessary, a little brine is added. After pouring off the supernatant liquid, the saline mass is boiled with 4—6 c.c. of alcohol, the liquid is decanted, and, after acidifying with sulphuric acid, the alcohol is set light to. One % of borax is thus readily detected. L. DE K.

Use of Sodium Paratungstate in the Estimation of Carbon Dioxide in Carbonates and Nitric Pentoxide in Nitrates by Loss on Ignition. FRANK A GOOCH and S. B. KUZIRIAN (*Amer. J. Sci.*, 1911, [iv], 31, 497—500).—The carbonates of calcium, strontium, and barium may be readily tested for the actual amount of carbon dioxide by fusing with five times the weight of sodium paratungstate and observing the loss in weight; nitrates may be similarly tested for the amount of nitrogen pentoxide by fusing with three to six times the amount of the flux.

The flux is prepared by fusing over a blast a mixture of equal parts of normal sodium tungstate and tungsten trioxide. The mass is then powdered and is ready for use. L. DE K.

Qualitative Analytical Treatment of Silicates with Boric Acid. ERWIN RUPP and F. LEHMANN (*Chem. Zeit.*, 1911, **35**, 565).—Jannasch's method (Abstr., 1896, ii, 219) for the treatment of silicates with boric anhydride in their quantitative analysis is extended to the qualitative analysis of these compounds. One gram of the finely-powdered silicate is intimately mixed with 5—6 grams of crystallised boric acid, and the mixture heated by the blowpipe for twenty-five to thirty minutes in a large platinum crucible. The resulting fusion is dissolved in dilute hydrochloric acid, when at the most only a trace of a sandy residue will be left, which may be neglected. The silica is made insoluble by evaporation to dryness, the residue taken up in warm dilute hydrochloric acid, and the filtrate from the silica treated in the usual manner. It should be noted that in the presence of boric acid the alkaline earths may be partly carried down in the ammonium sulphide group; they may be removed from the precipitate by washing with hot ammonium chloride solution, in which they are soluble. T. S. P.

The Titration of Alkali Carbonates in the Presence of Alkali Hydroxides and of Bicarbonates. J. TILLMANS and O. HEUBLEIN (*Zeitsch. angew. Chem.*, 1911, **24**, 874—876).—The authors show that the errors which occur in the determination of alkali carbonates in the presence of alkali hydroxides or of hydrogen carbonates according to the ordinary method of titration with an acid, using phenolphthalein and methyl-orange as indicators (compare Küster, Abstr., 1897, ii, 74; Lunge, Abstr., 1897, ii, 285, and Lunge and Lohhöfer, Abstr., 1902, ii, 105), are due to the loss of carbon dioxide, which escapes from the solution without combining with the carbonate to form hydrogen carbonate. The error can be eliminated by carrying out the phenolphthalein titration in a flask, which, after the addition of each lot of acid, is firmly stoppered and well shaken in order that the carbon dioxide may be completely absorbed by the liquid.

Good results may also be obtained by first determining the alkalinity of the solution with methyl-orange as indicator, adding the quantity of acid so determined to a fresh portion of the solution, and then titrating the carbon dioxide set free with sodium hydroxide and phenolphthalein in a stoppered flask, as above. The change from colourless to red is much sharper than the reverse change from red to colourless. T. S. P.

Assay of Silver by the Touch Stone. ALBERT STEINMANN (*Ann. Chim. anal.*, 1911, **16**, 165—167).—When applying the touch stone the metallic streak is treated with one or other of the various liquids that have been suggested, and from its action it is possible to judge the percentages of silver actually present.

The following liquid is recommended: 40 c.c. of nitric acid (D 1·27), 50 c.c. of glacial acetic acid, 50 c.c. of water.

It is recommended that the silver ware to be tested should be thoroughly polished; the streaks should be long and powerful, and the acid should be allowed to act until the streak becomes yellowish-brown, when it is instantly removed with a piece of blotting-paper. In the case of alloys containing zinc or cadmium, special comparative tests should be made. L. DE K.

Study of the Factors Influencing the Systematic Qualitative Estimation of Barium. LOUIS J. CURTMAN and EDWARD FRANKEL (*J. Amer. Chem. Soc.*, 1911, **33**, 724—733).—In ordinary systematic qualitative analysis it is impossible to detect small quantities of barium (up to 50 mg. in a 1 gram sample) by ammonium carbonate, owing to losses which occur at various stages.

It has been found that in the analysis of a solution containing 100 mg. of barium in 100 c.c., 1·4 mg. are lost in the precipitation of a typical metal of the copper group on account of the oxidation of hydrogen sulphide to sulphuric acid, 14·0 mg. are lost by the action of ferric chloride on hydrogen sulphide, 14·7 mg. are lost owing to the absorption of carbon dioxide during the precipitation of the metals of the iron group with ammonia, 2·2 mg. are lost in the precipitation of a typical metal of the ammonium sulphide group, and 2·8 mg. in the precipitation and filtration of zinc sulphide. Further losses are due to the presence of sulphates in the reagents employed. Moreover, ammonium carbonate fails to detect as much as 10 mg. of barium in presence of ammonium salts. E. G.

Estimation of Calcium Oxide in Sugar Refinery Products. JULIUS WEISBERG (*Bull. Assoc. chim. Sucr. Dist.* 1911, **28**, 933—938).—Sidersky's process for the estimation of organically combined calcium oxide in sugar refinery products (Abstr., 1910, ii, 548) is not preferable to the old hydrotimetric process usually employed in the refineries. L. DE K.

Schneider's Contribution for the Gravimetric Estimation of Zinc. RUDOLF GRUND (*Österr. Zeitsch. Berg. Huttenw.*, 1910, **58**, 591—592. Compare *Zeitsch. anal. Chem.*, 1883, **22**, 562).—Instead of passing hydrogen sulphide into the diluted neutral solution of a zinc salt, the author recommends that 50—100 c.c. of a concentrated aqueous solution of the gas be carefully poured down the side of the beaker; this forms a zone of zinc sulphide, which is slowly precipitated in large, flocculent masses. Gaseous hydrogen sulphide is then introduced to complete the reaction, and after a period of one to two hours filtration can be effected. F. M. G. M.

Estimation of Lead in Alloys Containing Antimony and Tin. A. G. BLAKELEY and EDWIN M. CHANCE (*J. Soc. Chem. Ind.*, 1911, **30**, 518—519).—Briefly, the process is as follows: About 0·5 gram of the alloy is heated with a minimum of aqua regia or hydrochloric acid and potassium chlorate. When nearly dry, the mass is warmed with 5 c.c. of hydrochloric acid and 20 c.c. of water are added, also a few crystals of tartaric acid. Twenty per cent. sodium hydroxide solution is now added in slight excess, and then 50 c.c. of sodium hydrogen sulphide solution (1 : 2), when the whole is kept on the boiling water-bath for half an hour. The lead sulphide is then collected and washed with dilute sodium hydrogen sulphide solution (1 : 100). The filter + contents is now heated in a Jena flask with 25 c.c. of dilute nitric acid (2 : 3), 20 c.c. of sulphuric acid are added, and the mixture heated until sulphuric fumes appear and the paper is entirely carbonised. After boiling for a few minutes' longer, the contents are allowed to cool slightly, and the carbon is oxidised by adding 0·1—0·2 gram of potassium permanganate and heating again. When cold, the solution, which should be pink or green, is diluted with 50 c.c. of water and heated to boiling, and the excess of permanganate destroyed by means of sulphurous acid. When cold, 25 c.c. of alcohol are added, and the lead sulphate washed, first with 10% sulphuric acid and then once with cold water; it is unnecessary to collect all the sulphate on the filter.

The lead sulphate is dissolved in boiling solution of sodium acetate (90 grams + 8 c.c. of glacial acetic acid per litre), and the solution, which should not be turbid (absence of bismuth), is neutralised with sodium hydroxide with phenolphthalein as indicator, and the pink colour is then again discharged with acetic acid. Ten c.c. of 10% potassium dichromate are added, and the liquid boiled for a few minutes. The lead chromate is washed with hot solution of sodium acetate (50 c.c. of cold saturated solution per litre), and then dissolved in cold dilute hydrochloric acid (1 : 2). The chromic acid liberated, which represents the lead, is then estimated by adding 2 c.c. of 50% potassium iodide solution and titrating with *N*/10-sodium thiosulphate, with starch as indicator; it is advisable to standardise the thiosulphate on pure lead foil, using 0·3 gram of the same, and operating as directed.

A slight modification of the process is described for use when a considerable amount of bismuth is present, but below 1% it does not affect the accuracy of the method. L. de K.

A New Method for Determining Copper in Pyrites or Burnt Pyrites. W. N. Iwanoff (*Chem. Zeit.*, 1911, **35**, 531).—Three grams of finely-powdered pyrites or burnt pyrites are intimately mixed with an equal weight of reduced iron, the mixture put into a glass tube, closed at one end and 7 cm. long and 1 cm. diameter, covered with a layer of reduced iron, and heated to a dull red heat for a few minutes. The hot tube is put into a conical flask, cracked by the addition of water, and the mass digested with hydrochloric acid until all the iron has dissolved. The copper is then precipitated with hydrogen sulphide, the precipitate collected, dissolved in nitric acid, and iron, etc., precipitated with ammonium hydroxide The copper in the filtrate is then determined electrolytically.

It is claimed that the method is more accurate and much more rapid than other methods. T. S. P.

Volumetric Estimations of Mercury Based on the Reduction to Metal. F. Reinthaler (*Chem. Zeit.*, 1911, **35**, 593—595).—Of the various methods proposed, the author prefers that of Feit with a slight modification. The solution, which should contain the metal as mercuric chloride or nitrate, is neutralised as far as possible with sodium hydroxide, and a definite volume of ordinary *N*/10-arsenious acid is added. The whole is then heated on the water-bath in a current of washed carbon dioxide, with frequent shaking, until the reduction to metal is complete, which usually takes from half an hour to an hour and a-half. The deposit should form a fine dark grey, mobile powder without a green shade. When cold, the excess of arsenious acid is titrated as usual with *N*/10-iodine; the mercury now present in numerous globules does not interfere, as it does not act on free iodine for a long time. L. DE K.

Analysis of Ferrotitanium Alloys Rich in Silicon. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 877).—Ferrotitanium alloys rich in silicon (12%) are not readily taken up by fusion with potassium hydrogen sulphate. One of the two following methods of treatment is recommended: (1) The alloy is roasted in a platinum crucible, the oxides evaporated down once with a few c.c. of hydrofluoric acid, and then submitted to fusion with potassium hydrogen sulphate. The fused mass then dissolves readily in not too dilute hydrochloric acid. (2) The roasted oxides are fused with sodium carbonate and nitrate in a platinum crucible, and the mass dissolved in the crucible with nitric acid. After removal of the crucible, complete solution, with the exception of the silica, is obtained in a few seconds by the addition of hydrochloric acid. Sulphuric acid is then added, and the whole evaporated until fumes appear, after which the residue is warmed with somewhat diluted hydrochloric acid until all the sulphates are dissolved; the solution is made up to a known volume, and the titanium determined in an aliquot portion after filtering off silica and removing any platinum.

The titanium and iron are best determined by Bornemann and Schirmeister's method (this vol., ii, 231). The carbon cannot be determined by direct combustion in oxygen, even when the alloy is mixed with lead peroxide; the alloy must first be treated in a current of chlorine, and then burnt in oxygen. The silicon is determined after taking up the alloy according to the second of the methods described above. T. S. P.

Application of the "Glow Reaction" to the Qualitative Detection of the Platinum Metals. LOUIS J. CURTMAN and P. ROTHBERG (*J. Amer. Chem. Soc.*, 1911, **33**, 718—724).—The following method of detecting metals of the platinum group is not so delicate as the potassium iodide test, but is recommended on account of its simplicity and the rapidity with which it can be carried out.

A piece of asbestos paper (about 3 mm. thick) is alternately dipped into the solution under examination and heated, until about 0·2 c.c. has been absorbed. The moist paper is heated to redness in the Bunsen flame, and while still hot is introduced into a mixture of illuminating gas and air issuing from a Bunsen burner. If platinum is present, the paper will glow for some time, and the glow can be renewed by again heating the paper and holding it in the stream of gas.

The test is sensitive to 0·002 mg. of platinum, 0·0005 mg. of palladium, 0·0009 mg. of rhodium, and 0·005 mg. of iridium, and is not interfered with to any great extent by the presence of other substances. Osmium and ruthenium do not respond to the test, owing, probably, to the volatilisation of the salts of these metals under the conditions of the experiment. E. G.

Judging Wines by the Low Alkalinity of the Ash. W. T. Baragiola and P. Huber (*Chem. Zentr.*, 1911, i, 1256; from *Mitt. Lebensmittelunters. Hyg.* 1, 158—169).—The authors have arrived at the conclusion that a low alkalinity number of the ash of wines should not be used for judging the quality of the sample unless the cause of the fall is known. It should, therefore, be ascertained whether there is any unusual amount of sulphate or chloride and phosphate present, which, of course, would lower the % of alkalinity in the ash without, however, causing a decreased alkalinity per litre of the wine.

L. de K.

Physico-chemical Analysis of Wine According to Dutoit. E. Philippe and H. Duperthuis (*Chem. Zentr.*, 1911, i, 1255; from *Mitt. Lebensmittelunters. Hyg.* 1, 111—138).—The authors have investigated the physico-chemical process proposed by Dutoit and Duboux (Abstr., 1910, ii, 552), which, except in the case of the alcohol, is based on the determination of the electrical conductivity, and think it offers no particular advantage, except in the estimation of the total acidity, as the neutralisation curve enables one to form a fair idea as to the quality of the sample. L. de K.

Estimation of Alcohol in Wine by means of the Critical Temperature. H. Duperthuis and E. Philippe (*Chem. Zentr.*, 1911, i, 1255—1256; from *Mitt. Lebensmittelunters. Hyg.* 1, 188—193).—The process given by Duboux and Dutoit (Abstr., 1908, ii, 136) is recommended, the results agreeing with those of the usual specific gravity process. As regards the mixtures employed by those writers, the authors prefer the mixture aniline and alcohol to the mixture nitrobenzene and alcohol. L. de K.

Assay of Sweet Spirits of Nitre. Otto Herting (*Pharm. Zeit.*, 1911, 56, 423).—In a stoppered 100 c.c. flask are placed 10 c.c. of water, 5 c.c. of a saturated solution of potassium chlorate, then 5 c.c. of the sample, and also 5 c.c. of 10% nitric acid. After shaking frequently for thirty minutes, the chloride formed in the reaction is estimated by adding 10 c.c. of *N*/10-silver nitrate and titrating the excess of silver by means of *N*/10-potassium thiocyanate, with iron-alum as indicator. One c.c. of silver solution = 0·0255 gram of ethyl nitrite. If % by weight is desired, the density of the sample should be ascertained. L. de K.

Assay of Sweet Spirits of Nitre. F. Dietze (*Pharm. Zeit.*, 1911, 56, 444—445).—A question of priority. The method recommended by Herting, based on the reduction of potassium chlorate by ethyl nitrite in presence of nitric acid (preceding abstract), was published by the author in 1897 (*Pharm. Zeit.*, 1897, 388), and has also been approved of by other writers. L. DE K.

Estimation of Glycerol. M. WAGENAAR (*Pharm. Weekblad*, 1911, **48**, 497—502).—A modification of Muter's process which is based on the solubility of cupric hydroxide in aqueous potassium hydroxide in the presence of glycerol; the copper is then titrated with potassium cyanide.

The author, however, states that the amount of glycerol is not strictly proportional to the cupric hydroxide dissolved, but that this depends on the degree of alkalinity and dilution. The new process is briefly as follows: 50 c.c. of glycerol solution (containing at most 1·2 gram of real glycerol) are placed in a tall stoppered cylinder and 25 c.c. of 4*N*-sodium hydroxide and 25 c.c. of *N*-copper sulphate are added, and the whole is thoroughly shaken. When the excess of cupric hydroxide has settled, 25 c.c. are pipetted off, 5 c.c. of 30% potassium iodide solution and 10 c.c. of 4*N*-sulphuric acid are added, and the copper is titrated with *N*/10-thiosulphate. When testing fats or fatty mixtures, a sufficiency is saponified with *N*/2-alcoholic potassium hydroxide, and then rendered acid with *N*/2-acid to Congo-red. After boiling off the alcohol, the fatty acids are removed by filtration, and the aqueous liquid is made up to 50 c.c. and treated with alkali and copper solution as directed. Reference is now made to an empirical table giving the amount of glycerol corresponding with from 1 to 30 c.c. of thiosulphate. The process may no doubt be applied to other substances having the property of forming alkaline copper solutions, such as sugar, mannitol, tartaric acid, etc. Each of these, of course, requires a separate empirical table. L. DE K.

Fehling's Solution. W. ROSENKRANZ (*Zeitsch. Ver. deut. Zuckerind*, 1911, 426—434).—The influence of the amount of alkali hydroxide in Fehling solution on the reduction is discussed; further, the effect of boiling the Fehling solution and the sugar under a condenser and so preventing concentration is shown to be considerable. Boiling under a condenser at various pressures has but little effect. The presence of sucrose increases the apparent reduction of invert sugar solutions, both under reduced pressure and at the ordinary pressure. Fehling's solution decomposes at 109·6° at a pressure of 1·4 atmospheres.

E. F. A.

Jolles's Polarimetric Estimation of Sugars based on the Use of Alkali. BRUNO BARDACH and SIEGMUND SILBERSTEIN (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 540—543).—A slight modification of Jolles's process (this vol., ii, 74).

A measured volume of the sugar solution is diluted with *N*-sodium hydroxide until the alkalinity of the liquid becomes decinormal. The liquid is polarised, a measured quantity introduced into a narrow beaker, and kept for twenty hours without interruption in a thermostat at 36—39°. The solution is then allowed to cool, the original volume is restored, and another polarisation is taken. Defecation with basic lead acetate is unnecessary. As the polarisation of dextrose is not entirely destroyed, but becomes slightly reversed, the following formulæ should be employed. In sucrose–dextrose mixtures the polarisation value (D) of the dextrose is found from $D = A - B - 0{\cdot}25$, and the value (S) for sucrose from $S = B + 0{\cdot}25$, A being the value before and B the value after the action of the alkali. L. DE K.

Estimation of Sugar and of Phosphoric Acid. Preparation of Methylglycuronic Acid. IVAR BANG (*Biochem. Zeitsch.*, 1911, **32**, 443—445).—*The Preparation of the Copper Solution in the Author's Sugar Titration Method.*—The thiocyanate is made by first dissolving the carbonate in water, and then adding the other constituents; 166·67 grams of copper sulphate are dissolved in 1 litre of water, and 150 c.c. of this solution are then added to the salt solution.

Estimation of Phosphoric Acid by Neumann's Method.—The phosphomolybdate precipitate is dissolved in excess of $N/2$-potassium hydroxide solution. Instead of getting rid of the ammonia by heating, it is converted into hexamethylenetetramine by formaldehyde, and the excess of alkali hydroxide can then be estimated by direct titration.

The Preparation of Menthylglycuronic Acid.—The urine of rabbits, after administration of menthol, is treated with ammonium sulphate to half saturation the mixture heated, and filtered. The ammonium glycuronate separates almost quantitatively on cooling in a pure condition. S. B. S.

Iodometric Estimation of Sugar in Urine. ALBERT FERNAU (*Chem. Zentr.*, 1911, i, 1012; from *Zeitsch. Allg. Österr. Apoth. Ver.*, 1911, **49**, 85—86).—The urine is diluted if it contains more than 0·8% sugar. The diluted solution is then treated with the two Fehling's solutions (I, copper sulphate; II, rochelle salt and sodium hydroxide), and heated for two minutes. It is then acidified by 25% sulphuric acid, and potassium iodide and starch are added. By the amount of iodine liberated by excess of the copper in acid solution, which is titrated by thiosulphate solution, the amount of copper reduction which has taken place can be determined. S. B. S.

Titration of Diabetic Sugar. IVAR BANG (*Pharm. Zeit.*, 1911, **56**, 436).—The author's method (titration with copper hydrogen carbonate and hydroxylamine, Abstr., 1907, ii, 136) may be safely applied to urines, and is recommended for that purpose by Hammarsten and other writers. The reason that some analysts have failed to get correct results with urines is probably due to the fact that their samples were not sufficiently diluted, as the process becomes untrustworthy when 10 c.c. of urine contain more than 0·06 gram of dextrose. L. DE K.

Estimation of Sugar and of Calcium in the Residues from Sugar Purification. LÉON LINDET (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 776—778).—A preliminary communication in which the author suggests that phenol should be added to decompose the calcium sucrate, the sugar then being determined by means of the polarimeter. E. J. R.

The Detection of Sucrose in Wine by Rothenfusser's Process. F. SCHAFFER and E. PHILIPPE (*Chem. Zentr.*, 1911, i, 1256; from *Mitt. Lebensmittelunters. Hyg.* 1, 303—311).—Rothenfusser's test for added sucrose in wines (blue coloration with diphenylamine, Abstr., 1910, ii, 463) is not characteristic for sucrose, but is also given by other saccharine matters, and cannot, therefore, be employed. L. DE K.

Detection of Sucrose in Wine, White Beer, etc. S. ROTHENFUSSER (*Zeitsch. Nahr. Genussm.*, 1911, 21, 554—555).—A provisional reply to Schaffer and Philippe (see preceding abstract). The author states, however, that minimal quantities of lævulose interfere with the diphenylamine test for sucrose. L. DE K.

Valuation of Turpentine Oils. PETER KLASON (*Chem. Zeit.*, 1911, 35, 537—539).—The value of turpentine oil in practice depends on the rapidity with which it absorbs oxygen, and the author has devised a method of determining the relative values of turpentine oils from this point of view, depending on the oxidation of cymyl mercaptan by the peroxide formed in the turpentine oil.

Fifty c.c. of the oil are distilled in a current of carbon dioxide, and 10 c.c. of the distillate are set aside in an open beaker in diffused light during twenty-four hours. Five c.c. of this oxidised oil are placed in a 30 c.c. flask with a like quantity of cymyl hydrosulphide solution (5% by volume) in alcohol. This quantity of cymyl mercaptan requires 13·3 c.c. of *N*/10-iodine solution when titrated by Klason and Carlson's method (Abstr., 1906, ii, 255). The flask is filled completely with alcohol, corked, and set aside during twenty-four hours. At the end of this time the contents are titrated with *N*/10-iodine solution, more alcohol being added if necessary to maintain complete solution. The difference between the number of c.c. of *N*/10-iodine used and 13·5 is proportional to the oxygen-absorbing capacity of the oil. For French turpentine oil, it is about 5 c.c., for "pine wood oil" about 3 c.c., and for "resin spirit," 1·5 c.c.

T. A. H.

Analysis of Camphor. WILHELM LENZ (*Arch. Pharm.*, 1911 249, 286—298).—In connexion with an examination of camphor oil and crude camphor produced in German East Africa, the author has investigated methods for the assay of camphor, and finds that the melting point, quantity of non-volatile residue, yield of oxime, and solubility in hydrochloric acid are useful criteria in gauging the purity of samples.

The camphor oil when kept during fourteen days at 0° deposited 4·4% of camphor. The moisture in the crude camphor was determined by dissolving a known weight of the camphor in light petroleum, separating the water in a centrifugal machine, and measuring its volume. Pure camphor melted at 178·75°. Synthetic camphor had $[\alpha]_D$ +1·76° in benzene, and this low rotation served to distinguish it from natural *d*-camphor ($[\alpha]_D = +41·87°$ in benzene under the same conditions). The impurities in the crude camphor examined caused it to have a slightly higher dextrorotation, $[\alpha]_D = +42{\cdot}17°$, than pure *d*-camphor. The non-volatile residue was determined by heating 5 grams of the camphor on the water-bath until the residue was odourless. The time required varied from eleven to sixteen hours, and the residue left varied from 0·02% in the case of good commercial Japanese camphor to 0·298% for the East African product. The yield of oxime obtained varied from 89% for synthetic camphor to 93% for good commercial camphor. Bohrisch's test (*Pharm. Zentr.-h.*, 1907, **28**, 527, 777) gave with the natural camphors reddish colorations changing to bluish-violet or bluish-green, whilst with synthetic camphor it gave a yellow coloration with a trace of vermilion-red. Good commercial camphor was completely soluble in concentrated hydrochloric acid, but synthetic camphor and the crude African camphor left noticeable quantities of undissolved matter with this solvent (compare Istrati and Zaharia, Abstr., 1899, i, 225).

T. A. H.

Estimation of Free Acid in Fats. EYVIND BÖDTKER (*Chem. Zeit.*, 1911, **35**, 548).—Five to 15 grams of fat are melted if necessary, and shaken in a stoppered bottle with 25 c.c. of alcohol, 50 c.c. of water, 2 or 3 drops of phenolphthalein are added, and the mixture titrated with *N*/10-sodium hydroxide to a deep red coloration. After shaking, the excess of alkali is titrated back with *N*/10-hydrochloric acid. The suggestion of Loebell to titrate in an alcoholic benzene solution of the fat is criticised as impossible.

E. F. A.

Estimation of Volatile Fatty Acids in Fæces. ROBERT S. MCCAUGHEY (*Zeitsch. physiol. Chem.*, 1911, **72**, 140—150).—A method is described, the principle of which is to obtain an alcoholic extract of the fæces, and this is distilled in a vacuum with steam after the addition of phosphoric acid. The distillate is titrated with decinormal sodium hydroxide. Previous results obtained by other methods are not trustworthy.

W. D. H.

Estimation of Tartaric Acid in Tartrates and Wines by Precipitation as Calcium Racemate. ANDRÉ KLING (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 893—903).—The process is briefly as follows: To the solution of the tartrate (which in natural products is always dextrorotatory) is added a sufficiency of lævorotatory alkali tartrate, thus forming a racemate which is then precipitated by addition of acid calcium acetate. The precipitate is washed with cold water and dissolved in boiling 4% hydrochloric acid, from which it is then reprecipitated by boiling with an excess of acid sodium and calcium acetate; any lævorotatory calcium tartrate contained in the racemate is thus got rid of.

When cold, the precipitate is washed and dissolved in boiling dilute sulphuric acid, and, while boiling, titrated with standard potassium permanganate which has been checked against tartaric acid. The result is, of course, divided by two.

L. DE K.

Rapid Method of Estimating Uric Acid in Urine. P. P. PIZZORNO (*Boll. Chim. Farm.*, 1911, **50**, 237—238).—A quantity of *N*/20-iodine solution is added to the urine (previously boiled and decolorised with animal charcoal), and the excess of iodine is estimated with thiosulphate. The difference represents the amount used in oxidising the uric acid to alloxan and urea. If the urine contains solid uric acid, this is brought into solution by adding sodium carbonate. Albumin is removed by acidifying the urine with acetic acid, adding sodium chloride, and boiling for half an hour.

R. V. S.

Assay of Bismuth Salicylate. HUBERT CARON and D. RAQUET (*Ann. Chim. anal.*, 1911, **16**, 177—179).—The author proposes the following process for the detection and colorimetric estimation of bismuth oxynitrate in commercial bismuth salicylate: 0·5 gram of the sample is boiled for ten minutes with 50 c.c. of *N*/10-sodium hydroxide, and after diluting to 100 c.c. the solution is filtered and 3, 10, or even 50 c.c. (according to the nitrate supposed to be present) are evaporated to dryness. The residue is well mixed with 1 c.c. of pure sulphuric acid and 10 c.c. of water, and then 10 c.c. of ammonia are added. Owing to the action of the nitric acid on the salicylic acid which is also present, a nitro-derivative is formed which dissolves in ammonia with a yellow colour. The colour is then matched with that obtained from a mixture containing a known weight of sodium nitrate.

L. DE K.

Schardinger's Milk Reaction. W. RULLMANN (*Biochem. Zeitsch.*, 1911, **32**, 446—472).—Germ-free, and germ-containing unheated milk, with thermostabile substances, both in combination and alone, decolorise Schardinger's methylene-blue–formaldehyde reagent in a few minutes at 45—50°. The aldehyde can be substituted by formic acid in equivalent quantity, but the reaction takes longer. The decolorisation in heated milk is due to thermostabile substances alone. The age of the germ-free milk exercises no influence on the reaction. If sodium hydroxide, ammonia, or phosphate is added to sterilised milk, the reaction is hastened, especially if lactose is added simultaneously; the latter alone exerts no action. Raw, pasteurised, and sterilised milk behave differently with regard to the decolorisation time. This difference may be partly due to a change in the inorganic constituents produced by heat, as well as to the injury to the enzymes. The author discusses the value of the Schardinger and other reactions for discriminating between raw and heated milk.

S. B. S.

Colour Reactions of Aromatic Aldehydes and their Application in the Analysis of Spirits. THEODOR VON FELLENBERG (*Chem. Zentr.*, 1911, i, 1254—1255; from *Mitt. Lebensmittelunters. Hyg.* 1, 311—350. Compare Abstr., 1910, ii, 805).—In addition to the higher alcohols, the terpenes which occur particularly in rum, but less in cognac, also give the reaction with salicylaldehyde and sulphuric acid. Aldehydes and acetals also give the test; the destruction of these three series is carried out by boiling with *N*/10-silver nitrate and *N*/10-potassium hydroxide; acetals should be first hydrolysed with sulphuric acid. The results of the investigation show that Komarowsky's colour reactions occur with all unsaturated substances, and also with those that are converted into unsaturated compounds by heating with sulphuric acid; unsaturated substances in which the CO_2H-group compound is adjacent to the double bond form an exception. The reaction also occurs with aldehydes and phenols in which the para-position is not substituted. Phenols then form colouring matters of the rosolic acid type, whilst alcohols give the reaction because they are converted into olefines, which then react. The reaction is given by all the aromatic aldehydes; salicylaldehyde is preferable to the others, as it, apparently, does not react with methyl and ethyl alcohols. By treatment with sodium hydroxide, the acetals, aldehydes, and terpenes are not always completely got rid of, but addition of silver nitrate causes their complete removal.

L. DE K.

Detection of Traces of Hydrogen Cyanide. G. DRUCE LANDER and A. E. WALDEN (*Analyst*, 1911, **36**, 266—270).—The authors have found that extremely dilute solutions of hydrogen cyanide (0·00002 gram, or less, per c.c.) may, after addition of alkali, be boiled down without suffering decomposition, and recommend the following test:

To the solution (or distillate) are added 2 drops of 10% sodium hydroxide solution, and the liquid is evaporated, finally in a test-tube, nearly to dryness. One drop of 2% ferrous sulphate solution is added, and after ten or fifteen minutes 2 to 3 drops of hydrochloric acid, when the whole is warmed gently and then cooled. A blue or bluish-green colour shows the presence of hydrogen cyanide. The process is quite equal in delicacy to (perhaps superior to) the picrate test.

L. DE K.

Estimations with Mercuric Nitrate. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1911, **249**, 253—259).—The method suggested by Cohn (Abstr., 1902, ii, 50) and applied by Rupp and Krauss (*ibid.*, 475) has been tried as a general method for the estimation of cyanides and haloid salts, by adding excess of standard mercuric nitrate and titrating back with ammonium thiocyanate, in presence of iron alum and nitric acid. Good results were obtained with hydrocyanic acid, alone or in presence of benzaldehyde cyanohydrin, cyanides, bromides, and iodides, including ferrous iodide in the pharmacopœial "syrup," but not with chlorides.

T. A. H.

Assay of Calcium Cyanamide ("Kalk Stickstoff"). R. MONNIER (*Chem. Zeit.*, 1911, **35**, 601—602).—*Estimation of Nitrogen Present as Cyanamide.*—One gram of the sample is mixed with 100 c.c. of water and stirred for two and a-half hours; 25 c.c. of the solution are evaporated in a dish, with addition of 10 c.c. of formic acid, to near dryness; the residue is made up with water to 25 c.c., 10 c.c. of this are introduced into the ureometer, and the nitrogen evolved by hypobromite from the urea generated is measured. A check experiment is then made with 10 c.c. of a urea solution containing about the same weight of urea as that found in the solution of the sample.

Estimation of the Total Nitrogen.—Concordant results are obtained by conversion into ammonia by heating 0·5 gram of the substance with 30 c.c. of pure sulphuric acid and 1 gram of anhydrous copper sulphate; addition of potassium sulphate, phosphoric oxide, or metallic mercury offers no advantage in this case. When, however, treated according to the process used for nitrates (heating with sulphuric acid with addition of salicylic acid and sodium thiosulphate, or zinc dust), decidedly higher results are obtained.

It is therefore certain that "Kalk Stickstoff" contains its nitrogen in at least three different forms. A specimen analysed by the author showed 21·5% of total nitrogen by the salicylic acid method, and 20·5% by the copper sulphate method; 18·98% were present as cyanamide.

L. DE K.

Improvement of the Micro-sublimation Process and the Detection of Arbutin in Plants. O. TUNMANN (*Ber. Deut. pharm. Ges.*, 1911, **21**, 312—319).—Glucosides such as arbutin cannot be sublimed, and consequently cannot be detected in plants by heating a small portion of the ground plant and applying ordinary microchemical methods to the sublimate. Arbutin is, however, readily hydrolysed by emulsin or by dilute hydrochloric or sulphuric acid, and the mixture when heated carefully on an object-glass gives a sublimate of quinol, which may be identified by its crystalline form and reactions, such as that with ammonia. The presence of arbutin in bearberry leaves and other plants can be demonstrated in this way by moistening the ground material with dilute hydrochloric acid, and after a few minutes heating it on an object-glass and collecting the sublimate of quinol on a second object-glass.

T. A. H.

Estimation of Cantharidin in Cantharides and its Tincture. HERMANN EMDE (*Arch. Pharm.*, 1911, **249**, 259—285).—This paper gives a critical résumé of work done independently by A. KNEIP, N. NEY, and F. REIMERS in a competition for the Hagen-Bucholz prizes of the Deutscher Apotheker-Verein in 1909–10. It gives a résumé of the chief methods so far devised for the estimation of the "total," "free," and "combined" cantharidin in cantharides, including those of Léger (Abstr., 1903, ii, 517), Singh (Abstr., 1907, ii, 994), Walbum (Abstr., 1909, ii, 839), and Greenish and Self (*Pharm. J.*, 1907, p. 324), with results obtained by the three workers named by the use of these various methods. As a result of his work Kneip suggests a new method in which the cantharides, acidified with hydrogen chloride in alcohol, is extracted with a mixture of light petroleum and benzene in a Soxhlet apparatus, and the extract so obtained freed from fat and other impurities by washing with a mixture of alcohol and light petroleum. This gives the "total cantharidin," the quantity "free" being estimated in like manner without acidifying the crude drug. Ney suggests a modified form of the Panchaud-Siegfried process, and Reimers a combination of the method devised by Fromme with that of the fifth German Pharmacopeia.

In an appendix to the paper the results of determinations by Kneip and by Reimers of moisture, fat, and ash in commercial cantharides are given. T. A. H.

A Reaction for Caulophyllin. JOHN F. H. GILBARD (*Analyst*, 1911, **36**, 270—271).—Five c.c. of an alcoholic extract obtained by digesting 0·1 gram of caulophyllin in 25 c.c. of 80% alcohol are filtered and evaporated on the water-bath in a flat porcelain capsule. The residue is taken up with 1 c.c. of water, and broken up with a flat-headed rod. Two c.c. of strong sulphuric acid are then added slowly and the mixture well stirred. An intense purple-blue colour is produced within five minutes; sometimes the colour is more of a reddish-purple. When testing a mixture of drugs, for instance, a compound pill, 0·1 gram of the pill is thoroughly extracted with 80% alcohol, the filtrate is evaporated, and the residue tested as directed. The extracts of many other drugs do not give the reaction. L. DE K.

Estimation of Urea in Urine. VALDEMAR HENRIQUES and S. A. GAMMELTOFT (*Chem. Zentr.*, 1911, i, 1450; from *Skand. Arch. Physiol.*, 1911, **25**, 153—168).—The process given by Levene and Meyer (defecation with phosphotungstic acid, and conversion of urea into ammonia by heating with sulphuric acid in an autoclave: Abstr., 1909, ii, 709) is recommended. L. DE K.

Identification of Veronal. ARMAND JORISSEN (*J. Pharm. Chim.*, 1911, [vii], **3**, 478—481).—The author suggests an extension of the test described in the Swiss Pharmacopœia for the identification of "veronal" (diethylbarbituric acid).

Three grams of potassium hydroxide are melted in a nickel capsule, and to this 3 grams of "veronal" are gradually added and the heating continued during ten minutes. The cold "melt" is dissolved in water (10 c.c.). This liquid gives (1) the Prussian blue reaction for cyanides, (2) carbon dioxide on addition of an acid, and the acidified solution on extraction with ether yields, after evaporation of the ether, oily drops having an odour of rancid butter and giving a wine-red coloration with ferric chloride. When "veronal" is mixed with quicklime and the mixture is gently heated on platinum foil, inflammable vapours are evolved, and the residue acquires a cinnabar-red coloration. T. A. H.

Identification of Cocaine and Some Cocaine Substitutes. FRANCIS J. SEITER and FREDERIC ENGER (*Amer. J. Pharm.*, 1911, **83**, 195—201).—The tests are based on the fact that a 2% solution of cocaine hydrochloride yields characteristic crystals on adding a 1% solution of either gold chloride, platinum chloride, or potassium permanganate; a 5% solution of chromic acid is also a valuable microchemical reagent. For the exact form of the crystals of the gold, platinum, and permanganate cocaine compounds, the micrographs in the original article should be examined, and for further details the tabular review of the microscopic tests should be consulted. A good chemical reagent for distinguishing cocaine and its substitutes is found in chlorine water. To 1 c.c. of a 1% solution of the alkaloid are added 2 c.c. of strong chlorine water. Cocaine gives no precipitate; α-eucaine, a milky turbidity; β-eucaine, a dense white turbidity; stovaine, a light milky turbidity; holocaine, a light yellow turbidity; acoine, a maroon precipitate and claret solution, but euphtalmine gives no reaction. L. DE K.

The Permanganate Test for Cocaine. FRANCIS J. SEITER (*Amer. J. Pharm.*, 1911, **83**, 265—268).—The author has improved this test and now operates as follows: To one c.c. of cocaine hydrochloride solution is added one drop of 25% sulphuric acid and 1 c.c. of saturated potassium permanganate solution. After some time, a drop of the liquid is removed to a slide, the cover glass is adjusted, the excess of liquid removed, and a drop of water drawn under the cover glass by means of a piece of filter paper placed on the opposite side. The slide is then examined under the microscope for the characteristic violet-red, rectangular plates of cocaine permanganate. One part of cocaine may thus be detected when dissolved in 3000 parts of water.

Accompanying natural alkaloids and also cocaine substitutes are at once oxidised with the exception of α-eucaine and β-eucaine. The α-compound yields violet-red crystals resembling ammonium magnesium phosphate in highly diluted solutions (limit 1 : 5000), but leafy crystals in 1% solutions, whereas the β-compound gives, in 1% solutions, minute violet-red globules which do not crystallise when kept. L. DE K.

Direct Estimation of Creatine in Pathological Urine. G. STANLEY WALPOLE (*J. Physiol.*, 1911, **42**, 301—308).—The pink colour given in alkaline solution by creatine and not by creatinine when a trace of diacetyl (dimethyl diketone) is added can be utilised for the colorimetric estimation of creatine in urine. The method is simple, rapid, and fairly accurate in cases where the Folin method was used as a control. W. D. H.

Polarimetric Estimation of Nicotine in Tobacco Extract. JOSEF VON DEGRAZIA (*Chem. Zentr.*, 1911, i, 1085; from *Fach. Mitt. österr. Tabakregie*, 1910, 87—90).—Thirty grams of the sample are mixed with 3·5 grams of calcium oxide and 10 c.c. of water, and the nicotine liberated is rapidly distilled in a current of steam. When the weight of the distillate is six times that of the amount of extract used, the nicotine is practically all recovered. After observing the rotation of the distillate in a 20 cm. tube in a Lippich half-shadow polarimeter, the percentage of nicotine is found from the equation $P = a.G.f/g$, in which G = weight of distillate, g = weight of the extract taken, and f = the rotation constant; this varies with the temperature, and a table in the original paper should be consulted.
L. DE K.

Estimation of Nicotine in Tobacco. JOSEF VON DEGRAZIA (*Chem. Zentr.*, 1911, i, 1085—1086; from *Fach. Mitt. österr. Tabakregie*, 1910, 149—152).—Twenty grams of finely powdered tobacco are treated in a 300 c.c. flask with 7 c.c. of potassium hydroxide solution (1 : 1), a few grams of sodium chloride, and 150 c.c. of boiling concentrated brine. After distilling off rapidly, 45 c.c., the remainder of the nicotine is distilled in a current of steam until the distillate measures 100 c.c. In the case of samples very rich in nicotine, a little more distillate should be collected. After introducing the steam, the heating of the flask should be interrupted for a while so as to dilute the residue somewhat. The distillate is then weighed and polarised (see preceding abstract). L. DE K.

Estimation of Nicotine in Tobacco and in Green Plants of "Nicotiana Tabacum." R. MELLET (*Chem. Zentr.*, 1911, i, 1561; from *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 117—120).—The finely cut up material (30 grams of dry tobacco or 250 grams of the green plant) is treated with boiling water in an air-tight flask, and then allowed to cool. After twenty-four hours, milk of lime is added, the stopper is again inserted, and the contents frequently shaken for another twenty-four hours. The liberated nicotine is then distilled in a current of steam until the volume of the distillate is about three times that of the original liquid. The distillate is acidified with sulphuric acid, strongly concentrated out of contact with the air, and then shaken with ether after adding potassium hydroxide. The ethereal solution is evaporated until the vapours no longer contain ammonia, and then allowed to evaporate spontaneously. The residue is then dissolved in water and titrated with *N*/10-sulphuric acid.

A number of check experiments made by the author have shown that 0·06 gram of nicotine should be added to the amount found.

L. DE K.

Estimation of Nicotine in Tobacco Extracts. WILHELM KOENIG (*Chem. Zeit.*, 1911, **35**, 521—522).—Twenty grams of the sample are mixed in a spacious glazed porcelain dish with ignited silver sand and 4 c.c. of aqueous sodium hydroxide (1 : 1), and to the half-dry mass is added so much burnt gypsum that an almost dry powder is obtained. This is rubbed in a mortar and transferred to a 250 c.c. stoppered bottle. On to this powder is then delivered, from a pipette, 100 c.c. of toluene, and the mixture is frequently shaken during two or three hours. Thirty or 40 c.c. are then poured off and filtered, the funnel being kept covered, and the filtrate is now examined in the 20 cm. polarimeter tube. The rotation divided by 3·36 = nicotine in the 100 c.c. of toluene solution. As the volume of the toluene is, of course, augmented by the nicotine present, a slight correction should be applied as follows: $x = g. \ 100 + g/100$; $g =$ grams of nicotine in 100 c.c. of toluene solution; $x \times 5 = \%$ nicotine in sample.

For the volumetric estimation, 25 c.c. of the toluene solution are placed in a stoppered flask containing 25—50 c.c. of *N*/10-hydrochloric acid diluted with 50—75 c.c. of water. After adding 25 c.c. of ether and 4 drops of iodoeosin (1 part in 500 parts of alcohol) and thorough shaking, the excess of acid is titrated, with constant shaking, with

N/10-sodium hydroxide; 1 c.c. of acid = 0·0162 gram of nicotine; the above correction for volume is then applied.

If the polarisation test alone is wanted, 10 grams of the extract may be diluted, if necessary, with, say, 5 c.c. of water, and, after adding 2 c.c. of alkali and some 50 glass beads, the nicotine may be extracted by shaking for two to three hours with 50 c.c. of toluene.

L. DE K.

Theory and Modification of the Malaquin Test for Strychnine. GEORGES DENIGÈS (*Bull. Soc. chim.*, 1911, [iv], **9**, 537—542).—Malaquin's colour reaction for strychnine (Abstr., 1910, ii, 165) is shown to depend on the action of a trace of nitric acid on a mixture of tetrahydrostrychnine and strychnidine, produced by the action of zinc and sulphuric acid on strychnine. Other oxidising agents may be used in place of nitric acid, and the author outlines a scheme for the detection of strychnine, which involves the reduction of the alkaloid with zinc and hydrochloric acid and the application of (1) sodium nitrite and (2) bromide to different aliquot portions of the reduced liquid, the former giving a rose-red, and the latter a reddish-purple coloration. The method of applying this improved Malaquin test is described in detail in the original. T. A. H.

Estimation of Theobromine and Caffeine. C. MONTHULÉ (*Ann. Chim. anal.*, 1911, **16**, 137—138).—0·2 Gram of the mixed alkaloids is dissolved in a small quantity of ammonia and introduced into a 100 c.c. flask, when 20 c.c. of *N*/10-silver nitrate are added. Should a precipitate form, this is redissolved by further addition of ammonia. After filling the flask up to the middle with water, a drop of phenolphthalein solution is added, and the ammonia is carefully neutralised with acetic acid. After diluting up to the mark and filtering, 30 c.c. of the liquid are titrated for silver by the Charpentier-Volhard process.

If *n* represents the number of c.c. of *N*/10-thiocyanate employed, the amount of theobromine in 100 grams of the mixture would be $(10 - n) \times 16·6$ (according to Kunze and Génin).

The caffeine may be recovered by taking a further portion of the above prepared neutralised solution, evaporating to dryness on the water-bath with addition of sodium chloride, and extracting with chloroform.

L. DE K.

New Applications of Amalgamated Aluminium in Analyses. E. KOHN-ABREST (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **28**, 938—943). Amalgamated aluminium, prepared by placing aluminium turnings for three minutes in a 0·5% solution of mercuric chloride, is recommended for the defecation of solutions containing much tannin and colouring matters. The effect is due to the formation of alumina with evolution of hydrogen. L. DE K.

Lecithins ex ovo, A Characteristic Colour Reaction for them and a Change which they Always Undergo. CARLO CASANOVA (*Boll. Chim. Farm.*, 1911, **50**, 309—313).—The emulsion of lecithins is freed from alcohol, and extracted with ether. The concentrated ethereal solution is treated with 2 c.c. of ammonium molybdate, then gradually with concentrated sulphuric acid. At the surface of contact of the two liquids, a cherry-red coloration appears, which becomes green and finally intensely blue. Cholesterol and phytosterol do not give this reaction. The lecithins alter readily in air, especially in aqueous suspension, and the change is accompanied by an increase in the quantity of free acid present. Alcoholic solutions are more stable. R. V. S.

The Use of Triketohydrindene Hydrate for the Detection of Proteins and their Cleavage Products. EMIL ABDERHALDEN and HUBERT SCHMIDT (*Zeitsch. physiol. Chem.*, 1911, **72**, 37—43).—The blue colour given by this reagent with proteins (Ruhemann, Trans., 1910, **97**, 2025) is also given by peptones, and a large number of amino-acids which are enumerated. Proline, oxyproline, and pyrrolidone-2-carboxylic acid do not give the reaction; they contain an imino- instead of an amino-group. The reaction is only given by those substances which contain a free amino- and a free carboxyl group. W. D. H.

Protein Estimation, and Peptic Digestion of Protein. F. WESTHAUSSER (*Zeitsch. physiol. Chem.*, 1911, **72**, 363—373).—The Stutzer-Burnstein method, and precipitation with tannin lead usually to the same result in protein estimations, and in the separation of protein and amide (asparagine) nitrogen. The results, however, are different if the products of hydrolysis liberated by pepsin are investigated. The applicability of such methods for the analysis of fæces is also described. W. D. H.

Estimation of Gliadin. J. E. GREAVES (*J. Biol. Chem.*, 1911, **9**, 271—293).—The concentration of alcohol-soluble proteins is decreased by filtering through or shaking with animal charcoal. Carefully made asbestos filters do not produce this effect; 100 c.c. of alcohol extracts 0·05% more gliadin from 8 grams of flour than it does from twice the amount of flour, but the extraction is not complete. The strength of the alcohol is a factor of importance; 74% is the best, and this extracts more gliadin when hot. Some flours contain sufficient nitrogenous substances soluble in ether to affect the accuracy of gliadin estimations. The Kjeldahl method is more accurate, although less rapid, than the polarimeter. W. D. H.

Hippuric Acid as the Cause of the Failure of the Spectroscopic Test for Hæmoglobin in Urine. F. ALEX. MCDERMOTT (*J. Amer. Chem. Soc.*, 1911, **33**, 992—995).—The presence of hæmoglobin in urine cannot be detected by means of the absorption spectrum unless the urine is quite fresh. It has been found that if blood is introduced into normal urine, the characteristic hæmoglobin spectrum is visible at first, but the absorption bands gradually fade and ultimately disappear. It is therefore evident that normal urine contains some substance which destroys hæmoglobin.

A study of the question has shown that uric acid and carbamide do not produce any effect on the absorption spectrum of water containing a little blood, but that hippuric acid causes the bands to disappear entirely in a few minutes. If the hippuric acid is neutralised with ammonia, it no longer has the power of destroying the hæmoglobin, and the absorption spectrum remains unaffected. These results indicate that when a specimen of urine, suspected of containing hæmoglobin, has to be left for some time before the application of the spectroscopic test, it should first be rendered slightly alkaline with ammonia. E. G.

Detection of Blood by means of Leucomalachite Green. Franz Michel (*Chem. Zeit.*, 1911, **35**, 389—390).—The reagent is prepared by dissolving 1 gram of leucomalachite green in 85 c.c. of glacial acetic acid, and diluting the solution with water to a volume of 250 c.c. One drop of the solution to be tested for blood is treated with 5 drops of the reagent, and 2 drops of a 1% hydrogen peroxide solution. Should blood be present, a green coloration develops within a short time. As it is not always possible to prepare a completely colourless solution of the reagent, a control test, using only the reagent and hydrogen peroxide, should be made. The test will detect the presence of 0·001 mg. of blood. Iron rust, saliva, bile, and proteins do not give a coloration with the reagent, but pus sometimes gives a slight reaction. W. P. S.

The Estimation of Diastase in Organs. H. Schirokauer and G. G. Wilenko (*Biochem. Zeitsch.*, 1911, **33**, 275—281).—Wohlgemuth's method was employed, into which two modifications were introduced, namely, the diastase was extracted from the well ground organs by agitating with saline for one hour in a shaking machine, and by shaking the digestion mixtures three times during the course of incubation (twenty-four hours) to avoid error due to sediment formation. Muscular tissue contained the largest amount of diastase, kidneys less, and liver the least of the organs investigated. S. B. S.

Estimation of Catalase. O. Laxa (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 417—420).—An apparatus is described for estimating catalase in milk; it consists of a graduated glass tube of 20 c.c. capacity, the lower end being drawn out to form a narrow jet, whilst the upper end is fitted with a tap. A mixture of the milk to be tested and hydrogen peroxide, in the proportion of 15 c.c. of the former to 5 c.c. of the latter, is filled into the apparatus, and the volume of oxygen liberated by the action of the catalase on the hydrogen peroxide in a given period of time is ascertained; this volume is a measure of the catalytic activity of the milk. It is claimed that the apparatus yields concordant and trustworthy results. W. P. S.

Colorimetric Detection of Some Oxidising Substances of the Body. W. Loele (*Chem. Zentr.*, 1911, i, 38; from *Munch. med. Woch.*, **57**, 2414—2416).—Certain cell granules have the property of forming coloured compounds with alkaline solution of phenol, which reaction can only take place in the presence of oxidising substances. Of the α-granules and the similarly behaving granules of the α-leucocytes, of the epithelia of the salivary glands, etc., it may be said that the granules contain an amino-base and an oxidising enzyme (Schultzer's oxydase).

On exposure to the air, α-naphthol-formol solution turns first green, then blue, and finally greyish-black. The colouring matter turns red with acids, and dissolves in chloroform. When blood-serum is added, the coloration is retarded; a 10% solution of peptone, or of Liebig's meat extract, or addition of bile has the same effect. The green colouring matter obtained behaves like a lacmoid. Boiled meat extract, however, is inactive, showing that, in this case, an oxidising enzyme is present. L. DE K.

The Reactions of Van Deen and Adler. CORRADO BONGIOVANNI (*Boll. Chim. Farm.*, 1911, **50**, 201—203).—Tarugi, finding that the blue coloration with hydrogen peroxide and guaiacum or benzidine was given also by thiocyanates, has advanced the view that these reactions of blood are due to thiocyanates, which act as peroxydases, yielding peroxygenated substances which oxidise the guaiacum or benzidine. The author shows that this is improbable, because the coloration is given by chromates, small quantities of bromine and other oxidisers, so that it cannot need the presence of peroxygenated compounds. Moreover, the red solutions obtained from thiocyanates and ferric salts, which may contain a peracid, do not give the benzidine reaction. R. V. S.

Titration of "Salvarsan" with Iodine Solutions. G. OTTO GAEBEL (*Arch. Pharm.*, 1911, **249**, 241—247).—It was shown previously (this vol. ii, 448) that ordinary methods for the estimation of arsenic could not be used for "salvarsan" (diaminodihydroxyarsenobenzene hydrochloride). In the present paper the interaction of iodine with this drug is considered, and it is shown that it may be estimated by titration with iodine provided an empirical factor is used in calculating the results.

The interaction of "salvarsan" with iodine takes place in accordance with the equation $As[C_6H_3(OH)\cdot NH_2,HCl]_2,2H_2O + 4I_2 + 4H_2O = 2[AsO(OH)_2\cdot C_6H_3(OH)\cdot NH_2,HCl] + 8HI$, but in practice only 7·5 atoms of iodine are used per mol. of "salvarsan" in place of 8 as required in this reaction. This is probably due to the reversibility of the reaction. The following method of carrying out the estimation is suggested, and under these conditions 1 c.c. of $N/10$-iodine is equivalent to 0·006326 gram of "salvarsan." A quantity of an 0·2 to 0 8% solution of the drug, equal to 0·1 gram, is mixed with 1 c.c. of starch solution and titrated with $N/10$-iodine solution until a permanent blue coloration is produced. T. A. H.

General and Physical Chemistry.

Optical Properties of Some Unsaturated Ketones. FREDERICK H. GETMAN (*Amer. Chem. J.*, 1911, **45**, 539—547).—In an earlier paper (Abstr., 1910, ii, 832) the surface tensions and densities of mesityl oxide, styryl methyl ketone, styryl ethyl ketone, and benzylidenepinacolin were recorded, and it was shown that these substances are non-associated. The refractive indices, dispersions, and absorption spectra have now been determined.

The refractive indices have been measured for the *D*, *C*, *F*, and *G* lines at various temperatures. In the case of styryl methyl ketone, styryl ethyl ketone, and benzylidenepinacolin (which melt at 40·2°, 37·5°, and 39·5° respectively), several readings were taken on the supercooled liquids; when the refractive indices are plotted against the temperatures, no discontinuity is apparent at the m. p. The molecular refractions have been calculated by the Gladstone and Dale and the Lorentz-Lorenz formulæ and compared, in each case, with the values computed from the refractivities of the elements as determined by Conrady (Abstr., 1889, 661) and Brühl (Abstr., 1891, 776). The two sets of values thus obtained agree fairly closely for mesityl oxide, but for the other compounds the observed values are much higher than the calculated; this optical exaltation is ascribed by Brühl to the relative positions of the unsaturated groups in the molecule (Trans., 1907, **91**, 115; Abstr., 1908, ii, 1002). Similar large differences between the molecular dispersions and those calculated from the atomic dispersions (Brühl, Abstr., 1891, 776) are shown by all the four compounds.

The ultra-violet absorption spectra of styryl ethyl ketone and benzylidenepinacolin have been studied, and the results plotted by Baly and Desch's method (Trans., 1904, **85**, 1039). The curves thus obtained have the same general form as that of styryl methyl ketone (Baly and Schaefer, Trans., 1908, **93**, 1813). E. G.

The Origin of Spectra. FRANK HORTON (*Phil. Mag.*, 1911, [vi], **21**, 214—219).—The five distinct line spectra which are exhibited by mercury vapour under different conditions of electrical discharge (compare this vol., ii, 559) are attributed to the re-combination of remainder atoms of different "electric atomic weight" with the appropriate number of electrons to form neutral systems. These systems differ probably from the atoms of the unionised gas and represent less stable arrangements of positive ions with one or more electrons revolving round them, each system, however, being electrically neutral. The periods of these systems will depend on the arrangement of the electrons around the central positive ion. For any one system there must be several positions of equilibrium, and consequently several periods. Since a definite minimum amount of energy will be required for the production of a particular positive ion, it follows that the corresponding neutral system, and the lines to which it gives rise, will appear when the energy is increased up to that value. In this way the appearance of the distinct line spectra under altered electrical conditions can be accounted for. The fact that compounds always give banded spectra seems to indicate that these are due, not to electrons, but to systems of atomic dimensions vibrating within the molecule. H. M. D.

The Carrier and the Emission Centre of Series Lines. JOHANNES STARK (*Jahrb. Radioaktiv. Elektronik*, 1911, **8**, 231—240; *Ber. Deut. physikal. Ges.*, 1911, **13**, 405—416).—A theoretical paper in which the author maintains the correctness of the hypothesis that the line spectra are due to positive ions. The actual centres of emission and absorption are supposed to be the parts of the atoms from which valency electrons have been removed. H. M. D.

Spectroscopic Investigations in Connexion with the Active Modification of Nitrogen. I. Spectrum of the After-Glow. ALFRED FOWLER and (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1911, *A*, **85**, 377—388).—The spectrum of the after glow of pure nitrogen is described in detail, and wave-length measurements showing the series relationships of the various bands are recorded. The bands appear to fall into three groups, the first of which contains three bright bands in the red, yellow, and green, and these have been found to be identical with some of the bands in the first positive group of nitrogen.

The second group consists of a series of eleven bands in the violet and ultra-violet extending from $\lambda = 4312$ to $\lambda = 2503$; these are degraded towards the red end of the spectrum and have double heads. Other fainter series of bands of similar structure also belong to this group.

The third group consists of a series of flutings, degraded towards the more refrangible end, which correspond in every way with Deslandres' third positive group of nitrogen bands.

The effect of introducing a condenser into the discharge circuit is to reduce the intensity of the first positive bands, to intensify the second, and to abolish those of the third positive group. At the same time a new series of seven bands makes its appearance in the ultra-violet from $\lambda = 2904$ to $\lambda = 2256$. These have not been described previously, and it is suggested that they should be termed the "fourth positive" group.

When the discharge is such as to give only the line spectrum of nitrogen, there is no after-glow effect. H. M. D.

The Ultra-violet Bands of the Carbon Monoxide Spectrum. PETER WOLTER (*Zeitsch. wiss. Photochem.*, 1911, **9**, 361—387).—Wave-length measurements have been made of the bands in the ultra-violet spectrum emitted by Geissler tubes containing carbon monoxide. By means of Geissler tubes furnished with a Wehnelt cathode, as described by Konen and Jungjohann (*Physikal. Zeitsch.*, 1910, **11**, 112), the author has succeeded in obtaining spectra of high intensity with a continuous current discharge.

The wave-length data are examined in reference to Deslandres' laws, and although an approximate agreement is found, the author arrives at the conclusion that these do not afford a sufficiently accurate representation of the structure of the bands. H. M. D.

Spectra of Combustion of Hydrocarbons and of Different Metals. JEAN MEUNIER (*Compt. rend.*, 1911, **152**, 1760—1762).—A Bunsen burner supplied with hydrogen instead of coal gas can be made to give a well-defined inner cone similar to the green one shown in the ordinary way when the air supply of a Bunsen is increased. The spectrum of this cone shows lines of calcium from floating dust. The principal lines of the spectra given by different metals burning in air are mentioned. W. O. W.

Circular Double Refraction of Sodium Chlorate. GEORGES MESLIN (*Compt. rend.*, 1911, **152**, 1666—1668).—Fresnel's triprism of quartz has been imitated with sodium chlorate to ascertain whether the double refraction produced in the direction of the axis in the former case would also be exhibited by an optically active substance not doubly refracting in the ordinary way. The assemblage consisted of a prism of dextrorotatory crystals having an angle of 137°, with two lævorotatory prisms of angle 68°30′. Observations with the mercury arc showed that the yellow, green, and violet lines were doubled by the prism, the two components being circularly polarised in opposite directions. W. O. W.

Molecular Structure and Optics of Large Liquid Crystals. OTTO LEHMANN (*Ann. Physik*, 1911, [iv], **35**, 193—219).—By means of a special form of crystallisation microscope the author has examined the structure of liquid crystals of ethyl *p*-azoxybenzoate of about 1 mm. diameter. The appearances presented in ordinary and polarised light between parallel, crossed, and half-crossed nicols are illustrated and described in detail. Observations were also made with *p*-azoxyphenetole containing a little azobenzene, with *p*-azoxyanisole admixed with *p*-azoxyphenetole, resin, and oil, and with *p*-azoxyphenetole admixed with methylene iodide and resin. H. M. D.

Anomalous Magnetic Rotation Dispersion and Selective Absorption. G. J. ELIAS (*Ann. Physik*, 1911, [iv], **35**, 299—346).—Measurements have been made of the rotation dispersion for various substances which exhibit selective absorption, with special reference to the magnitude of the dispersion in the neighbourhood of the absorption bands.

Detailed results are recorded for aqueous solutions of praseodymium nitrate, neodymium nitrate, samarium nitrate, and erbium nitrate. Observations were also made with liquid air, water, aqueous solutions of potassium permanganate and cobalt chloride, and with uranium glass. The data are discussed in reference to the hypothesis put forward to account for the magnetic rotation of the plane of polarisation. H. M. D.

A Method of Optical Control for Magneto-chemical Analyses. PAUL PASCAL (*Compt. rend.*, 1911, **152**, 1852—1855. Compare this vol., ii, 91, 183, 251, 252).—From Drude's modification of the Ketteler-Helmholtz dispersion formula (*Ann. Physik*, 1904, [iv], **14**, 677) the author deduces the simplified expression :

$$N = 1841 \times 10^{-14}.Mr_1r_2(1/\lambda_1^2 - 1/\lambda_2^2)/d(r_1 - r_2),$$

in which M is the molecular weight, d the density of a substance having refractive index n, λ_1 and λ_2 are the two wave-lengths for which n has been measured, whilst $r = n^2 - 1 + k\lambda^2$. N is found to be nearly equal to the sum of the valencies of the atoms composing the molecule, and its difference from this number, Δ, when not zero, is shown to be closely connected with the constitutive properties of the substance. Δ has been determined for several hydrocarbons and their halogen derivatives, and from the results conclusions have been arrived at concerning the number of electrons influencing n, which agree closely with those previously deduced from magnetic measurements.

Generally speaking, ethylenic linkings and ring-formation diminish the number of active electrons. Benzenoid hydrocarbons behave optically and magnetically as though no double linkings are present. Halogens diminish the number of electrons active in the optical sense, and, except in the case of fluorine, they also produce a diminution in diamagnetism. According to Drude's electronic theory of light the optical effect is due to mutual saturation of supplementary valencies, and the same explanation has already been adopted by the present author to account for the diamagnetic deficits in halogen compounds.

W. O. W.

Nature of the Photochlorides of Silver and their Potential in Light. KONRAD SICHLING (*Zeitsch. physikal. Chem.*, 1911, **77**, 1—57).—The preparation of photochlorides of silver containing silver chloride and amorphous silver in varying proportions is described. From the results of solubility and of potential measurements the conclusion is drawn that the photochlorides are solid solutions of silver chloride and amorphous silver. The "half chloride," Ag_2Cl, is doubtless present, but is not a predominant component of the system. It is probable that colloidal silver and silver chloride are miscible in all proportions. There is a definite region of stability of the photochlorides towards crystalline silver and silver chloride.

In the first experiments on the influence of light on the potential of the photochlorides, the latter were absorbed in gelatin, but later it was found more advantageous to use colloidal silicic acid as the absorbing agent. Platinum net was used as electrode, platinum chloride solution as electrolyte, and the potentials were measured against the silver/silver chloride electrode, the latter being kept in the dark. The Uviol lamp and the Nernst light were used as sources of illumination. With the former, alterations of potential up to $\frac{1}{2}$ volt were observed, illumination rendering the electrode more positive.

The influence of the composition of the photochloride mixture, of the intensity and colour of the light, and of the temperature were investigated in detail. Photochlorides containing the components in any proportion appear to be sensitive to light. On exposure to white light, the potential gradually rises to a maximum and then diminishes somewhat. On then removing the source of light the potential gradually falls, in some cases becomes negative, and then slowly returns to the potential before illumination. Blue and yellow have much the same effect as white light, green light has a less powerful action, and red light produces a negative potential. The maximum potential rises in an approximately logarithmic manner with the intensity of illumination. The temperature-coefficient is negative.

G. S.

[Nature of the Photochlorides of Silver and their Potential in Light.] Emil Baur (*Zeitsch. physikal. Chem.*, 1911, **77**, 58—65. Compare preceding abstract).—In order to explain the complicated form of the potential curve obtained on illuminating a photochloride and then withdrawing the source of light (maximum in light, minimum in the dark, with subsequent slow return to the original potential), three processes are necessary, a positive, a negative, and an annulling. The positive process is the absorption of light energy by the silver chloride in the photochloride, whereby it becomes unstable; the annulling process is the gradual "acclimatisation" of the photochloride to light, whereby the stimulating effect of the latter diminishes. The negative action which has been observed for red light is ascribed by the author to the silver in the photochloride, also assumed to be sensitive to light, and it is shown that the results can be accounted for in this way.

The results obtained by Sichling are further shown to afford an explanation of certain phenomena observed in photography, such as solarisation. G. S.

Photochemical Reactions in Aqueous Solution. Alfred Benrath (*Annalen*, 1911, **382**, 222—235).—The action of ultra-violet (mercury) light on aqueous solutions is not so marked as its action on gases (Berthelot and Gaudechon, Abstr., 1910, i, 349; ii, 564, 606, 814; this vol., ii, 240, 242; Stoklasa and Zdobnicky, this vol., i, 178). The effects are similar to those of ordinary light, but more pronounced. All carboxylic acids are decomposed according to the scheme $R{\cdot}CO_2H \longrightarrow RH + CO_2$. In the case of β-ketonic acids, this decomposition occurs in the dark when solutions of the acids are heated; α-ketonic acids are decomposed when exposed to sunlight in glass vessels. Other acids are decomposed but slowly under these conditions, but decompose more readily in the presence of fluorescent salts, such as those of uranium. All acids decompose when exposed in quartz vessels to the effect of the rays from a mercury lamp. Sulphonic acids behave in a similar manner; for example, an aqueous solution of sulphanilic acid is decomposed into aniline and sulphuric acid. An aqueous solution of ether does not yield alcohol when exposed to ultra-violet light. Esters, on the other hand, are hydrolysed, whereas ester formation has not been observed. Halogen derivatives are hydrolysed; thus bromobenzene and water yield phenol and hydrobromic acid. Monochloroacetic acid yields first glycollic acid, but this is oxidised to glyoxylic acid, which is decomposed into formaldehyde and carbon dioxide. Dichloroacetic acid yields glyoxylic acid or its decomposition products, and trichloroacetic acid yields chloroform and carbon dioxide. Chloroform in aqueous suspension or aqueous alcoholic solution is oxidised to formic acid or its decomposition products. The only manner of preventing the decomposition of chloroform is to keep it in the dark. Carbon tetrachloride and water yield carbon dioxide and hydrochloric acid. Choral hydrate is decomposed by water into carbon dioxide and formaldehyde. For hydrolytic decomposition of ketones compare Ciamician and Silber (Abstr., 1907, i, 587; 1908, i, 277, 555; 1909, i, 306, 396).

When aqueous solutions of α- or β-hydroxy-acids are exposed to ultra-violet light in the presence of ferrous salts, ketonic acids are first formed, and these are then decomposed into carbon dioxide and aldehydes or ketones. It is not advisable to seal the tubes while they are exposed to the light, as the pressure of the carbon dioxide may be appreciable. Lactic, α-phenyl-lactic, malic, and mandelic acids behave in this way. Citric acid yields acetone and carbon dioxide, acetonedicarboxylic acid probably being formed as an intermediate product. Tartaric acid is oxidised to carbon dioxide, formaldehyde, glyoxylic acid, and glyoxal.

The velocity of a photochemical reaction can be studied, in many cases, by means of the change in electrical conductivity, provided the solutions are less concentrated than normal. This is shown in the case of the reduction of ferric chloride by means of ethyl alcohol, where the value Δ/t (increase in conductivity per minute) rises rapidly and finally becomes constant. The hydrolysis of chloroform by water is a pure photochemical reaction, and the values for Δ/t are nearly constant, but tend to diminish as t increases. This may be due to the fact that the hydrogen chloride formed acts as a catalyst.

The hydrolysis of methyl acetate and of monochloroacetic acid has been studied in a similar manner. In the latter case a 0·6*N*-solution was used, and the values for Δ/t increased with t, and finally attained a maximum.

Experiments have been made on the absorbing values of different liquids for the active light rays. This was effected by surrounding the narrow quartz cylinder containing the mixture under investigation within a quartz mantle and filling the space between the two vessels with the liquid. Water is the liquid most transparent to the active rays, and the benzene hydrocarbons the least. The following comparative numbers are given: Water, 100; methyl alcohol, 94; ethyl alcohol, 93; glycerol, 56; acetic acid, 31; *iso*propyl alcohol, 27; *iso*butyl alcohol, 20; *iso*amyl alcohol, 14; ethyl acetate, 8; methyl acetate, 5; benzene, 3; toluene, 3. J. J. S.

Variations in the Distribution of α-Particles. E. C. SNOW (*Phil. Mag.*, 1911, [vi], **22**, 198—200).—The theory of ideal frequency curves developed by Karl Pearson has been applied to the experimental results in the paper by Rutherford and Geiger (Abstr., 1910, ii, 917) bearing the same title, to measure the "goodness of fit" of the experimental results with theory. The "fit" is described as fair for the $\frac{1}{8}$-minute interval and better for the $\frac{1}{4}$-minute interval experiments. Those authors' conclusion, that the variations of emission are not greater than is to be expected on a random distribution, is not controverted. F. S

Energy Transformations of *X*-Rays. WILLIAM H. BRAGG and HARRY L. PORTER (*Proc. Roy. Soc*, 1911, *A*, **85**, 349—365).—According to the corpuscular theory of *X*-rays, the passage of these through matter gives rise to cathode rays which alone cause ionisation. Since the speed of a cathode ray is determined by the hardness of the *X*-ray from which it is derived, it is permissible to speak of a zinc cathode ray as determining the quality of the zinc *X*-ray. Homogeneous tin *X*-rays were allowed to fall normally on plates of copper and zinc, and the energy of the zinc cathode rays and the copper cathode rays were measured in terms of the ionisation they produce. Allowing for the energy appearing as copper *X*-rays and zinc *X*-rays, it was found that the rate of production of cathode rays is proportional to the absorption of the primary tin *X*-rays in the metal. If plates of metals other than copper and zinc were used, or tin replaced by arsenic or zinc, this proportionality was still found to exist This suggests that when *X*-rays are absorbed by matter their energy is fully accounted for by the energy of the cathode rays. If characteristic *X*-rays are formed, these result from the transformation of the cathode rays.

In order to show that ionisation is not directly due to *X*-rays, the ionisation due to cathode rays produced in silver was compared with the ionisation produced by the passage of the same beam of *X*-rays through oxygen. Tin *X*-rays were passed into a chamber closed by one, two, or more sheets of silver foil. From the curve showing the relation between cathode ray radiation and the thickness of the silver, the amount of such radiation produced in the silver could be found in terms of that emerging. When tin *X*-rays were passed into this chamber containing oxygen, it was found that the ionisation due to the cathode rays produced in the silver (as obtained by that emerging from the silver) was 34·3 times the ionisation produced by the *X*-rays in an equal weight of oxygen. Experiments also show that the absorption coefficient of tin *X*-rays in silver was thirty-six times greater than that in oxygen, weight for weight. According to the corpuscular theory this means that the cathode ray production in silver is thirty-six times greater than that produced in oxygen, and these results, therefore, indicate that the whole of the ionisation in oxygen must be attributed to the cathode rays. H. M. D.

Chemical Action of Canal Rays. VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1911, **17**, 393—398).—Referring to the experiments of Dechend and Hammer (this vol., ii, 454) the author describes a number of observations of the action of canal rays on metals and salts. In general, the changes observed are independent of the nature of the gas in which the rays are produced, although they take place more readily in a gas of higher molecular weight. The author thinks that the changes are probably due either to the mechanical effects of the impact of atoms moving at a high velocity or to the heat developed by the impact; specific chemical reactions of the rapidly moving atoms have not as yet been definitely recognised.
T. E.

The Transformation of the Actinium Emanation. HANS GEIGER (*Phil. Mag.*, 1911, [vi], **22**, 201—204).—The occurrence of double scintillations, using the α-rays of the actinium emanation, gave rise to the presumption that the change of the emanation was either accompanied by the expulsion of two α-particles, or that it was duplex, the period of the α-ray product of the emanation being less than 0·1 second (Geiger and Marsden, Abstr., 1910, [ii], 92). Experiments on the range of the α-rays of the actinium emanation have shown that the α-rays consist of two types, the ranges of which, in air, are 5·7 and 6·5 cm., the range of the α-ray of the active deposit being 5·4 cm. The α-ray of actinium-*X* has a range of 4·4 cm., Hahn having ascribed to actinium-*X* the longer-ranged α-ray given by the emanation. Further evidence has been obtained that the α-ray of 6·5 cm. range is due to a product of the emanation, having a period of the order of 1/500th second, that due to the emanation itself having the range of 5·7 cm. An arrangement was used whereby only the longest range α-rays could reach the screen from a tube with a thin mica window in which actinium emanation circulated. Inside the tube was placed an electrode, so that no α-rays proceeding from the electrode could escape from the mica window. Application of a field to the inner electrode and the tube greatly reduced the number of α-rays reaching the screen, showing that the product of the emanation gives α-rays and carries a charge. From the field necessary to effect a certain reduction in the number, and by assuming that the radioactive atoms possess the same migration constant as positive ions, a rough estimate of the order of the period of the product was obtained. F. S.

A New Radium Perpetuum Mobile. Heinrich Greinacher (*Ber. Deut. physikal. Ges.*, 1911, **13**, 398—404).—This apparatus is in principle the same as in that of the Curies' first demonstration of the negative charge carried by the β-rays of radium. A metal plate, completely embedded in paraffin wax, absorbs the β-rays from a radium source and becomes negatively charged. The plate is connected, by a fine wire embedded in paraffin wax within a metal tube, with the needle of a "binant electrometer" placed at a considerable distance to avoid the ionisation of the air around the needle by the radium. The "binant electrometer" is a kind of quadrant electrometer with a single pair of opposite quadrants, one carrying a platinum wire for discharging the needle when the deflection attains a certain value. The needle is charged up negatively, and discharged alternately at a definite constant rate if an external separate radium preparation is placed upon the embedded metal plate, or brought near to it, so that β-rays penetrate to the plate. The instrument is arranged for use with a mirror and scale for lecture demonstration, and possesses the advantage that it can be worked with any available preparation of radium.

F. S.

A Readily Absorbable, Ionising Radiation Emitted by Radium-*C*. Louis Wertenstein (*Compt. rend.*, 1911, **152**, 1657—1660. Compare Abstr., 1910, ii, 817).—The radiation giving rise to strong ionisation, to which attention has previously been drawn, appears to be produced by the projection of radium-*D* from radium-*C*, since its intensity is always proportional to the amount of radium-*C* on an active disk, and it is only slightly deviated by a magnetic field of moderate intensity. W. O. W.

The Estimation of Radium Emanation by the Ionisation Current. W. S. TITOFF (*Physikal. Zeitsch.*, 1911, 12, 476—480).—Details are given of a comparison of Mache's method and Elster and Geitel's apparatus with Schmidt's method and instruments in the estimation of radium emanation in the water of a thermal spring of W. Siberia. The values obtained by the former method were more constant and somewhat lower than those obtained by the latter, using the strength of the ionisation current in the electroscope as the basis of comparison. The conditions for using the ionisation current as a measure of the quantity of radium emanation are discussed, and the importance is emphasised of passing the gas from the spring-water through cotton-wool and a drying agent before admitting it to the electroscope. Under proper conditions the two methods give similar results. F. S.

Effect of Electric and Magnetic Fields on the Spontaneous Charging of Polonium. The Penetration Power of δ-Rays. FR. HAUSER (*Physikal. Zeitsch.*, 1911, 12, 466—476).—In a vacuum a polonium plate charges itself positively, the δ-rays carrying away more negative electricity than compensates for the positive charges of the α-rays. The limiting potential attained, if the plate is perfectly insulated, is about 24·5 volts, whilst a potential of 3·91 volts suffices to reduce the loss of negative electricity to half-value. This was determined by measuring the rate of loss of charge when the polonium was charged both positively and negatively, with and without a magnetic field sufficient to return the δ-rays to the plate. The limiting potential E is given by $E = mv^2/2e$, where m, v, and e refer to the mass, velocity, and charge of the δ-ray. The secondary rays produced by the impact of the α-rays on brass have a value for mv^2/e certainly not greater than for the δ-rays. From the rate of charging of the polonium plate and its surroundings with and without a magnetic field, it is deduced that per α-particle expelled about 60 δ-particles are expelled, and that each α-particle produces about 17 secondary negatively-charged particles by impact on brass. By measuring the rate of charging of a polonium plate covered with thin aluminium foil, it was deduced that the δ-particles have a penetration power of from 1/7th to 1/11th of the penetration power of the α-rays of polonium. F. S.

A Method of Investigating the Quantity of Radium in Rocks and Minerals, etc. JOHN JOLY (*Phil. Mag.*, 1911, [vi], 22, 134—150).—The emanation is removed from the rock or mineral by fusion with sodium and potassium carbonates or with borax. This is accomplished in a platinum crucible, electrically heated by a resistance wire within a porcelain crucible, and covered with a quartz bell-jar. The crucible rests on an iron plate standing in water on feet, and the quartz bell-jar is made air-tight by dipping in mercury contained in an annular groove in the iron plate. The expelled gases are collected in a rubber bag and discharged into the electroscope, arrangements being provided for sending a current of air through the apparatus at the close of the fusion.

The results obtained show that this method removes more emanation and indicates a higher radium-content than the solution method. Acid rocks especially, owing to the intense effervescence, yield their emanation easily, but the same result may be attained with basic rocks by addition of boric acid. The new method showed in two series of Irish granites a mean radium-content 46% higher than the solution method, whilst with basic rocks much larger increases, up to four times the earlier results, were obtained. No radium could be detected in the reagents used by the new method, and no appreciable loss of emanation could be observed from a sample of rock after being kept in a closed vessel for a month. The advantages of the fusion method are its quickness, the small bulk of the materials employed, and greater certainty against contamination of the materials tested. F. S.

A New Radioactive Mineral Spring at Brambach i.V. Heinrich Fresenius and A. Czapski (*Chem. Zeit.*, 1911, **35**, 722—723).—The radioactivity, measured at the spring, was found to be 2270 Mache units. Experiments made on water which had been kept for some days showed that the half-period was 3·02—3·13 days, which is less than that corresponding with pure radium emanation (3·71—3·86 days). Further measurements lead the authors to the conclusion that the 2270 Mache units are chiefly due to radium emanation, but that another radioactive substance is present which has a shorter life-period than radium emanation.

The waters of this spring are by far the most radioactive known. T. S. P.

Radioactive Springs of Exceptionally High Activity at Brambach in the Saxon Vogtland. M. Weidig (*Zeitsch. öffentl. Chem.*, 1911, **17**, 221—224. Compare the preceding abstract).—The radioactivity of the new spring is given as 1965 Mache units. The radioactivities of the waters from six other springs at Brambach are also given; they vary from 81 to 361 Mache units. T. S. P.

Charges on Ions in Gases. John S. Townsend (*Phil. Mag.*, 1911, [vi], **22**, 204—211).—The evidence in favour of the view that positive ions carrying double charges are produced in gases in certain circumstances is reviewed, the opposite conclusion (Millikan and Fletcher, this vol., ii, 573) being criticised. Various criticisms of the author's results (*loc. cit.*) are replied to. F. S.

Corpuscular Ionisation of Saline Vapours and the Re-combination of Ions in the Flame. Georges Moreau (*Compt. rend.*, 1911, **152**, 1664—1666. Compare this vol., ii, 455).—In the production of ions in a flame charged with the vapour of a salt, under the conditions previously described, the saturation current, Q, is not experimentally attainable, but can be deduced from observations made with fields of low intensity. With intense fields, return of corpuscles to the cathode through diffusion is comparatively insignificant, and consequently the number of salt molecules, p, dissociated by each cathodic corpuscle is given by the expression $p = Q/Q'$, where Q' is the observed current.

It is found that p does not vary with the acid radicle of the salt, and only within narrow limits with the metallic radicle. The value of p, however, changes with the incandescent substance coating the cathode, its temperature, and the duration of heating. At about 1500°, p does not exceed 20 for lime or 10 for strontium oxide, barium oxide, or sodium carbonate. The coefficient of re-combination of ions varies between 5000 and 20,000 electrostatic units, according to the nature of the salt and material of the cathode. It follows that re-combination occurs once in about 500 collisions. W. O. W.

Experiments with Liquid Helium-*D*. Change of the Electrical Resistance of Pure Metals at Very Low Temperatures. V. Disappearance of the Resistance of Mercury. H. Kamerlingh Onnes (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 113—115. Compare this vol., ii, 487, 575).—More accurate measurements have been made of the resistance of mercury at helium temperatures. At 4·3° abs. the resistance is 0·0021 of the value for solid mercury at 273° abs., whereas at 3° abs. it is only 0·0000001 of the value at 273°. Further lowering of the temperature to 1·5° abs. produces no measurable alteration in the resistance. These results indicate that the upper limit to be ascribed to the resistance, which still remains at helium temperatures, is very much smaller than the limit deduced from the earlier determinations.

H. M. D.

Dissociation of Sulphuric Acid and the Mobility of the Hydrogen Sulphate Ion. Karl Drucker (*Zeitsch. Elektrochem.*, 1911, **17**, 398—403. Compare Abstr., 1907, ii, 610; 1910, ii, 937; and this vol., ii, 362).—It would be possible to calculate the dissociation constant k_2 of the change $HSO_4' \rightleftharpoons H^{\cdot} + SO_4''$ from measurements of the conductivity of sulphuric acid if the fraction of the acid dissociated according to the equation $H_2SO_4 = H^{\cdot} + HSO_4'$ and the mobility of the HSO_4' ion were known. Earlier writers have attempted to calculate k_2 by assuming values for these quantities; it appears, however, that the value assumed for the mobility of HSO_4' affects the result very little; the degree of the first stage dissociation is the important factor. The writer has therefore studied sodium hydrogen sulphate. New measurements of the depression of freezing point and of the concentration of hydrogen ions by means of a concentration cell show, in good agreement with each other, that a 0·1*N*-solution of sodium hydrogen sulphate contains 0·049 gram-mol. of $H^{\cdot}$ ion per litre. Combining these results with the migration and conductivity measurements of Noyes and Stewart (Abstr., 1910, ii, 937), the value of the mobility of the HSO_4' ion at 25° is found to be 39. The values of k_2 are then calculated from the conductivity of sodium hydrogen sulphate solutions on the assumptions (1) that the first stage dissociation is complete, (2) that it is equal to that of sodium chloride, and

(3) that it is equal to that of sodium sulphate. The final conclusion drawn is that the most probable value of k_2 is 0·017. Sulphuric acid of less than 0·041*N* strength contains the ions HSO_4' and SO_4'', but other ions are formed in stronger solutions. The first stage dissociations of sulphuric acid and of sodium hydrogen sulphate are almost the same as those of hydrochloric acid and of sodium chloride.

T. E.

Conductivity of Aqueous Solutions of Sodium Chloride, Hydrochloric Acid, and their Mixtures.

WILLIAM C. BRAY and FRANKLIN L. HUNT (*J. Amer. Chem. Soc.*, 1911, 33, 781—795).—This work was undertaken in order to study, for two salts of widely different conductivities, the validity of the method of calculating the specific conductivity of mixtures of salts with a common ion which is based on the principle that the degree of ionisation of each salt in such a mixture is equal to that which it has when present alone in a solution of the same total ion concentration (compare Mackay, this vol., ii, 366).

The conductivity has been determined at 25° of 0·001—0·2*N*-solutions of sodium chloride and of hydrochloric acid, and of mixtures of these substances in which the concentrations were varied systematically. The specific conductivities of the mixtures were calculated by the rule to which reference has already been made. It is shown that large variations in the degrees of ionisation produce scarcely any change in the calculated specific conductivities, provided that the conductance of each ion is assumed to depend on the total equivalent ion concentration.

The specific conductivities calculated in this way were in all cases greater than the values obtained experimentally. The difference is about 1·6% of the actual specific conductivity when the concentration of each substance is 0·1*N* in the mixture, and is less at lower concentrations. It is suggested that the conductance of an ion may depend on its actual concentration rather than on the total ion concentration, and it is shown that a satisfactory agreement can be obtained between the measured and calculated values by assuming that this is true for the hydrogen ion, and that hydrochloric acid is ionised to about the same extent as potassium chloride.

The ratio of the specific conductivities at 25° and 18° has been determined for 0·01*N*-potassium chloride, 0·05*N*-hydrochloric acid, and for sodium chloride solutions of concentrations from 0·001*N* to 0·1*N*. The results for the potassium chloride and hydrochloric acid solutions agree with those recorded by Déguisne, but those for the sodium chloride solutions are about 0·15% higher.

E. G.

Conductivity and Ionisation of Certain Salts at 18° and 25°.

FRANKLIN L. HUNT (*J. Amer. Chem. Soc.*, 1911, 33, 795—803).—It has been shown by Noyes (Abstr., 1908, ii, 348) that the empirical dilution law $(C\gamma)^n/C(1-\gamma)=$ a constant, in which *n* has values varying between 1·4 and 1·6, holds closely for dilute aqueous solutions of salts of different types over a wide range of temperature. In continuation of this work, the conductivity and ionisation at 18° and 25° have been determined of solutions of potassium and lead bromates, silver and thallous sulphates, magnesium nitrate, lead chloride, and sulphuric acid.

When the empirical dilution law holds over a definite range of concentration for some value of n, the curve obtained on plotting $1/\Lambda$ against $(C\Lambda)^{n-1}$, where Λ is the equivalent conductivity, must be a straight line. The results of the experiments have been plotted in this way, and the curves for each salt are found to be closely similar at 18° and 25°. By means of these curves, the value of n was chosen which gave the best straight line over any range of concentrations. Probable values of Λ_0 at 18° and 25° were then calculated, and these agreed well with the final values except in the case of lead chloride.

The degrees of ionisation of the uni-bivalent salts decrease in the same order as the values of n increase. The value of n is high for lead chloride, and this salt is less ionised than the other salts. The values of the equivalent conductivity and the percentage ionisation of the salts are given at various concentrations. The degree of ionisation of each salt at 25° is rather less than at 18°, but the difference decreases with decreasing concentration, and is almost negligible for very dilute solutions. The degree of ionisation is almost the same for magnesium nitrate and chloride, and for potassium bromate and nitrate. It is slightly less for barium bromate than for barium nitrate, and for thallous sulphate than for silver sulphate. Thallous and silver sulphates are somewhat less ionised than lead nitrate, and these salts are all much less ionised than most other uni-bivalent salts. Lead and cadmium chlorides are still less ionised. The silver, thallous, lead, and cadmium salts evidently occupy a position intermediate between typical strong electrolytes and weak electrolytes, such as mercuric chloride. E. G.

Conductivity and Dissociation of Organic Acids in Aqueous Solution between 0° and 35°. E. P. WIGHTMAN and HARRY C. JONES (*Amer. Chem. J.*, 1911, **46**, 56—112).—In continuation of the work of White and Jones (Abstr., 1910, ii, 821) the electrical conductivity and dissociation of a further number of organic acids have been determined from 0° to 35°. The conclusions drawn from the earlier work are confirmed, and in addition it is shown that for weak acids which are not hydrated the temperature-coefficients of conductivity increase rapidly with dilution and decrease rapidly with rise in temperature. When the acids are hydrated, the temperature-coefficients of conductivity are larger, and are less affected by dilution and alteration of temperature. Organic acids with the largest dissociation constants have also the largest temperature-coefficients of conductivity. The strong organic acids (for example, benzenesulphonic acid) do not obey the Ostwald dilution law.

The acids which have been investigated consist mainly of substituted fatty acids and substituted benzoic acids. The experimental data are quoted in detail. G. S.

Electrical Conductivities of Solutions in Acetic and Propionic Acids. AL. N. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 526—534. Compare Abstr., 1910, ii, 1027; this vol., ii, 247).—The author has measured the molecular conductivities at

25° of solutions of various dilutions of aniline, dimethylaniline, pyridine, quinoline, dimethylpyrone, water, acetanilide, lithium and zinc bromides, and calcium and zinc iodides in acetic acid (dielectric constant, 6·46) (compare Patten, Abstr., 1903, ii, 57); and of aniline, pyridine, quinoline, and lithium bromide in propionic acid (diel. const. 3·15). Solutions of the organic acids, even of trichloro- or tribromo-acetic acids in acetic or propionic acids, exhibit no conductivity.

The specific conductivities found for solutions of aniline, dimethylaniline, and quinoline in acetic acid agree with those given by Patten (*loc. cit.*), who, however, gives a higher value for pyridine solutions than is found by the author; the pyridine used by the latter boiled within 0·7°, and that used by Patten within 3°.

With the majority of the solutions examined, the conductivity does not change with lapse of time. Although in solutions of aniline in acetic acid, acetanilide and water (which are found to conduct but slightly) are gradually formed, yet this reaction is so slow at 25° that some days are necessary for the conductivity to fall by a few per cent.; this result confirms Menschutkin's observations on the velocity of formation of acetanilide (Abstr., 1882, 1084). Still slower should be the reaction between aniline and propionic acid, but here another change, accompanied by increase of the conductivity, takes place, and the same is the case with solutions of quinoline (but not of pyridine) in propionic acid; all these changes are, however, slow.

All the solutions in acetic and propionic acids examined show diminution of conductivity on dilution; this is very marked with the more concentrated solutions, and gradually becomes less and less so as the dilution increases.

The probable cause of these anomalies is the formation of complex conducting compounds (compare Steele, McIntosh, and Archibald, *Zeitsch. physikal. Chem.*, 1906, **55**, 183), and this is confirmed by the observation that acetic acid favours the formation of complex compounds in a high degree; indeed, many salts undergo polymerisation in this solvent. If the formula of the complex compound capable of electrolytic dissociation is mA, pB (where A and B represent a mol. of the solute and solvent respectively), then the function KV^m (K being the specific conductivity, and V the dilution) should increase with dilution like the molecular conductivity (KV) of aqueous solutions. For many solutions in acetic acid, this function will be KV^3, so that the formulæ of the complexes will be: $3C_5H_5N,pCH_3{\cdot}CO_2H$; $3ZnBr_2,pCH_3{\cdot}CO_2H$, etc.; p remains undetermined, but is probably greater than unity.

For solutions of dimethylpyrone, lithium bromide, and calcium iodide in acetic acid, the function KV^2 already increases with the dilution, the complexes being therefore: $2C_7H_8O_2,pCH_3{\cdot}CO_2H$; $2LiBr,pCH_3{\cdot}CO_2H$, etc.

Solutions in propionic acid exhibit considerably more rapid diminution of the molecular conductivity on dilution than those in acetic acid, so than m is greater than 3; but the determination of the value of m necessary for the function KV^m to increase with dilution is impossible in this case, as the theory developed by Steele, McIntosh, and Archibald is applicable solely to relatively dilute solutions, whilst only the more concentrated solutions in propionic acid exhibit conductivity. This theory finds confirmation in the change in the conductivity of acetic and propionic acid solutions with change of temperature (compare following abstract).

The dielectric constant of propionic acid is very small, being less than that of either chloroform (4·95) or ether (4·37), but, in spite of this, concentrated solutions of aniline, pyridine, or lithium bromide in this acid are conducting; in *iso*amyl acetate (diel. const. 4·79), lithium bromide shows very slight conductivity, whilst solutions in dimethylaniline are insulators (Patten, *loc. cit.*). On the other hand, amylamine (dielect. const. 4·5) approaches propionic acid in the conductivity of its solutions (compare Kahlenberg and Ruhoff, Abstr., 1903, ii, 464), and in the rapidity with which the molecular conductivity falls on dilution.

The dielectric constant of ethyl benzoate (6·62) is almost equal to that of acetic acid; yet a solution of lithium bromide in the latter conducts some hundreds of times as well as one of equal dilution in the former solvent; solutions of calcium and zinc iodides in these two solvents show similar relations. The conductivities of organic bases and of potassium acetate in acetic acid are so high that, in concentrated solutions, they exceed the conductivity of acetic acid in water. Like propionic acid, acetic acid gives solutions approximating in conductivity to those in primary amines with similar dielectric constants, *e.g.*, aniline and ethylamine (compare Shinn, Abstr., 1907, ii, 926).

These results confirm the inapplicability of the Nernst-Thomson law to solvents with low dielectric constants, and indicate that the principal factor governing their dissociating power is their chemical nature.

T. H. P.

Abnormal Conductivity Changes. Al. N. Sachanoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 534—546).—The author has further examined solutions in acetic and propionic acids (see preceding abstract) in order to test the sufficiency of Steele, McIntosh and Archibald's theory (*Zeitsch. physikal. Chem.*, 1906, **55**, 179; Abstr., 1907, ii, 840) to account for the anomalous changes in the conductivity of such solutions.

The results show that at 100° the number of molecules of the solute (*m*) entering into the composition of the complex molecule is less than at 25°, this being the cause of the characteristic difference between the molecular conductivity curves at 100° and at 25°. The molecular conductivity at 100° changes less by far than that at 25° on dilution; the relative change of conductivity from 25° to 100° is different for solutions of different concentrations.

At 25° the complex compounds conducting the current in acetic acid solutions will be of the form: $3C_5H_5N,pC_2H_4O_2$; $3C_6H_5\cdot NH_2,pC_2H_4O_2$, etc., whilst at 100° the value of *m* is diminished to two: $2C_5H_5N,pC_2H_4O_2$; $2C_6H_5\cdot NH_2,pC_2H_4O_2$.

T. H. P.

Influence of Alkyl Substituents on the Electrical Conductivity of Malonic Acid. William B. Meldrum (*J. Physical Chem.*, 1911, **15**, 474—488. Compare Walker, Trans., 1892, **81**, 696).—The conductivity of 18 mono- and di-alkyl substituted malonic acids was determined, and the monobasic dissociation constants were calculated by Ostwald's formula. These results combined with those of Walden (1891) enable the following conclusions to be drawn. The introduction of one alkyl group into malonic acid decreases the dissociation, this influence being greatest for the methyl and least for the ethyl group. *n*-Propyl and *n*-butyl produce an intermediate effect. The *iso*alkyl malonic acids are usually more dissociated than the corresponding normal compounds. The *iso*butyl group has an abnormal influence, lowering the constant considerably when alone and raising it when in conjunction with other groups.

The introduction of a second alkyl group into a monoalkylmalonic acid is accompanied by an increase in the dissociation above that of malonic acid, except in the case of two methyl groups.

It is suggested that one alkyl group diminishes the reinforcing influence of the carboxyl groups on each other, whereas a second alkyl group serves to bring the two carboxyls into close proximity again.

R. J. C.

Conductibility Accompanying Chemical Reactions. G. Reboul (*Compt. rend.*, 1911, **152**, 1660—1661).—The reactions examined were allowed to proceed in such a way that there was but little surface disturbance and only slight rise in temperature. For this purpose, chlorine diluted by an inert gas was passed over sodium, antimony, copper amalgam, etc. In no instance was there a marked production of ions.

W. O. W.

Electrical Induction in Chemical Reactions. L. G. Winston (*Amer. Chem. J.*, 1911, **45**, 547—553).—A discussion is given of the mechanism of chemical reactions based on the conception of electrostatic induction, the rearrangement of the atoms being compared with the distribution of positive and negative electricity in a neutral body by induction. The conditions best suited for induction are found in organic chemistry, and the hypothesis is applied to the explanation of the formation of homologous compounds by the substitution of a radicle for a hydrogen atom, and to the elucidation of tautomeric changes, the formation of polymerides, and the function of a catalyst.

E. G.

Elimination of Liquid Potentials in Measurements of Electrode Potentials. Niels Bjerrum [and, in part, (Frl.) J. Bjerrum] (*Zeitsch. Elektrochem.*, 1911, **17**, 389—393).—Liquid potentials may be calculated with greater accuracy by Henderson's theory than by that of Planck (this vol., ii, 182). The former theory indicates that when a solution of potassium chloride is used to separate two dilute solutions, the liquid potential is the sum of two parts, one of which is due to the unequal mobilities of potassium and chlorine ions, and the other to the unequal mobilities of the anions and cations of the dilute solutions. The latter portion is almost twice as great with a half-saturated solution of potassium chloride as it is with a saturated solution, whereas the first portion is approximately the same. By making two measurements with the two solutions of potassium chloride and extrapolating, the variable potential may be eliminated; the constant part must be calculated. In examples given it varies from -0.18 to $+0.72$ millivolt. A solution of ammonium nitrate gives larger values for this constant potential, owing to the greater difference in the mobilities of the ions. These conclusions are confirmed by a number of measurements. T. E.

Self-induction with the Semi-insulator in Relation to Concentration Cells. CHARLES M. VAN DEVENTER (*Chem. Weekblad*, 1911, **8**, 468—472. Compare van Deventer and van Lummel, Abstr., 1908, ii, 12, 558).—A contribution to the author's theory of the "leaking insulator." A. J. W.

Electrochemistry of Hydronitric Acid [Azoimide] and its Salts. I. Corrosion of Some Metals in Sodium Trinitride Solution. J. W. TURRENTINE (*J. Amer. Chem. Soc.*, 1911, **33**, 803—828).—A study has been undertaken of the electrochemical behaviour of azoimide and its salts (the trinitrides) with special reference to the relation of the N_3^- ion to other ions. In the present paper, an account is given of the electrochemical corrosion of magnesium, aluminium, zinc, iron, nickel, tin, lead, cadmium, copper, and silver in sodium azoimide solution. The experiments were made with each metal in both unstirred and stirred solution. The electrolytic bath was a 2% solution of sodium azoimide, and the cathodes usually consisted of platinum wires. The anodes were weighed before the experiment, and after they had been subjected to corrosion were cleaned, dried, and again weighed.

In the case of magnesium, the results show that the electrochemical equivalent of this metal is twice as great as would be expected in accordance with Faraday's law. Aluminium, zinc, and cadmium also give anode efficiencies of considerably more than 100%. In order to explain these phenomena, it is suggested that the metals dissolve electrochemically at a valency lower than that usually assigned to them with formation of compounds which are readily oxidised. This hypothesis is supported by the fact that reduction products of the N_3^- ion, such as ammonia, hydrazine, and nitrogen, are found in the region of the anode, the presence of which indicates that some reducing agent is formed at the anode. As an example of the change which occurs, reference may be made to the behaviour of magnesium. It is supposed that magnesious azoimide, MgN_3, is formed at the anode, and that this causes the reduction of the azoimide ion with formation of ammonia, hydrazine, and nitrogen in accordance with the equation: $8MgN_3 + 10H_2O = 3MgN_6 + 5Mg(OH)_2 + 2NH_3 + N_2H_4 + N_2$.

Nickel and lead become passive in unstirred solutions, whilst aluminium, iron, nickel, tin, lead, and silver become passive, or nearly so, in stirred solutions. E. G.

An Electrical Tungsten-resistance Oven for Chemical Purposes. FRANZ FISCHER and ERICH TIEDE (*Ber.*, 1911, **44**, 1717—1720).—The oven is very similar in principle to that described by Pring and Hutton (Trans., 1906, **89**, 1591) and Greenwood (Trans., 1908, **93**, 1483), except that the resistance of carbon or iridium is replaced by a tube formed from compressed tungsten, the upper part of the centre of the tube being cut away to form a hollow for holding a magnesia crucible. Surrounding the resistance is a glass globe, connected with a Gaede mercury pump, and kept cool by a continuous stream of cold water flowing over it.

With the above apparatus, 1·5 grams of tin could be distilled in five minutes, the tungsten tube being heated to near its vaporising temperature. The tin collected partly on the edge of the magnesia crucible, and partly as a black mirror on the cool surface of the glass globe. T. S. P.

Researches on Magnetism. III. Para- and Dia-magnetism at Very Low Temperatures. H. KAMERLINGH ONNES and ALBERT PERRIER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911. **14**, 115—122).—Measurements of the magnetic susceptibility of gadolinium sulphate, ferrous sulphate, dysprosium oxide, and electrolytic bismuth have been made at temperatures ranging from room temperature down to 14° abs. In the case of gadolinium sulphate, the product of specific susceptibility and absolute temperature is constant down to 17° abs. in accordance with Curie's law. A slight diminution in the value of the product is found at 14° abs.

For ferrous sulphate, Curie's law is satisfied down to 64° abs., but at lower temperatures, deviations are found which increase in magnitude as the temperature falls. In the case of dysprosium oxide, the temperature susceptibility product begins to exhibit divergences at 170° abs., and at liquid hydrogen temperatures the susceptibility is only about half what it should be according to Curie's law. Between 20° and 14° abs. the susceptibility varies inversely as the square-root of the absolute temperature, which relationship was also found for liquid oxygen at temperatures between 90° and 63° abs. It is probable therefore that this behaviour is characteristic of all substances for a certain temperature range.

The data for bismuth show that the linear relationship between the susceptibility and the temperature, which has been found at higher temperatures, ceases to be valid at very low temperatures. At liquid hydrogen temperatures the susceptibility is nearly independent of the temperature. H. M. D.

Rationality of the Proportions of the Molecular Magnetic Moments and the Magneton. PIERRE WEISS (*Arch. Sci. phys. nat.*, 1911, [iv], **31**, 401—438).—By application of Langevin's kinetic theory of dia- and para-magnetism to the magnetisation data for para- and ferro-magnetic solids and for dissolved para-magnetic substances, it is found that the magnetic moment of an element varies in such a way that the several values can be represented by simple ratios. For different elements, the magnetic moments are also related in a simple manner, and these facts lead the author to put forward the hypothesis that magnetisation is of atomic character. The indivisible elementary magnetic unit is termed a magneton. This is supposed to be a constituent of the atoms of all elements. The elements, for which available magnetisation data indicate the validity of the magneton hypothesis, are iron, nickel, cobalt, chromium, manganese, vanadium, copper, mercury, uranium, and the metals of the rare earths. From observations on the magnetisation of iron and nickel at the temperature of liquid hydrogen and Perrin's value for the number of atoms in a gram-atom of an element ($68{\cdot}5 \times 10^{-22}$), the author calculates the moment of the elementary magneton to be $16{\cdot}4 \times 10^{-22}$.

H. M. D.

Specific Heat of Different Gases and Vapours. R. THIBAUT (*Ann. Physik*, 1911, [iv], **35**, 347—377).—The sound-wave method of determining $k = C_p/C_v$ described by Behn and Geiger (Abstr., 1908, ii, 99) has been used to determine the specific heat of carbon dioxide, hydrogen sulphide, sulphur dioxide, carbon disulphide, and ethyl ether at room temperature. Measurements of the heat capacity of the vapours of benzene, methyl alcohol, ethyl alcohol, and chloroform at about 350° have also been made by the differential calorimetric method described by Nernst (*Zeitsch. Elektrochem.*, 1910, **16**, 96).

The sound-wave method is unsuitable in the case of gases or vapours for which C_p is very large. At high temperatures, C_p increases as the number of atoms in the molecule increases, and for gases which contain the same number of atoms in the molecule it increases with the molecular weight. With rise of temperature, C_p increases more quickly as the ratio of the number of atoms in the molecule to the molecular weight increases. Carbon dioxide and sulphur dioxide have approximately the same molecular heat; this is also the case for water and hydrogen sulphide, but there is a considerable difference between the values for carbon dioxide and carbon disulphide. In the case of carbon dioxide, sulphur dioxide, and hydrogen sulphide, the specific heat ratio differs appreciably according to whether the measurement is made at a pressure of 1 or $\frac{1}{3}$ atmosphere.

H. M. D.

Transition Temperatures of Sodium Chromate as Convenient Fixed Points in Thermometry. THEODORE W. RICHARDS and GEORGE LESLIE KELLEY (*J. Amer. Chem. Soc.*, 1911, **33**, 847—863). —In earlier papers (Richards and Churchill, Abstr., 1898, ii, 555; 1899, ii, 354; Richards and Wells, Abstr., 1903, ii, 411; 1906, ii, 727; and Richards and Wrede, Abstr., 1908, ii, 16), it has been shown that the transition temperatures of certain crystallised salts, such as sodium sulphate, sodium bromide, and manganous chloride, can be so easily observed and constantly maintained as to form convenient fixed points in thermometry.

Sodium chromate has now been studied from this point of view and is regarded as of particular value, since it has three transition temperatures in the neighbourhood of 20°, a temperature at which thermometers frequently need to be verified.

Pure sodium chromate can be prepared by treating pure recrystallised sodium dichromate with rather less than the calculated quantity of sodium carbonate and completing the neutralisation by means of sodium hydroxide solution with the aid of phenolphthalein.

The existence of the three hydrates, $Na_2CrO_4,10H_2O$; $Na_2CrO_4,6H_2O$, and $Na_2CrO_4,4H_2O$, has been confirmed. The points at which each of these hydrates is converted into each of the other two can be accurately determined. The addition of heteromorphous substances lowers the transition temperatures as usual. Successive additions of sodium sulphate (which yields an isomorphous decahydrate) cause successive elevations of the transition temperature of the decahydrate-hexahydrate which are roughly proportional to the amounts added. In some cases an elevation of about 4° was observed. The transition temperatures, on the international hydrogen scale, are approximately as follows: decahydrate-hexahydrate, 19·525°; decahydrate-tetrahydrate, 19·987°; hexahydrate-tetrahydrate, 25·90°. E. G.

Fusibility Curves of Gaseous Mixtures: Systems Formed by Carbon Dioxide and Hydrogen Sulphide with Methyl Alcohol and Methyl Ether. GEORGES BAUME and F. LOUIS PERROT (*Compt. rend.*, 1911, **152**, 1763—1765. Compare Abstr., 1909, ii, 545; 1910, ii, 825; this vol., i, 414).—The fusibility curves of carbon dioxide with methyl ether or methyl alcohol, and of the latter with hydrogen sulphide show no maxima. That of the system methyl ether–hydrogen sulphide has a distinct maximum at $-148·5°$, corresponding with the compound OMe_2,H_2S. The curves are reproduced in the original paper, which also contains a diagram of the apparatus employed. W. O. W.

Influence of Pressure on the Melting Points of Certain Metals. JOHN JOHNSTON and L. H. ADAMS (*Amer. J. Sci.*, 1911, [iv], **31**, 501—517).—An apparatus is described by means of which chemical and physical changes can be investigated at temperatures up to 400° and under pressures up to 2000 atmospheres. This apparatus has been used to determine the influence of pressure on the melting point of tin, bismuth, lead, and cadmium. Up to 2000 atmospheres, the melting point varies with the pressure according to a linear equation. The rise of temperature per atmosphere was found to be as follows: tin 0·003275°. cadmium 0·006288°, lead 0·008026°. In the case of bismuth the melting point falls to the extent of 0·003548° per atmosphere. The measured changes of the melting point with pressure are shown to be in satisfactory agreement with the values calculated from the respective latent heats of fusion and the volume changes which occur on melting. The melting points at atmospheric pressure were determined both with copper–constantan and platinum–platinum rhodium couples, and found to be: tin 231·0°, bismuth 270·7°, cadmium 320·4°, and lead 326·7°. These temperatures refer to a scale obtained by measurements of the boiling points of naphthalene and benzophenone and the melting point of zinc. H. M. D.

Determination of Melting Points of Crystalline Liquids. H. STOLTZENBERG (*Zeitsch. physikal. Chem.*, 1911, **77**, 73—74).—Into the melting-point tube a glass rod, bent horizontally at the upper end, is inserted, and in the capillary layer thus formed between rod and tube, melting points of crystalline liquids can be observed very sharply. Further, in such a tube alterations in the height of the meniscus connected with transitions from one phase to another can readily be observed. G. S.

Molecular Complexity of Salts in Phenol. CURT B. HARTUNG (*Zeitsch. physikal. Chem.*, 1911, **77**, 82—90).—The molecular weights of sodium acetate, aniline and dimethylamine hydrochlorides, tetramethylammonium iodide and the potassium and rubidium salts of oximinodiketohydrindene (a weak acid) in phenol have been determined by the cryoscopic method in different dilutions. The salts of the two weak acids show an abnormally great molecular depression in $N/10$-solution, which cannot be due to electrolytic dissociation, as in the same dilution the i value for tetramethylammonium iodide is nearly unity. The results are ascribed to "phenolysis" of the salts, analogous to hydrolysis. The curve obtained for the two salts of oximinodiketohydrindene by plotting i values as ordinates against dilutions as abscissæ show distinct minima, a result which is ascribed to association between solute and solvent with a consequent diminution of "free" solvent, which is of importance in concentrated solution. G. S.

Method for Determining Heat of Evaporation as Applied to Water. THEODORE W. RICHARDS and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1911, **33**, 863—888).—The recorded values of heats of vaporisation of various liquids are very discordant, owing partly to the use of impure materials and partly to the employment of faulty methods. A satisfactory method has now been devised, and is fully described. A modification of Kahlenberg's form of Berthelot's apparatus is employed in conjunction with the adiabatic method of calorimetry (Abstr., 1905, ii, 677; 1907, ii, 604; 1908, ii, 806; 1910, ii, 391, 930) and the use of a Dewar vessel as vaporiser.

It has been found that a serious error, amounting to about 0·1% of the total per minute, is caused by premature condensation in the narrow zone between the vaporiser and the condenser. This error was reduced as far as possible by modifications in the apparatus, and was finally eliminated by conducting experiments at different rates and extrapolating the results to a hypothetical instantaneous experiment in which the disturbing effect may be regarded as zero.

The heat of vaporisation of a gram of water was found to be 538·9 Cal._{21°, or 2·251 kilojoules per gram. A gram-molecule therefore requires 9·707 Cal._{21° or 40·54 kilojoules when the vaporisation is carried out at 100° ($O = 16{\cdot}000$, 1 $\text{Cal.}_{21^\circ} = 4{\cdot}177$ kilojoules). This result compares satisfactorily with those of previous investigators, and proves that the method is trustworthy and suitable for general use.

The method has been applied to other liquids, and has given concordant results. E. G.

The Specific Gravities of the Elements Considered in their Relation to the Periodic System. ARTHUR JOHN HOPKINS (*J. Amer. Chem. Soc.*, 1911, **33**, 1005—1027).—The relationships between atomic weights, densities, specific volumes, atomic volumes, and position numbers in the periods are discussed, and the view put forward that the position number is the fundamental property of an element, the density, valence, and all properties dependent on these being functions of the position number. A slightly modified arrangement of the periodic system is suggested in the second part of the paper. H. M. D.

Relation of Vapour Pressure to Specific Gravity in Binary Liquid Mixtures. ANTONY G. DOROSCHEWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 656—670).—In discussing the relation of the vapour pressure (P) of a mixture of two liquids to the specific gravity, the author compares the deviation dP of the actual vapour pressure from the value calculated according to a straight line law with the corresponding deviation (contraction) dV for the volume of the mixture. It is known (Young, Trans., 1902, 768; Kuenen, "Theorie der Verdampfung und Verflüssigung," 1906, 137) that, for liquids which have a straight line vapour pressure curve, the contraction (and the heat effect of mixing) is very small, so that when $dP=0$, dV approaches 0; as the contraction was determined at an appreciably lower temperature than the vapour pressure, it may be that, at identical temperatures, when $dP=0$, dV also $=0$.

Kuenen regards mixtures of methyl and ethyl alcohols as having a rectilinear vapour pressure curve, but calculation by means of Haywood's results (Abstr., 1900, ii, 64) shows that the straight line value is greater than the experimental by an amount almost constant for all solutions, namely, 29 mm.

Consideration of the somewhat insufficient data available points to the conclusion that when dP is zero, dV is zero, and when dP is constant, dV is also constant. Further, a maximum or minimum value of dP corresponds with a maximum or minimum value of dV.

The mixtures showing the most regular relations between dP and dV are those of ethyl alcohol and water, probably owing to the fact that they have been more completely and accurately studied than others.

The connexion between dP and dV is manifested in a general way, but there are certain peculiarities of dP for which no peculiarities of dV exist. Thus, in cases where a maximum of vapour pressure is not very well defined, for example, in mixtures of ethyl alcohol and water, the contraction curve shows no peculiarity at a corresponding point.

The conclusion is drawn that a maximum vapour pressure indicates a special molecular process in the solution. T. H. P.

The Weight of a Falling Drop and the Laws of Tate. VII. The Drop Weights of Some of the Lower Esters and the Surface Tensions and Molecular Weights Calculated from Them. J. LIVINGSTON R. MORGAN and FREDERICK W. SCHWARTZ (*J. Amer. Chem. Soc.*, 1911, **33**, 1041—1060. Compare Abstr., 1908, ii, 356, 668; this vol., ii, 372, 584, 585).—The drop weight method of determining surface tension has been applied to various esters of the lower fatty acids with a view of comparing the results with those obtained by the method of capillary rise. In general, the agreement is quite satisfactory, but deviations are found in the use of methyl formate, amyl formate, and ethyl acetate.

When the equation $w(M/d)^{\frac{2}{3}} = k_B(t_c - t - 6)$ is applied to the drop weight data with the object of finding a value of t_c which is independent of the temperature of observation t, using, in all cases, the value of k_B found for benzene ($t_c = 288·5°$), it is found that methyl acetate, ethyl acetate, propyl acetate, methyl butyrate, methyl *iso*butyrate, methyl propionate, ethyl propionate, and amyl formate have a normal molecular weight. Only in the case of methyl acetate does the calculated t_c agree with the observed critical temperature, the calculated values being higher in all the others except methyl, ethyl, and propyl formates. In these three cases, rise of temperature appears to cause some change to take place which can be removed by sudden cooling, but persists when the cooling is effected slowly, leading to a higher drop weight than that found for the unheated liquid.

H. M. D.

The Weight of a Falling Drop and the Laws of Tate. VIII. The Relationship Existing between the Weight of the Drop, the Diameter of the Tip from which it Falls, and the Surface Tension of the Liquid. J. LIVINGSTON R. MORGAN and JESSIE Y. CANN (*J. Amer. Chem. Soc*, 1911, **33**, 1060—1071. Compare preceding abstract).—The weights of falling drops of benzene, quinoline, pyridine, ethyl ether, and carbon tetrachloride have been determined at 27·8°, using sixteen different tips varying in diameter from 3·05 to 7·86 mm. In the case of the smaller and larger tips, the drop formation is abnormal, and values are obtained for the drop weights which are too large. All liquids are found to give satisfactory results with a tip of 4·5 mm. diameter, and if liquids, like carbon tetrachloride, which have a very small surface tension and large density are excluded, equally good results are obtained by the use of tips with diameters between 4·5 and 5·5 mm. The general conclusion which the authors draw from these measurements is that the weight of a falling drop is rigidly proportional to the diameter of the tip from which it falls, if the drop formation is not visibly abnormal.

H. M. D.

The Compression of Liquids at High Pressures. (Hon.) CHARLES A. PARSONS and S. S. COOK (*Proc. Roy. Soc.*, 1911, *A*, **85**, 332—348).—The compressibility of water, ethyl ether, paraffin, and graphite has been measured by means of an apparatus in which the pressure could be raised to more than 6000 atmospheres. This apparatus consisted of a gun steel mould, placed under a heavy hydraulic press, water being supplied to the upper side of the ram by a three-throw hydraulic pump driven by an electric motor. The pressure on the ram was recorded by a Bourdon gauge, and the depression of the liquid in the mould was measured by a pair of multiplying callipers.

The following isothermal coefficients of compressibility were obtained for pressures of 1, 2000, and 4500 atmospheres respectively: water (4°) 50, 25, and $22{\cdot}5 \times 10^{-6}$; ethyl ether (35°) 165, 42·5, and 18×10^{-6}; paraffin oil (34°) 87, 34, and 17×10^{-6}.

Measurements of the cooling effect produced by adiabatic expansion were also made, and from these the authors calculate the magnitude of the internal pressure. For water this is 2150 atmospheres, for ethyl ether 2440, and for paraffin 2920.

The experiments with Atchison and Ceylon graphite indicate that this does not behave as a fluid under high pressures, but that it attains a greater degree of consolidation as the pressure increases. By immersing the graphite in water, its bulk compressibility was found to be about $6{\cdot}5 \times 10^{-6}$ in atmospheric units. H. M. D.

The Adsorption of Some Substances by Starches. Hoyes Lloyd (*J. Amer. Chem. Soc.*, 1911, **33**, 1213—1226).—The adsorption of hydrogen chloride, sodium chloride, and sodium hydroxide from aqueous solution by cassava, arrowroot, potato, rice, and maize starch granules has been investigated. The rapidity with which equilibrium is attained indicates that the effect is one of adsorption. With 50 grams of starch and 100 c.c. of solution, five minutes' stirring was found to suffice for the completion of adsorption. The influence of temperature is very small, and on this account the experiments could be carried out at room temperature.

The adsorption of the three electrolytes varies with the different starches, but not nearly so much as might be expected, considering the great differences in the size of the granules. Sodium hydroxide is adsorbed to a much greater extent than either hydrogen or sodium chloride. In the case of hydrogen chloride, adsorption takes place in accordance with the exponential adsorption formula up to a concentration of $0{\cdot}4N$. Within this range divergent results were, however, obtained when maize starch granules were employed.

H. M. D.

The Dissociation Equilibrium $S_8 \rightleftarrows 4S_2$ O. J. Stafford and H. von Wartenberg (*Zeitsch. physikal. Chem.*, 1911, **77**, 66—74).—When heat is conveyed between two surfaces at different temperatures through a dissociating gas, the thermal conductivity should be much higher than for a non-dissociating gas, since, in the former case, dissociation is taking place at the hot wall and re-combination at the cold wall, and therefore an extra transport of heat due to the heat of dissociation occurs. The authors have used this principle in order to settle the question whether any intermediate stages (for example, S_6) occur in the dissociation $S_8 \longrightarrow 4S_2$. As a matter of fact, the curve obtained by plotting the thermal conductivity as ordinates against the temperatures as abscissæ shows one pronounced maximum only, and this at first sight appears to show that only the molecules S_8 and S_2 are present. This is opposed to the results of Preuner and Schupp (compare Abstr., 1910, ii, 118), and the authors point out that in this curve there is a rapid alteration in the molecular complexity with temperature, so that the different maxima which might be anticipated for the various stages of the dissociation have coalesced to a single maximum. Bearing in mind this limitation, the measurement of the thermal conductivity is a useful method for determining the condition of a dissociating gas. G. S.

Measurement of Surface Tension by the Method of Capillary Rise. JULES E. VERSCHAFFELT and (Mlle.) L. VAN DER NOOT (*Bull. Acad. roy. Belg.*, 1911, **5**, 383—394).—It is shown that the variation of the capillary rise and the form of the capillary surface with the radius of the tube is such that it may be represented in each case by a single curve applicable to all liquids. For this purpose the curves must be plotted on a scale which is proportional to $1/a$, a^2 being the capillary constant of the liquid.

Measurements of the capillary rise of water, benzene, ethyl ether, and carbon disulphide have been made in tubes of radius varying from 0·094 to 1·56 mm., and the data are shown to be in agreement with the above deduction. A similar result is found in respect of the form of the capillary meniscus for the same liquids. H. M. D.

Relation of Osmotic Pressure to Temperature. V. The Measurements. HARMON N. MORSE, WILLIAM W. HOLLAND, E. G. ZIES, C. N. MYERS, W. M. CLARK, and E. E. GILL (*Amer. Chem. J.*, 1911, **45**, 554—603. Compare this vol., ii, 191, 375, 473).—An account is given of a series of determinations of the osmotic pressure of solutions of sucrose of 0·1, 0·2, 0·3, 0·4, and 0·5 weight-normal concentration at 0°, 5°, 10°, 15°, 20°, and 25°.

In four of the determinations, membranes of nickel ferrocyanide were used instead of those of copper ferrocyanide, and behaved in a satisfactory manner.

The rotatory power of the solutions remained constant in all the experiments recorded, and it is therefore evident that none of them were vitiated by leakage through the membranes, and that no inversion of the sucrose occurred in the cells. In one experiment, a cell maintained the concentration of the solution and the consequent osmotic pressure for more than eight weeks. This demonstrates the durability of the membranes, and shows that it is not necessary to stir the solutions. It also proves that osmotically active membranes may be made truly semi-permeable. The temperature of the solutions did not usually fluctuate more than 0·01°, and in no case more than 0·02°.

The ratio of osmotic pressure to gas pressure is constant for each concentration. This ratio in the 0·01*N*-solution was 1·082—1·084 at 5°, 10°, 15°, 20°, and 25°, but at 0° was 1·106, the osmotic pressure being higher at 0° than at 5°. It is pointed out in this connexion that at 0° the 0·1*N*-solution is within less than 0·2° of its f. p.

The conclusion is drawn from these experiments that, if the 0·1*N*-solution at 0° is excepted, the osmotic pressures of all solutions containing from 0·1 to 1·0 gram-mol. of sucrose per litre of water obey Gay-Lussac's law between 0° and 25°. E. G.

Osmotic Phenomena in Non-conducting Media. PAUL BARY (*Compt. rend.*, 1911, **152**, 1766—1767. Compare this vol., ii, 590).—A rubber membrane vulcanised with sulphur chloride is semi-permeable towards a solution of sulphur in benzene, and, in general, permeable towards substances dissolved in liquids capable of swelling the material. If a porous vessel containing a solution of acetylcellulose in tetrachloroethane is surrounded with the same solvent, no transfer of liquid occurs in either direction. A substance such as hexachloroethane, which is soluble both in acetylcellulose and tetrachloroethane, will traverse the dividing septum, however. These experiments are quoted in support of the conception of colloids put forward in a previous communication, and all semi-permeable membranes are considered to be composed of colloidal materials, their permeability being proportional to the solubility of the dissolved substance in the membrane. W. O. W.

Osmotic Pressure of Colloids. III. Dialysis and Osmosis of Solutions of Dyes. WILHELM BILTZ and F. PFENNING (*Zeitsch. physikal. Chem.*, 1911, **77**, 91—116. Compare Abstr., 1910, ii, 22, 693).—The results of the dialysis experiments have already been published (compare this vol., ii, 375); for the conductivity and osmotic pressure measurements, orange TA extra and "cloth-red" GA, salts of monosulphonic acids; brilliant-Congo, derived from a trisulphonic acid, and Congo-blue and Chicago-blue, salts of tetrasulphonic acids, were used. They were first freed as far as possible from inorganic salts by dialysis. The conductivity measurements appear to show that they behave as normal electrolytes, the molecular conductivity in great dilution being for the monosulphonates 100—150, for the disulphonate (Congo-red) 213, for brilliant Congo 363, and for the tetrasulphonates 451—532. On the other hand, Ostwald's rule regarding the dependence of the molecular conductivity on the basicity of the acid does not apply.

The osmotic measurements were made as already described, pure water and also salt solutions being used as an exterior liquid. The results show that a dye solution is highly complicated, as products of association, electrolytic dissociation, and hydrolysis occur in equilibrium. In the monosulphonates, association and hydrolysis are of most importance, and the observed molecular weight is much higher than the calculated. With disulphonates electrolytic dissociation approximately balances association, so that the compounds appear to be unimolecular; with tri- and tetra-sulphonates, on the other hand, electrolytic dissociation is of most importance, and the observed molecular weights are smaller than the calculated. An explanation is given for the fact that, in spite of polymerisation, the monosulphonates show the normal conductivity of binary electrolytes. G. S.

Concentric Stratification in Filter Paper. E. LENK and H. BRACH (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 325—326).—The formation of a precipitate in concentric rings is readily observed when a sheet of thick filter paper is moistened with a solution of potassium dichromate, and silver nitrate solution is allowed to drop slowly on to the paper at a fixed point. The effects are quite similar to those which are obtained with solidified gelatin films, but the rings are developed much more quickly when filter paper is employed.

H. M. D.

Weak Electrolytes, and towards a Dynamical Theory of Solutions. WILLIAM SUTHERLAND (*Phil. Mag.*, 1911, [vi], **21**, 17—66. Compare Abstr., 1902, ii, 300; 1907, ii, 599).—An attempt is made to elaborate a theory of solutions on a molecular kinetic basis. The motions of the molecules in a liquid mixture are supposed to be mutually influenced, and this has an effect on all those properties of the mixture which depend on the relations of a molecule to its immediate neighbours, such as cohesion, density, viscosity, and the like. The kinetic principle is applied to the calculation of the densities of solutions of ethyl alcohol and acetic acid in water and of the contraction which occurs in their formation. Its application to the refractivity, dielectric capacity, viscosity, specific heat, heat of solution, and surface energy in the case of mixtures of water with ethyl alcohol and the first four members of the series of fatty acids is also examined. The interpretation of the dilution law as applied to weak electrolytes is also discussed, and shown to be in agreement with the author's views. According to these, the changes in most of the physical properties which occur when ethyl alcohol or fatty acids are admixed with water are due to changes in the water itself, trihydrol being converted into dihydrol and dihydrol into hydrol. H. M. D.

Formation of Solid Metallic Solutions by Diffusion in the Solid State. GIUSEPPE BRUNI and D. MENEGHINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 671—674).—Nickel and copper form solid solutions in all proportions (compare Guertler and Tammann, Abstr., 1907, ii, 174; Kurnakoff and Schemtschuschny, Abstr., 1907, ii, 525), and the curve representing the conductivity as a function of concentration shows a somewhat flattened minimum corresponding with 40—60% by weight of copper.

In order to ascertain whether these alloys can be formed by diffusion of the solid metals, the authors have subjected a nickel wire, coated electrolytically with a compact covering of copper, to a temperature of about 1000° in an atmosphere of dry hydrogen, this temperature being about 80° below that at which the copper melts. The resistance of a certain length of the wire was measured from time to time. The resistance (0·026 ohm) at first diminished very slightly and subsequently increased, slowly in the beginning, then very rapidly, and finally slowly again, a constant value of about 0·21 ohm being approached. The wire showed no signs of fusion, and had the appearance and conductivity of constantan. T. H. P.

Validity of the Boyle-Gay-Lussac Laws for Colloidal Solutions. II. THE SVEDBERG and KATSUJI INOUYE (*Zeitsch. physikal. Chem.*, 1911, **77**, 145—191. Compare Abstr., 1910, ii, 772).—The validity of the laws in question has been further tested by ultramicroscopic observations with solutions of colloidal gold and of gamboge on the basis of the principles already described. The main conclusions are as follows. The compressibility diminishes with increasing concentration and with increase in the size of the particles ; in very great dilution the gas laws are accurately followed. There is a considerable deviation between the observed and calculated frequency numbers in concentrated solutions, but the agreement becomes better with increasing dilution and is ultimately exact. The influence of a number of substances, such as carbamide, sucrose, and certain electrolytes, on the compressibility has been determined; in no case does the effect exceed the limits of experimental error. Further, it is shown that the compressibility is independent of the viscosity of the dispersion medium, and Dalton's law of independent partial pressures is also valid. Finally, as the compressibility ratio is much greater for the gamboge system than for colloidal gold for the same size of particle, it follows that the compressibility depends on the nature of the disperse phase.

The experimental data are quoted in great detail. G. S.

Phenomena of Crystallisation in Ternary Systems. I, II, and III. Isomorphous Ternary Mixtures with a Miscibility Gap. Nicola Parravano and G. Sirovich (*Gazzetta*, 1911, **41**, i, 417—453, 478—489, 569—620).—The authors discuss equilibria in ternary systems with a miscibility gap in the solid state. The paper does not lend itself to abstraction, but the main results arrived at are briefly as follows.

Where a gap of miscibility occurs in which is exhibited only one solid triangle, and if the gap is maintained throughout the crystallisation, it always gives origin to a point of invariant equilibrium. This point may be of three kinds: (*a*) A eutectic point, in which case a liquid may deposit the three solid phases. In this point meet the three curves of univariant equilibrium, which all fall towards it. The eutectic point is always found within the solid triangle. (*b*) A transition point of the first order, and then a liquid may react with a solid phase, previously separated, to give rise to two other solid phases. Two curves of univariant equilibrium fall towards this point and meet in it, whilst a third, also of univariant equilibrium, falls away from it. (*c*) A transition point of the second order, a liquid then reacting with the two phases previously deposited, giving rise to the third solid phase. Only one curve of univariant equilibrium falls towards this point and two away from it.

The curves of univariant equilibrium, in their turn, may give rise to the three following cases: (*a*) the curve falls continuously from one end to the other, in which case it can either arrive at or start from the invariant point; (*b*) the curve presents a minimum of temperature, one of its ends then starting from the invariant point; (*c*) the curve exhibits a temperature maximum, when it reaches the invariant point at one end. The authors treat only of the first of these three cases.

Where, instead of one gap, there are two distinct ones, the above considerations apply to each separately. Where the two gaps touch, there results a single more complex gap; this case is also discussed.

T. H. P.

Phenomena of Crystallisation in Ternary Systems. IV. Certain Cases of Solubility Gaps.

Nicola Parravano and G. Sirovich (*Gazzetta*, 1911, **41**, i, 621—644. Compare preceding abstract).—Of the innumerable cases of solubility gaps in ternary systems, the authors discuss the following ten :

(1) The miscibility gap concerns only one binary system ; (2) two binary systems exhibit miscibility gaps, whilst the third forms a continuous series of mixed crystals ; (3) all three component binary systems exhibit miscibility gaps ; (4) one of the binary systems does not form mixed crystals, each of the other two giving continuous series ; (5) two of the binary systems do not form mixed crystals, while the third gives a continuous series ; (6) two of the binary systems do not give mixed crystals, the third exhibiting a miscibility gap ; (7) none of the three binary systems forms mixed crystals ; (8) two of the binary systems form no mixed crystals, the third showing two miscibility gaps ; (9) four solid phases are formed, the three components and a binary compound ; (10) no mixed crystals are formed, but a ternary compound. T. H. P.

Criterion of the Formation of a Compound in the Condensation of Two Gases.

E. Briner (*Zeitsch. physikal. Chem.*, 1911, **77**, 245—249).—An answer to the criticisms of Scheffer (this vol., ii, 379). The main point at issue is the bearing of dissociation on the proof of the formation of a compound between two gases on condensation. The author considers that when condensation takes place at the same composition at different temperatures a compound which is only very slightly dissociated is formed, but when the compound is highly dissociated the process of liquefaction may closely resemble that of mixture of two gases which do not combine chemically. G. S.

Equilibrium in the System: Lead Nitrate and Pyridine.

James H. Walton, jun., and Roy C. Judd (*J. Amer. Chem. Soc.*, 1911, **33**, 1036—1041).—The solubility of lead nitrate in pyridine has been determined at various temperatures between −19·4° and 110°. The proportion of lead in the solution and solid phases was estimated by adding to ammonium acetate solution, boiling until the pyridine had been removed, and then titrating with a standard solution of ammonium molybdate, using tannic acid as an indicator. The solubility data show that three compounds are formed within the above range of temperature. Up to 51°, $Pb(NO_3)_2,4C_5H_5N$ is the stable solid phase, but this is then converted into $Pb(NO_3)_2,3C_5H_5N$, and at 96° the latter is transformed into $3Pb(NO_3)_2,2C_5H_5N$. H. M. D.

Law of Moduli in the Variation of the Coefficient of Distribution.

Nicolas de Kolossovsky (*Bull. Soc. chim. Belg.*, 1911, **25**, 234—238).—It is shown by experiments on the distribution of acetic acid between ether and aqueous salt solutions that in not too concentrated solution each ion acts independently as regards its effect in altering the distribution of the acid ; in other words, the law of moduli is followed. The coefficients of lowering for a number of ions, positive and negative, are given in the paper. G. S.

Influence of the Masses of the Reacting Substances on the Formation of Oxonium Dibromides in Different Organic Solvents.

WLADIMIR W. TSCHELINZEFF and W. K. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 620—632).—The authors have studied the effect of increasing the proportion of the ether on the formation of oxonium dibromides in the eight solvents employed in their previous experiments (this vol., i, 256).

The results show that in the majority of cases, increase of the amount of ether is accompanied by only a slight increase in the amount of oxonium compound formed. If two mols. instead of one of ether are used to one mol. of bromine, an appreciable increase in the heat effect is observed, and the increases in the amount of oxonium dibromide formed are, in general, inversely as the amounts formed by equimolecular proportions of the reacting compounds. Corresponding changes are produced by using 3—5 mols. of ether. On the basis of the amount of dibromide formed from 5 mols. of ether and one molecule of bromine, ethyl bromide and benzene change places in the series of solvents given (*loc. cit.*). T. H. P.

Influence of the Concentration of the Reacting Substances on the Formation of Oxonium Dibromides in Different Organic Solvents.

WLADIMIR W. TSCHELINZEFF and W. K. KONOWALOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 633—650. Compare preceding abstract).—The following table shows the effect of varying the concentrations of ether and bromine on the percentage yield of oxonium dibromide obtained in different solvents :

Solvent.	Yields of dibromide formed when the reacting substances have the concentrations :			Ratios of the yields.
	2·5*N*.	1·5*N*.	0·9*N*.	
CS_2	15·3	10·4	6·4	2·7 : 1·6 : 1
CCl_4	26·7	15·5	10·1	2·6 : 1·5 : 1
C_2H_5Br	54·2	6·1	4·6	11·8 : 1·3 : 1
Light petroleum	63·3	43·4	14·5	4·4 : 3·0 : 1
$C_2H_4Br_2$	67·9	3·7	1·2	56·6 : 3·1 : 1
$CHCl_3$	68·0	38·6	17·7	3·8 : 2·2 : 1
C_6H_6	69·6	10·5	5·6	12·4 : 1·9 : 1
C_6H_5Br	82·3	40·8	10·8	7·6 : 3·8 : 1

Only with carbon disulphide and carbon tetrachloride does the yield increase proportionately to the concentration of the reacting substances. The results show clearly that, with change of concentration, the arrangement of solvents in the order of their retarding influences on a chemical reaction also changes essentially ; further, that the special influence of the solvents does not vanish with ever increasing dilution.

Further experiments with the various solvents show that there exist three regions of concentration of the reacting substances, distinguished by the following relations : in the first, the region of low concentrations, the reaction is retarded so much that it is only sensible in the first few moments, and, although it begins, it comes almost immediately under the influence of the medium, which opposes the chemical affinity ; in the second region, the strength of the chemical forces begins to overcome the retarding influence of the solvent, in consequence of which the process proceeds further, although still slowly; finally, in the third region of concentration, the chemical forces preponderate to such an extent that the retarding action of the solvent only begins to be felt near the end of the reaction, when the concentration of the reacting substances diminishes. T. H. P.

Application of the Phase Rule in Stereochemistry and the Recognition of Racemic Compounds. ALBERT LADENBURG (*Ber.*, 1911, **44**, 1677. Compare this vol., ii, 265; Van der Linde, this vol., ii, 477; Kruyt, *ibid.*).—The author maintains that his method for the recognition of racemic compounds is applicable to liquid racemates. F. B.

Hydrolysis of Metallic Alkyl Sulphates. W. A. DRUSHEL and G. A. LINHART (*Amer. J. Sci.*, 1911, [iv], **32**, 51—60).—Kremann (Abstr., 1910, ii, 596) has found that the hydrolysis of barium ethyl sulphate is retarded by the addition of dilute (*N*/2) hydrochloric acid, and was unable to find a velocity constant to represent the behaviour of the reaction. The authors find, on the contrary, that the hydrolysis of the ester is accelerated by hydrochloric acid in all dilutions. Both ethyl hydrogen sulphate and the barium salt are hydrolysed extremely slowly by water even at 60°.

When hydrochloric acid is added to a solution of barium ethyl sulphate, double decomposition takes place with formation of a certain amount of ethyl hydrogen sulphate. On the assumption that the two esters (the acid and the barium salt) are of equal stability, and that the rate of hydrolysis is proportional to the total acid and ester concentrations, a comparatively simple formula is derived which represents satisfactorily the course of the reaction, especially when allowance is made for the different degrees of ionisation of the reacting substances.

In strong aqueous hydrochloric acid (2—4*N*), the formation of barium sulphate is probably chiefly due to the hydrolysis of the ethyl sulphuric acid (equation below) to sulphuric acid, and its subsequent combination with the barium chloride liberated from the barium ethyl sulphate by double decomposition: $Ba(SO_4Et)_2 + 2HCl \rightleftarrows BaCl_2 + 2HSO_4Et$. G. S.

Influence of Neutral Salts on the Velocity of Reaction. G. POMA (*Gazzetta*, 1911, **41**, i, 353—383).—After a theoretical summary of this question, the author describes his own experiments on the influence exerted on the hydrolysis of ethyl acetate by hydrochloric, hydrobromic, hydriodic, and nitric acids by varying proportions of potassium, sodium, lithium, barium, strontium, and magnesium salts having similar anions to the acids. The experiments were carried out at 20°.

The results show that all the chlorides used cause the catalytic power of the hydrogen ions to increase to approximately the same extent, the differences nearly coinciding with the limits of experimental error. Using the method indicated by Kay (Abstr., 1900, ii, 198) to calculate the diminution in the dissociation of hydrochloric acid produced by the presence of chlorides, it appears that the percentage increase of the reaction constant increases with the concentration and more rapidly than it. Indeed, the increases divided by the ionic concentrations tend to constancy and to non-dependency on the dilution. The increment of the reaction velocity is greater for salts of the bivalent than for those of the univalent metals, and, among the latter, it increases with diminution of the atomic weight of the alkali metal. Similar results are given by bromides in presence of hydrobromic acid.

The combined results of the whole series of measurements show that the influence of neutral salts on the velocity of reaction depends in high degree on the nature of their anions, the influence of the cations either being non-existent or else coming within the limits of experimental error. The salts examined have the following order of diminishing influence : chlorides, bromides, nitrates, iodides.

These results are in opposition to the view that the influence of neutral salts on the process of hydrolysis is to be referred to an actual concentration of the solution, owing to the formation of solvates. This action exhibits no apparent parallelism with the electro-affinity of the ions into which the neutral salts dissociate, and hence none with their tendency to form complex compounds.

Salts like potassium chloride which do not form solid hydrates, even at low temperatures, exhibit the maximum accelerating effect on the velocity of reaction, whilst those which, like barium bromide, strontium nitrate, etc., crystallise with various amounts of water, show the least influence.

The marked differences in the intensities of the accelerating action exerted by salts similar in constitution and properties tend to exclude a purely physical explanation.

The explanation advanced by Arrhenius that there exists in solution a chemical equilibrium between the active and inactive forms of the substratum, an equilibrium which may be displaced by variations of temperature and ionic concentration, thus remains probably accurate.

T. H. P.

The Development of the Atomic Theory. IV. Dalton's Physical Atomic Theory. V. Dalton's Chemical Theory. VI. The Reception Accorded to the Theory Advocated by Dalton.

Andrew Norman Meldrum (*Mem. Manchester Phil. Soc.*, 1911, **55**, No. 5, 1—22 ; No. 6, 1—18 ; No. 19, 1—10. Compare this vol., ii, 267).—Historical. T. S. P.

Tabular Grouping of the Elements on the Basis of the Periodic System.

Eduard von Stackelberg (*Zeitsch. physikal. Chem.*, 1911, **77**, 75—81).—An arrangement of the elements is described, which, when represented on a plane surface, differs from Mendeléeff's arrangement mainly in that each long period occupies one line and the elements of the two short periods are so placed that the first four come on the extreme left above the first four elements of the long periods, the last four on the extreme right above the last four elements of the long periods, so that blanks are left in the middle of the short periods.

Hydrogen is put in the same vertical row as the alkali metals. The advantages of this method of arrangement are discussed. G. S.

Mendeléeff's "Cubic" Periodic System of the Elements and the Arrangement of the Radio-elements in this System. A. van den Broek (*Physikal. Zeitsch.*, 1911, 12, 490—497).—A "cubic" system suggested by Mendeléeff when only 58 elements were known, is advocated in place of the present "plane" system to embrace the many new series of elements now known in consequence of the discovery of the rare-gases, the recent investigations of the rare-earths, and the disintegration of the radio-elements. The elements are arranged in ascending order of atomic weight in 8 vertical columns, each with 3 vertical lines of elements and 5 horizontal columns, each with 3 horizontal lines of elements. Beginning with horizontal row *A*1, the 8 elements (He—F) occupy the left-hand sub-columns of the 8 vertical columns; in the next horizontal row *A*2 the 8 elements (Ne—Cl) occupy the middle sub-columns; in the next horizontal row *A*3 the next 8 elements (A—Mn) occupy the right-hand sub-columns. At the 25th element (Fe), horizontal column *B*1 commences, the elements being in the left-hand vertical sub-column, and so on for, in all, 120 possible elements. With this arrangement Na, Cu, Ag, and Au, do not appear in the same vertical row, and the differences between the short and long periods of the old system disappear. The "theoretical" atomic weight of the 120 possible elements (excluding hydrogen) are multiples of two up to 240. The sum of all the differences between the actual and "theoretical" atomic weights of all the known elements is very nearly zero. All the α-ray producing radio-elements known and the new rare-earths can be accommodated. On the old system there are 38 elements for 18 places between *W* and *U*; on the new, counting only the α-ray producing disintegration products among the radio-elements, there are 24 elements for 24 places. The Lothar Meyer curves of atomic volume and melting points are simpler on the cubic system than on the old system. F. S.

Radioactivity as a General Property of Matter. Theodor Wulf (*Physikal. Zeitsch.*, 1911, 12, 497—500).—A great number of the known atomic weights are separated by 4 units, the mass of the α-particle. If the known atomic weights are divided by 4 and arranged in columns from 0 to 9 according to the value of the decimal, of the first 25 elements, 11 have the decimal 0, 9 have the decimal 7, the remaining 5 having other values for the decimal. Of the remaining 57 elements, 9 have the decimal 0 and 11 the decimal 7, the remaining 37 elements being distributed over the other values. Of the whole elements, 20 have the decimal 0 and 20 the decimal 7. This suggests that the atomic weights are made up of two series, $4n$ and $4n-1$. Similar generalisations have been made by Rydberg (1886) before the discovery of radioactivity, who pointed out that the elements with even valency fall in the $4n$ series and those with odd valency in the $4n-1$ series. These relations suggest that the whole elementary system results by disintegration from the heaviest elements, the helium atom being the fundamental unit. F. S.

Observations not in Good Agreement with the Existence of Atoms and Molecules. GAETANO MAGNANINI (*Gazzetta*, 1911, **41**, i, 383—384).—The author has already pointed out (*Annuario Univ. Modena*, 1899–1900, **48**) that, not only the consequences of thermodynamics (principle of mobile equilibrium), but, what is more important, chemical phenomena at high temperatures, do not readily accord with the fundamental conception of the atomic and molecular structure of matter.

The chemical association occurring in endothermic reactions : *e.g.*, the formation of ozone from oxygen, of hydrogen peroxide from hydrogen, of oxides of nitrogen from their elements, etc., would not only be unforeseen, but would not be easily explained if, starting from thermodynamical results, they were regarded purely from the point of view of the theory of heat—from the ideas concerning the effects of variation of temperature on the movements of the atomic or molecular particles. It seems probable that the principal reason of the universal acceptance of the atomic and molecular hypothesis lies in its simplicity. T. H. P.

Van't Hoff's Hypothesis and the Dissolved Molecule. ALBERT COLSON (*Bull. Soc. chim.*, 1911, [iv], **9**, 576—583).—To explain peculiarities in the behaviour of certain salts the author suggests that the dissolved particle is generally an aggregate of chemical molecules in accordance with Raoult's law, but independent of the degree of dissociation as measured by conductivity. This suggestion is in harmony with Cahour's rule.

The chief facts cited in favour of this view are as follows: The lowering of freezing point produced by quantities represented by the formulæ $H_2SO_4,(ZnSO_4)_2,Cr_2(SO_4)_3$ and $Cr_4O(SO_4)_5$ is the same, and in its amount does not depend on the conductivity of the solutions. It has been shown already (Abstr., 1908, ii, 45) that chromium sulphates in solution show conductivities independent of their state of ionisation, since the violet sulphate, which is the most ionised, in solution shows the lowest conductivity. Zinc chloride in solution always give results indicating the presence of molecules more complex than $ZnCl_2$. Ferric chloride and certain of the trioses and tetroses give depressions corresponding to molecular weights which are too low.

It is pointed out finally that Mathias' theory of the constitution of liquids show that Raoult's law does not imply identity of molecular particles for gases and liquids, but merely that there should be a certain constancy in the association which gives rise to liquid molecules. Conductivity appears to be a characteristic of particles which, disintegrated by dissociation, hydrolysis or double decomposition, revert to the molecular state. T. A. H.

Relation of Temperature and Molecular Attraction. JAMES E. MILLS (*Phil. Mag.*, 1911, [vi], **21**, 84—113).—Kleeman's views (Abstr., 1910, ii, 492) in regard to the nature of molecular attraction are criticised and shown to be at variance with the relationship $\lambda/\sqrt[3]{d}-\sqrt[3]{D}$ = constant, where λ is the internal heat of vaporisation, d and D the densities of the liquid and saturated vapour respectively at the temperature of vaporisation. For a large number of substances, data are recorded which show that $\lambda/\sqrt[3]{d}-\sqrt[3]{D}$ is nearly independent of the temperature. A further table of data is given to show that Dieterici's relationship $\lambda=CRT\ln d/D$ is in remarkably good agreement with experiment at higher temperatures, but that deviations occur at very low vapour pressures.

The third part of the paper is devoted to a theoretical discussion of the relationship between temperature and molecular attraction. The chief result of this is to justify the author's previous conclusion that change of temperature does not change the nature or the magnitude of the force of molecular attraction. The temperature merely determines the orbit that the molecules will follow in obedience to the attractive force. H. M. D.

Molecular Attraction. IX. Molecular Attraction and the Law of Gravitation. James E. Mills (*J. Physical Chem.*, 1911, **15**, 417—462. Compare Abstr., 1909, ii, 862).—The author's equation connecting internal latent heat with molecular attraction was found to hold with twenty-five non-associated substances. It follows from this equation that the individual forces acting between the molecules as they expand from distance S_1 to distance S_2 apart vary as $\mu M/S^2$, where M is the mass of substance considered, and μ is a constant. If the total force exerted by one molecule on its neighbours is considered, this is equal to $f=\mu m/S^2$, where m is the molecular weight and S the average distance apart of the molecules.

The equation developed by Helmholtz, giving the amount of energy liberated by the contraction of the sun under Newtonian gravitation, can be applied to the contraction of a sphere of saturated vapour to a liquid, and by use of a suitable constant the latent heat can be calculated on the assumption that molecular force like gravitation varies inversely as the square of the distance apart of the molecules.

It is suggested that molecular and gravitational force are identical in nature. The ether in the neighbourhood of the molecule is in a state of stress, the intensity of which is $f=\mu m/S^2$. The author considers that all the usual definitions of mass assume that Newton's law holds. If mass is defined as the attraction exerted by matter instead of the quantity of matter, Newton's law becomes identical with the above law of molecular force; that is, the total gravitational force of a particle with respect to the rest of the universe is a definite quantity depending only on the specific reaction between that particle and the ether. R. J. C.

The Electron Conception of Valence. II. The Organic Acids. K. George Falk (*J. Amer. Chem. Soc.*, 1911, **33**, 1140—1152. Compare Falk and Nelson, this vol., ii, 101).—A theoretical paper, in which the author suggests a classification of organic acids according to the direction of the valences (as determined by the seat of the negative corpuscles) by which the *a*-carbon atom is combined with the other atoms or groups in the molecule. Three classes are thus obtained in which the valence directions are represented respectively by $\begin{smallmatrix}\rightarrow\\\rightarrow\\\rightarrow\end{smallmatrix}\mathrm{C{\cdot}CO_2H}$, $\begin{smallmatrix}\leftarrow\\\rightarrow\\\rightarrow\end{smallmatrix}\mathrm{C{\cdot}CO_2H}$, and $\begin{smallmatrix}\leftarrow\\\leftarrow\\\rightarrow\end{smallmatrix}\mathrm{C{\cdot}CO_2H}$. The ionisation constants of the first group are less than 0·01, those of the second range from 0·1 to 0·4, and those of the third are greater than 2. In certain cases substituents may exert constitutive effects which give rise to intermediate values of the ionisation constants.

The ionisation constants of unsaturated acids are also supposed to be determined by the additive action of the valence directions, and these effects are discussed in detail. H. M. D.

Polarity of Elements and Radicles Measured in Terms of a Logarithmic Function of the Ionisation Constant. C. G. Derick (*J. Amer. Chem. Soc.*, 1911, 33, 1152—1162).—An element or radicle is said to possess positive or negative polarity according to whether it increases the hydroxyl or the hydrogen ion concentration when it is substituted for one of the atoms of hydrogen in water. In other words, a positive radicle increases the affinity constant K_b, whilst a negative radicle increases the constant K_a for water. Since the free energy change (A) and the affinity constant (K) are connected by the equation $A = RT\ln K$, it follows that the free energy of ionisation is a logarithmic function of K. For nearly all organic compounds, $RT\ln K$ is negative, and the greater the positivity or negativity of a substituting radicle, the greater will be the ionisation. Radicles of greatest polarity will therefore have the smallest values for the free energy of ionisation. On this account, the author suggests the expression $-1000/\log K$ as a convenient measure of the polarity. Polarity values, expressed in this way, have been calculated for a large number of organic radicles, and these numbers are tabulated alongside the values of K. H. M. D.

Application of Polarity Measured in Terms of a Logarithmic Function of the Ionisation Constant. I. The Use of Polarity in the Explanation of the Reactions of Aldehydes and Ketones. C. G. Derick (*J. Amer. Chem. Soc.*, 1911, 33, 1162—1167. Compare preceding abstract).—The mechanism of the spontaneous dehydration of the dihydroxy-forms of aldehydes and ketones is discussed in terms of the author's conception of polarity. If the substitution of negative radicles for hydrogen in neutral aldehydes or ketones decreases the hydroxyl ion concentration to the value for pure water, the dihydroxy-form should be completely stable; in other circumstances the aldehyde or ketone must exist for the most part in the inactive dehydrated condition. It is shown that the carboxyl group is probably more negative than chlorine, and on this account the substitution of the carboxyl group for hydrogen in neutral aldehydes and ketones should make the dihydroxy-form stable at the ordinary temperature. Glyoxalic and mesoxalic acids are referred to as substances in which this influence is operative.

The formation of oximes, hydrazones, and semicarbazones is also examined by reference to the conception of polarity. By taking ammonia as unity, the following polarity values have been calculated: ethylamine 1·452, methylamine 1·433, hydroxylamine <1, semicarbazine 0·447, phenylhydrazine 0·592, hydrazine 0·855. For molecules which are less positive than ammonia, the formation of additive compounds is followed by dehydration, whilst molecules which are more positive than ammonia yield stable hydroxy-additive compounds.

H. M. D.

Application of Polarity Measured in Terms of a Logarithmic Function of the Ionisation Constant. II. Scale of Combined Influence of Substitution in Organic Compounds.

C. G. Derick (*J. Amer. Chem. Soc.*, 1911, **33**, 1167—1181. Compare preceding abstracts).—In this paper the author criticises the views of Michael (Abstr., 1900, i, 321; 1906, i, 550, 781; 1907, i, 170) and Flürscheim (Trans., 1909, **95**, 718) relative to the nature of intramolecular action, and maintains the suitability of the so-called polarity values as a measure of the combined direct and indirect influences of substituting radicles on a given atom in the molecule. The relative influence of a substituting atom or group on the ionisation of an acid is obtained by taking the ratio of the polarity values ($-1000/\log k$) of the substituted and unsubstituted acids and subtracting from this the combined influence of the other atoms in the molecule which is equal to unity.

This combined relative influence has been calculated for a large number of substituted organic acids and the values are tabulated. For the β-, γ-, and δ-substituted normal fatty acids, the values representing the influence of various substituents are as follows: chlorine, 0·187, 0·063, 0·023; bromine, 0·210, 0·047, 0·017; iodine, 0·167, 0·035, 0·008; hydroxyl, 0·073, 0·018, —; carboxyl, 0·160, 0·111, 0·083. In no case is the influence less in the β-position than in either the γ- or δ-positions. This result is not in agreement with the conclusions drawn by Michael.

H. M. D.

Application of Polarity Measured in Terms of a Logarithmic Function of the Ionisation Constant. III. Correlation of Chemical Structure with Ionisation.

C. G. Derick (*J. Amer. Chem. Soc.*, 1911, **33**, 1181—1189. Compare preceding abstracts).—It is shown that a general relationship exists between the numbers which are supposed to represent the influence of substitution on the ionisation of organic acids. The "place factors" for chlorine when substituted for hydrogen in normal fatty acids in the α-, β-, γ-, and δ-positions are respectively 0 6825, 0·1873, 0·0627, and 0 0229. These numbers are approximately in the ratio: $1 : 1/3 : 1/3^2 : 1/3^3$. This relationship between the "place factors" is found to hold equally well when hydrogen is replaced by bromine, iodine, hydroxyl, or phenyl. It is not exhibited by acids which contain two carboxyl groups, and for these the deviations increase as the distance between the two carboxyl groups increases. This seems to indicate that both carboxyl groups undergo ionisation.

By means of the above rule of thirds it is possible to calculate the ionisation constants of substituted fatty acids if the α-"place factor" for the given substituent is known. Examples are given to show the degree of accuracy with which this may be carried out.

When two or more hydrogen atoms of a fatty acid are substituted by negative atoms or groups, the influence on the ionisation can be deduced by adding together the "place factors" for the different substituents. This is the case whether the rule of thirds is obeyed or not. H. M. D.

A Self-regulating Gas Burner. FRITZ HANFLAND (*Chem. Zeit.*, 1911, 73, 669).—A patent burner, now obtainable, is described, by the use of which steam-ovens, sterilisers, etc., may be kept at constant temperature somewhat above 100°, the principle involved being similar to that of an arrangement described by Ulsch (*ibid.*, 1895, 51, 1183). The mercury regulator is built into the base of the burner, which is therefore self-contained. J. D. K.

Constant Level Water-Bath. H. MINIOT (*J. Pharm. Chim.*, 1911, [vii], 3, 585—586).—The adjustable tube in the usual constant level apparatus is replaced by two tubes, one of which, provided with a perpendicular vent, just rotates easily inside the other, which is provided with a helical vent. The inner tube takes the water supply, and, as it is rotated, the position of its perpendicular vent in relation to the helical vent of the outer tube, which communicates by a side arm with the bath, determines the water level. Both tubes are enclosed in a third, which has a side-arm to carry away the excess of water. T. A. H.

Arrangement for Collecting the Condensed Water from the Outside of Reflux Condensers. L. DEDE (*Chem. Zeit.*, 1911, 35, 723).—A glass cup is fitted on to the bottom of the condenser, below the inlet tube for the water. The water condensing on the outside of the condenser collects in the cup and runs off through an outlet tube fused into the bottom thereof. T. S. P.

The General Application of the Geryk Air Pump to Vacuum Distillations. G. DOBY (*Chem. Zeit.*, 1911, 35, 756).—In using the Geryk pump for vacuum distillations, the author inserts absorption flasks containing concentrated sulphuric acid, and calcium chloride and phosphoric oxide tubes, to prevent water and alcohol getting at the pump. This method has the drawback that the sulphuric acid rapidly becomes hot and must be changed very often; to obviate this a reflux condenser, preferably three Soxhlet double surface condensers in series, is inserted between the receiver of the distillation apparatus and the absorption flasks. With this arrangement, 8—10 litres of alcohol can be distilled in eight hours under a pressure of 8—10 mm., and a bath temperature of 40—50°, without the sulphuric acid becoming warm in the least. T. S. P.

Safety-valve for Water Pumps. ARMAND BERG (*Bull. Soc. chim.*, 1911, [iv], 9, 621—623).—The author describes a device for insertion between a water-pump and apparatus under evacuation. The device is designed to (1) prevent entry of water into the apparatus should the water pressure fail and a back-flow occur, and (2) re-

establish action when the water pressure becomes normal. The device is figured, and its mode of action described in detail in the original.
T. A. H.

A Safety Wash-Bottle GUSTAV HAPPE (*Chem. Zeit.*, 1911, **35**, 656).—The gas delivery tube of the wash-bottle is enlarged considerably in diameter within the bottle so that it is more than capable of taking the whole of the washing liquid, and a safety funnel is also fused in it. Liquid cannot therefore be sucked back into the bottle, nor can the washing liquid rise up into the inlet tube for the gas. The gas delivery tube is open to its full width at the bottom, in order to prevent any stoppage by the formation of crystals, and the bottom of the tube is also made zig-zag, so as to break up the gas bubbles.
T. S. P.

A Self-acting Wash-Bottle. JOHANN HAIN (*Chem. Zeit.*, 1911, **35**, 697).—The jet-tube of the wash-bottle is elongated to such an extent that when filled with the liquid in the bottle it acts as a siphon.
T. S. P.

Cutting Tubes by Etching. JAROSLAW MILBAUER (*Chem. Zeit.*, 1911, **73**, 669) —A wet string is tied in a single knot round the (porcelain) tube, supported horizontally on fork rests. One end of the string is placed in a suitable vessel above the tube containing aqueous hydrofluoric acid (preferably mixed with 1/3 vol. of hydrochloric acid), the other in an empty vessel below. As etching proceeds the string is tightened, unevenness being avoided by turning the tube and shifting the knot round. When etched far enough, the tube is wrapped in a cloth and severed by bending.

Quartz tubes may be readily cut in like manner. J. D. K.

Preparation of Indigotin as a Laboratory Exercise and as a Lecture Experiment. FRANZ MICHEL (*Chem. Zeit.*, 1911, **35**, 755—756).—Ten parts of phenylglycine-*o*-carboxylic acid, or the corresponding amounts of the sodium or potassium salt, are dissolved in 10—12 parts of a solution of sodium hydroxide (1 : 4 or 6), and the solution evaporated rapidly to dryness on the water-bath. The powdered residue is then added, stirring well meanwhile, to 8—14 parts of paraffin wax (m. p. *ca* 60°) heated at 250—270° in a nickel crucible. The reaction is complete when the fusion has become strongly yellow. The cold product may then be extracted with hot water under exclusion of air (or after addition of sodium hyposulphite), or the paraffin may be dissolved away with chloroform, etc. The indoxyl-containing products are then oxidised to indigotin by boiling the aqueous solution in the air, a 90% yield of indigotin being obtained.

Indirubin may be obtained as follows: the fusion is dissolved in boiling 10% acetic acid, the filtrate from the paraffin made strongly alkaline with ammonia, and the indigotin precipitated by oxidation with a rapid current of air. Extraction with ether then dissolves the indirubin, indigotin remaining undissolved.

For a lecture experiment, 0·5—1 gram of the dry mixture of phenylglycine-*o*-carboxylic acid and sodium hydroxide is heated in a test-tube until water vapour is no longer evolved, and the fusion has become yellow. After cooling, the mass is boiled with 4—5 c.c. water, the test-tube is half-filled with water, and shaken in the air, when indigotin is deposited. T. S. P.

Inorganic Chemistry.

The Replacement of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperatures and Pressures. II. WLADIMIR N. IPATIEFF and W. WERKHOWSKY (*Ber.*, 1911, **44**, 1755—1758).—Having found previously (Abstr., 1909, ii, 564) that the replacement of metals from aqueous solutions of their salts by hydrogen at high temperatures and pressures is accompanied by the formation of oxides, hydrates, and basic salts, the authors concluded that hydrolysis was a very important factor in the reaction. They now show that the reaction between copper sulphate and hydrogen takes place according to the equation:

$$CuSO_4 + H_2 = Cu + H_2SO_4.$$

The formation of a basic salt and of cuprous oxide is due to secondary reactions.

At 25 atmos. and 90° a *N*/10-solution of copper sulphate, in an atmosphere of hydrogen, gives a deposit of a basic salt,

$$CuSO_4,2Cu(OH)_2,$$

after ten to fifteen hours. On further heating, cuprous oxide is formed at the expense of the basic salt, which finally disappears. After forty to fifty hours, crystals of copper begin to form, and the cuprous oxide gradually disappears, until after four to seven days only copper remains. Increase of pressure accelerates the above process, diminution in pressure retarding it, as also does rise in temperature. At 90° and under 200 atmos., complete deposition of the copper takes place.

When sufficient sulphuric acid is present, precipitation of a basic salt and of cuprous oxide does not occur as a preliminary to the deposition of copper. The formation of the basic salt is due simply to hydrolysis, and occurs when a normal solution of copper sulphate is heated in the air under ordinary pressure at 100°; the formation of cuprous oxide takes place only in the presence of hydrogen. The final disappearance of basic salt and cuprous oxide in the experiments recorded above is due to their solution in the sulphuric acid liberated by the replacement of the copper by hydrogen. T. S. P.

Decomposition of Water by Metals. MIROSLAW KERNBAUM (*Compt rend.*, 1911, **152**, 1668—1670).—It is well known that hydrogen and hydrogen peroxide are produced when finely divided zinc, magnesium or aluminium are shaken with water. Hydrogen peroxide is not formed, however, when all traces of free oxygen are excluded. The reaction probably follows the course: (1) $Zn + H_2O = Zn + \overset{-}{OH} + \overset{+}{H}$; (2) $Zn + 2(\overset{-}{OH}) = Zn(OH)_2$; (3) $2\overset{+}{H} + O_2 = H_2O_2$; (4) $Zn + H_2O_2 = Zn(OH)_2$. When oxygen is absent, reactions (3) and (4) do not occur. The decomposition of water by the electric current and by negative electrons emitted by metals is discussed. W. O. W.

Formation of Oxidising Agents in Air Under the Influence of Ultra-violet Light. W. G. Chlopin (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 554—561; *Zeitsch. anorg. Chem.*, 1911, **71**, 198—205. Compare Kernbaum, Abstr., 1909, ii, 364, 714, 717; Courmont, Nogier, and Rochaix, Abstr., 1909, ii, 723; Berthelot and Gaudechon, Abstr., 1910, i, 349; ii, 564, 606).—The author's experiments show that the ordinary moist air of a room, after subjection for a few minutes to the action of ultra-violet light, shows the presence of ozone, hydrogen peroxide, and nitrogen trioxide. T. H. P.

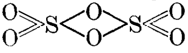
Molecular Weights and Constitutional Formulæ of Nitric and Sulphuric Acids. Giuseppe Oddo and Giovanni Anelli (*Gazzetta*, 1911, **41**, i, 552—568).—It has been shown (Oddo and Scandola, Abstr., 1910, ii, 1035) that in cryoscopically absolute sulphuric acid (that with the highest freezing point, 10·43°, absolute sulphuric acid not existing in the liquid state), methyl sulphate is partly decomposed to form the acid ester, $MeH_3S_2O_8$. The determination of the molecular weight of methyl sulphate in acetic acid or benzene gives results corresponding with Me_2SO_4, and thus excludes the view that the formation of the tri-acid sulphate depends on the existence of a double molecule of methyl sulphate. It hence becomes necessary to assume that sulphuric acid itself has the double formula $(H_2SO_4)_2$.

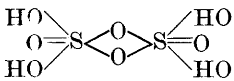
In view of the discordant results which have been obtained by different investigators for the molecular weight of sulphuric acid, the authors have made the three following series of measurements.

I. The vapour density of cryoscopically absolute sulphuric acid, determined by Victor Meyer's method in anthracene or triphenylmethane vapour, gives the molecular weight 101·9 or 100·9. Hence, at 10—20° above the b. p., the vapour of sulphuric acid must represent a mixture of the molecules $(H_2SO_4)_2$, H_2SO_4, SO_3, and H_2O in thermal equilibrium, since the acid undoubtedly undergoes dissociation into SO_3 and H_2O even at the ordinary temperature. This result is confirmed by similar measurements of sulphuric acid containing varying proportions of water, the values obtained for the molecular weight being 119, 100·2, and 103·2. With acid containing an excess of the trioxide, the vapour tube is attacked, dissociation of the trioxide into dioxide and oxygen taking place.

II. The molecular weight of the purest obtainable nitric acid was determined cryoscopically in nitrobenzene (compare Ampola and Carlinfanti, Abstr., 1897, ii, 12) and in ethylene bromide (compare Raoult, Abstr., Abstr., 1884, 952), which are regarded as associating solvents, but the values obtained were only slightly higher than those corresponding with the single molecule HNO_3. Similar values were obtained in acetic (Raoult, *loc. cit.*) and chloroacetic acids (compare Mameli, Abstr., 1910, ii, 182). With ethylene bromide, sulphuric acid containing a little water (m. p. 10·52°) causes the separation of an aqueous layer at the surface, but in nitrobenzene its molecular weight corresponds with the molecule $(H_2SO_4)_2$. In acetic, chloroacetic, and formic acids, sulphuric acid also gives the doubled molecular weight. The conclusion is hence drawn that ordinary sulphuric acid corresponds with ordinary sulphur trioxide, which is dimeric (compare Oddo, Abstr., 1901, ii, 650), and that monosulphuric acid, H_2SO_4, corresponding with the anhydride, m. p. 14·8°, b. p. 46·2°, is not known in the free state. A similar state of affairs exists with the sulphurous compounds, monosulphurous anhydride being known, but not the corresponding acid. An explanation is thus obtained of the considerable interval between the boiling point of sulphuric acid (338°) and those of the anhydride (46·2°) and sulphuryl chloride (69·1°), the differences being much less with the corresponding nitric acid derivatives: N_2O_5, 47°; NO_2Cl, 5°; HNO_3, 86°.

III. To prepare triacid salts, $MH_3(SO_4)_2$, it is only necessary to dissolve the normal sulphates or chlorides in the calculated quantity, or rather more, of cryoscopically absolute sulphuric acid and allow the solution to dry on a porous tile in a vacuum over phosphoric anhydride. To prepare the corresponding salts of organic bases, the calculated quantities of cryoscopically absolute sulphuric acid and the base are poured separately into light petroleum; the sulphate immediately separates as an oil, and can be caused to crystallise. A similar result can be obtained by mixing the base and acid directly in the calculated proportions. These compounds will be described later.

Regarding the constitution of ordinary dimeric sulphur trioxide as represented by:  (compare Oddo, Abstr., 1901, ii, 650), that of ordinary sulphuric acid is best expressed by the annexed formula. A mesohydric formula (compare Oddo, Abstr., 1907, ii, 15) is also suggested.



T. H. P.

Action of the Silent Electrical Discharge on Dry and Moist Ammonia. Adolphe Besson (*Compt. rend.*, 1911, 152, 1850—1852).

—When ammonia and hydrogen dried over potassium hydroxide are submitted to the action of the silent electrical discharge, traces of a substance capable of reducing copper sulphate solution are formed. This may be hydrazine, but the amount was insufficient for identification. In presence of water vapour a small quantity of hydroxylamine is formed. A mixture of ammonia and oxygen under like conditions gives no reducing substance, but forms ammonium nitrate and nitrite.

W. O. W.

Anhydrous Hydrazine. I. A Convenient Apparatus for the Preparation of Anhydrous Hydrazine. C. F. Hale and Fred F. Shetterley (*J. Amer. Chem. Soc.*, 1911, 33, 1071—1076).

—A form of all-glass apparatus is described for carrying out the dehydration of hydrazine hydrate. It consists of a 500 c.c. flask connected by a ground glass joint with a Vigreux distillation column, which at its upper end is fused to a Liebig's condenser, and this communicates with a graduated cylindrical receiver, which is provided at its lower end with a tap, whilst the upper end is connected with a suitable form of pump. An inlet tube for introducing hydrogen is fused through the walls of the 500 c.c. flask. The results of experiments on the dehydration by means of barium oxide, barium hydroxide, and sodium hydroxide are recorded. According to these, barium oxide appears to give the best results, whilst barium hydroxide is very much less efficient. H. M. D.

Aqua Regia. William C. Moore (*J. Amer. Chem. Soc.*, 1911, **33**, 1091—1099).—The behaviour of aqua regia as an oxidising agent is discussed in reference to experiments on the oxidation of mercuric sulphide, lead sulphide, and arsenious sulphide, and of solutions of ferrous ammonium sulphate by nitric acid and by solutions containing hydrogen, nitrate, and chloride ions. The preliminary results show that there are differences in the rates of oxidation which may be due to the influence of excess of hydrogen ions or to a catalytic action of the chloride ion. In the oxidation of ferrous salts the chloride ion appears to act as a negative catalyst. H. M. D.

Action of Syrupy Phosphoric Acid on Alloys Prepared by the Electric Furnace. Max Wunder and B. Janneret (*Compt. rend.*, 1911, **152**, 1770—1771).—Certain metals and alloys difficult to attack in the ordinary way are readily dissolved when in a finely divided condition, by heating with phosphoric acid, D 1·75. Silicon after three hours' treatment at 230° gives a colourless liquid, with a gelatinous substance in suspension. Zirconium is dissolved in a few minutes, tungsten less rapidly. Ferrosilicon, ferrotitanium, ferrozirconium, ferrovanadium, silicomanganese, titanium nitride, boron nitride, and ferrosilicon containing aluminium all give clear liquids. Carborundum is entirely decomposed in three hours, giving a syrupy liquid containing a gelatinous precipitate. Carbon in the alloys remains undissolved. Addition of water or acids to the above solutions, produces no precipitate. W. O. W.

Compounds of Sulphur and Phosphorus. II. Syntheses with Yellow Phosphorus. Julius Mai (*Ber.*, 1911, **44**, 1725—1727. Compare this vol., ii, 484).—Hot solutions of sulphur in aromatic hydrocarbons readily dissolve yellow phosphorus, and at higher temperatures the products of reaction are obtained in the crystalline form.

To prepare P_4S_7, a cold saturated solution of 3 grams of phosphorus and 5·2 grams of sulphur in carbon disulphide is added to 20 grams of naphthalene heated to 110°; the temperature is gradually raised to 195°. The sulphide crystallises out on cooling, and is purified by extraction of the naphthalene with carbon disulphide, benzene, and light petroleum successively.

The pentasulphide, P_4S_{10}, is prepared similarly, using 4 grams of phosphorus, 13 grams of sulphur, and 35 grams of naphthalene.

Naphthalene as a solvent can be replaced by xylene, using iodine as a catalyst, but even with excess of sulphur the heptasulphide, P_4S_7, only is obtained.

Attempts to prepare the trisulphide, P_4S_3, in the above manner met with no success. T. S. P.

Allotropic Modifications of Arsenic and its Melting Point. PIERRE JOLIBOIS (*Compt. rend.*, 1911, **152**, 1767—1769. Compare Güntz and Broniewsky, Abstr., 1907, ii, 948).—From observations by the thermal method the existence of only two allotropic modifications of arsenic is admitted. The ordinary grey variety is stable up to its m. p., 850° (± 10°). This was determined in a quartz tube by means of a thermocouple. A yellow vapour began to be visible at 700°, and the liquid remained turbid up to 1100°. The unstable form of arsenic prepared by the action of stannous chloride on a solution of arsenious oxide in hydrochloric acid undergoes an irreversible transformation into the grey variety at 285°; it appears to be identical with the lustrous modification formed when the element is distilled in a vacuum. W. O. W.

The Adsorption of Arsenic by Aluminium and Ferric Hydroxide. GEORG LOCKEMANN and M. PAUCKE (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 273—288).—The results of the experiments with ferric hydroxide have been described previously (this vol., ii, 485). When aluminium hydroxide is precipitated from a solution containing arsenic as arsenite or arsenate, the arsenic is adsorbed by the precipitated hydroxide. The removal of the arsenic takes place more readily at 80—90° than at the ordinary temperature. From solutions which contain less than 20 mg. of arsenic per 100 c.c., the arsenic can be completely removed by the precipitation process, but the quantity of hydroxide requisite for this is very large, the ratio $Al(OH)_3$:As increasing from about 15,000 in the more concentrated solutiohs to about 100,000 in the most dilute solutions investigated. Arsenic is also partly removed by adsorption when solutions of egg-albumin and blood-serum are coagulated. Adsorption effects are further found when arsenic solutions are shaken up with animal charcoal. H. M. D.

The Boric Acids. ALFRED HOLT (*Mem. Manchester Phil. Soc.*, 1911, **55**, No. 10, 1—9).—The experiments described in this paper were carried out to see whether the meta- and pyro-acids were really definite compounds or mixtures, and whether any other acids existed.

In the first series of experiments, a weighed amount of orthoboric acid was heated in a platinum dish at constant temperatures of 98°, 120°, and 150° respectively, and the loss in weight determined from time to time. The second series of experiments consisted in the determination of the melting points of mixtures of orthoboric acid and boric anhydride, intimate mixtures of these two substances being heated in sealed capillary glass tubes. The changes in vapour pressure on heating orthoboric acid at 70° and 180° were next examined. Finally, cryoscopic measurements were made on the molecular condition of the boric acids in aqueous solution; three portions of the ortho-acid were heated until one had the composition of metaboric acid, the second of pyroboric acid, and the third was completely dehydrated. Solutions of these portions, as well as the ortho-acid, were then prepared of such strength that each contained the same amount of boric anhydride per c.c. of water.

The results arrived at are as follows: Metaboric acid is probably a definite compound, or hydrate of boric anhydride. No clear evidence can be found for the existence of any acid containing less water than metaboric acid. Only orthoboric acid can exist in solution, under which conditions it is present in simple molecules. Metaboric acid cannot be regarded as an equimolecular mixture of orthoboric acid and boric anhydride. Fused mixtures of orthoboric acid and boric anhydride, in which the molecular ratio of the latter to the former compound exceeds 4 : 1, can exist in a vitreous metastable and a crystalline form.

Orthoboric acid is readily soluble in hot glacial acetic acid, from which it separates out unchanged on cooling. The pyro-acid and boric anhydride are insoluble, whilst metaboric acid dissolves to a very slight extent, the solution depositing the ortho-acid on cooling.

T. S. P.

Preparation of Selenium Boride from Iron and Manganese Borides. J. HOFFMANN (*Chem. Zeit.*, 1911, **35**, 713).—When iron boride (ferroboron) is heated in selenium vapour, a porous mass similar in appearance to ferrous sulphide is obtained, which is contaminated by a yellowish-grey product. The latter substance is selenium boride, B_2Se_3, as shown by its interaction with water. A similar action takes place when iron boride is heated in a current of hydrogen selenide, but the method is not a convenient one, as the temperature required is very near the softening point of hard glass.

Manganese boride reacts with selenium vapour at a red heat, forming a homogeneous yellow to yellowish-green mass, which is a mixture of selenium boride and manganese selenide. T. S. P.

Pyrogenic Reactions of Carbon Dioxide with Carbon Disulphide and Hydrogen Sulphide. RICHARD MEYER and SIEGFRIED SCHUSTER (*Ber.*, 1911, **44**, 1931—1944).—In the elementary analysis of organic sulphur compounds, Meyer and Stadler (Abstr., 1884, 1215) found that carbon monoxide was sometimes produced. Its formation was explained by the reduction of carbon dioxide by sulphur dioxide formed during the combustion. The authors in question obtained small quantities of carbon monoxide when they passed a mixture of carbon and sulphur dioxides over glowing copper spirals, but the present authors find that only a trace of carbon monoxide is formed when such a mixture is passed through a red-hot tube, whether the tube is empty or filled with copper. It is possible that carbon disulphide is produced during the combustion of the sulphur compounds, and the authors find that considerable quantities of carbon monoxide are produced when a mixture of carbon dioxide and disulphide is passed through a red-hot tube, the reaction being $CO_2 + CS_2 \rightleftarrows 2CO + S_2$; it is reversible. Possibly also the reaction $CO + S \rightleftarrows COS$ takes place.

Other gases, such as hydrogen sulphide and water vapour, might be present in the combustion tube, and the authors find the following reactions to take place at a red-heat: $CO_2 + H_2S \rightleftarrows CO + H_2O + S$. Hydrogen is formed at the same time by the reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2.$$

The following reactions take place between carbon disulphide vapour and moist carbon dioxide at a red-heat: (1) $CO_2 + CS_2 \rightleftarrows 2CO + 2S_2$; (2) $CO + S + H_2O \rightleftarrows CO_2 + H_2S$. Subsidiary reactions are: (3) $CO + S \rightleftarrows COS$, and (4) $H_2S \rightleftarrows H_2 + S$.

Mixtures of sulphur dioxide and carbon disulphide, both dry and in the presence of water vapour, and moist or dry mixtures of carbon dioxide and sulphur vapour do not give rise to carbon monoxide when heated.

It is, therefore, probable that the formation of carbon monoxide observed by Meyer and Stadler was due to the action of carbon disulphide, or other volatile organic sulphur compound, on carbon dioxide; also, possibly, the reaction between carbon dioxide and hydrogen sulphide may play some part. T. S. P.

Carbon Telluride, CTe_2. ALFRED STOCK and HERBERT BLUMENTHAL (*Ber.*, 1911, **44**, 1832—1838).—When an arc is formed under carbon disulphide between a tellurium cathode and a graphite anode (compare Abstr., 1905, ii, 315), the tellurium is rapidly vaporised, and condenses, for the most part, in the form of a fine black powder. At the same time the carbon disulphide becomes yellow to brownish-red in colour, and acquires a penetrating, very disagreeable odour. On exposure to daylight, the filtered solution soon, in direct sunlight immediately, deposits a black precipitate. If the yellow solution is concentrated by evaporation on the water-bath, and then heated in a sealed evacuated tube at 175° for forty-eight hours, a greyish-black deposit is obtained, the carbon disulphide not being affected.

Investigation of this greyish-black deposit showed it to consist of carbon and tellurium. It was analysed by heating in a vacuum to sublime the tellurium from the carbon, and weighing the carbon and tellurium separately, the carbon also being burned to dioxide and weighed. The results point to the formula CTe_2 for the unstable compound dissolved in the carbon disulphide, which is readily decomposed by exposure to light or a high temperature.

On evaporation, the yellow solution in carbon disulphide leaves a viscid, brown residue, which will again dissolve to a yellow solution if immediately treated with the solvent, but otherwise becomes solid and greyish-black in a few seconds, decomposing into carbon and tellurium. The same solution at $-100°$ gives glistening, brown crystals, which dissolve on slightly raising the temperature.

The solution of carbon telluride has an unbearable penetrating odour, even when so dilute as 0·1%. Smelling a somewhat stronger solution for only a short time is enough to impart an intense odour of garlic to the breath for several days. T. S. P.

Preparation of Colloidal Silicic Acid. ERICH EBLER and M. FELLNER (*Ber.*, 1911, **44**, 1915—1918).—Completely clear and stable colloidal solutions of silicic acid are obtained when silicon tetrachloride vapours, diluted with an indifferent gas, are passed into water through a mercury trap, the water being continuously stirred. A solution obtained by treating 500 c.c. of water with 10—20 grams of silicon tetrachloride could, after dialysis, be concentrated until it contained 9% of silica without gelatinising. The specific conductivity of a solution obtained from 40 grams of silicon tetrachloride and 2000 c.c. of water was $\chi_{18} = 1 \cdot 7 \times 10^{-5}$ after dialysing for twenty-two days.

Colloidal solutions of silicic acid obtained by Graham's method from sodium silicate and hydrochloric acid still contain sodium after very prolonged dialysis. T. S. P.

Hydrates of Potassium Thiosulphates, their Solubility, and Transition Points. INOHIKO JO (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, **3**, 41—49).—The solubility has been determined at 0° and between 17° and 89°, and from the curve obtained the transition points of the hydrates, namely, 35·0°, 56·1°, and 78·3°. The course of the curve indicates another break between 0° and 17°. The composition of the long-known hydrates has also been confirmed by analysis of the residues at intermediate temperatures, namely: $K_2S_2O_3,2H_2O$; $3K_2S_2O_3,5H_2O$; $K_2S_2O_3,H_2O$; $3K_2S_2O_3,H_2O$. Above 78·3° the salt is anhydrous. J. D. K.

Sodium Potassium Carbonates. YUKICHI OSAKA (*Mem. Coll. Sci. Eng. Kyōtō*, 1911, **3**, 55—61).—Two double salts are described in the literature of the subject: $Na_2CO_3,K_2CO_3,12H_2O$ and

$$2Na_2CO_3,K_2CO_3,18H_2O.$$

The author has determined the solubility of the mixed carbonates at 25°, and draws the conclusion that the only double salt that can exist in presence of its solution corresponds with the former. His results agree closely with those obtained at 24·2° by Kremann and Zitek (Abstr., 1909, ii, 572), who, however, give $6H_2O$, which the author has traced to an error in calculation. J. D. K.

Reaction between Sodium and Mercury. LOUIS KAHLENBERG and DAVID KLEIN (*J. Physical Chem.*, 1911, **15**, 471—473).—The liberation of hydrogen when sodium is dissolved in mercury has often been observed, and Lockyer (*Chem. News*, 1879, **40**, 101) found it impossible to obtain sodium free from hydrogen even by heating it in a vacuum. The authors find that if clean dry sodium of ordinary quality is dissolved in mercury in absence of water no hydrogen whatever is liberated. No hydrogen could be detected in the sodium in ordinary use. R. J. C.

The "De-salting of Sea-Water" According to Aristotle. EDMUND O. VON LIPPMANN [and ERNST ERDMANN] (*Chem. Zeit.*, 1911, **35**, 629—630).—Erdmann has investigated the percolation of a 3% salt solution through porous pots and through the so-called Italian pitchers, which are used in the summer for cooling water. In both cases it was found that the water which percolates through the fresh vessels when immersed in the salt solution is salt. When, however, a pitcher was used which had previously been immersed in fresh water for some time and then dried before being immersed in the salt water, in forty-five minutes 50 c.c. of water had percolated through, which was quite sweet, and gave only a very slight opalescence with silver nitrate. The pitcher had retained so much of the fresh water in which it was previously immersed that the hydrostatic pressure caused by immersion in the salt water forced it to percolate into the interior.

The above observations offer an explanation of a statement of Aristotle that when a corked empty vessel is immersed in sea-water, the water which percolates through is fresh. According to the Greek version the vessel used was made of wax (*ἀγγεῖον χήρινου* = wax vessel; but since wax is completely impervious to water, the author suggests that the rendering should be *ἀγγεῖου χέραμου* = earthenware vessel). T. S. P.

Reciprocal Solubility of Sodium Carbonate and Sodium Hydrogen Carbonate in Water. EDOUARD HERZEN (*Bull. Soc. chim. Belg.*, 1911, **25**, 227—234).—De Paepe (this vol., ii, 489) has deduced from his experimental results on the reciprocal solubility of sodium carbonate and hydrogen carbonate in water that the former dissociates into $Na^{\cdot}$ and $NaCO_3'$ ions, the latter into $H^{\cdot}$ and $NaCO_3'$ ions. The author points out the impossibility of the existence of any appreciable amount of $H^{\cdot}$ ions in alkaline solution, and shows, on the basis of an extension to ternary electrolytes of van't Hoff's treatment of equilibrium in salt solutions, that the results of de Paepe are fully in accord with the usual assumptions that the ions chiefly present in such solutions are $Na^{\cdot}$, $NaCO_3'$, CO_3'', and HCO_3'. G. S.

An Allotropic Form of Silver. DRAGOMIR PALITSCH (*Bull. Acad. roy. Belg.*, 1911, **5**, 395—414).—Zinc silver alloys containing 7—10% of silver were prepared, and the zinc extracted at low temperature by means of hydrochloric acid. The silver remains behind in the form of a greyish-white powder, which assumes a metallic appearance when compressed. From measurements of the density, the rate at which it dissolves in mercury, the heat of solution in mercury, and the difference of potential which is set up in contact with a solution of a silver salt, the author draws the conclusion that this form of silver represents an allotropic modification. H. M. D.

Nature of the Photochlorides of Silver. KONRAD SICHLING (*Zeitsch. physikal. Chem.*, 1911, **77**, 1—57). EMIL BAUR (*ibid.*, 58—65). —See this vol., ii, 680, 681.

Plastic Calcium Fluoride. ROBERT COHN (*Zeitsch. angew. Chem.*, 1911, **24**, 1209. Compare Atterberg, this vol., ii, 605).—When calcium fluoride is precipitated by the addition of milk of lime or of calcium carbonate to a very dilute aqueous solution of hydrofluoric acid, it forms a white, deliquescent mass. If this is collected and powdered after drying in the air or by gentle warming, the powder obtained can be rolled into wire after the addition of 20—25% of water, whereas with 30% of water the mixture obtained flows. Calcium fluoride is thus a plastic substance. T. S. P.

Isomorphous Mixtures of Anhydrous Calcium, Magnesium, and Iron Carbonates. W. DIESEL (*Zeitsch. Kryst. Min.*, 1911, **49**, 250—277).—Working on the lines suggested by G. Linck for the artificial production of dolomite (this vol., ii, 294), solutions of calcium chloride, magnesium sulphate, magnesium chloride, ammonium sesquicarbonate, and ferrous-ammonium sulphate were mixed together in various proportions and of various strengths, the experiments being preformed in an atmosphere of carbon dioxide. The gelatinous precipitates after some hours became crystalline, taking the form of minute spherules with weak negative birefringence. The precipitates, dried and filtered in an atmosphere of carbon dioxide, were analysed, and it was found that whilst calcium and iron carbonates mixed together in all proportions, only little magnesium carbonate (not more than 5%) enters into the composition of the spherules. The filtrates from these precipitates contained no iron, only little calcium, and much magnesium. The size and form of the spherules vary with the amount of iron they contain. Determinations of the sp. gr. show that the calcium carbonate is present in the spherules as vaterite (a spheroidal form of calcium carbonate with D 2·54). Vaterite is more active than aragonite, and aragonite more active than calcite, in precipitating iron from a solution of ferrous sulphate. When a mixed magnesium-calcium carbonate is placed in a ferrous sulphate solution, the magnesium is replaced by iron more quickly than is the calcium. L. J. S.

The Ternary System $CaO-Al_2O_3-SiO_2$. A Study of the Constitution of Portland Cement Clinker. EARNEST S. SHEPHERD and GEORGE A. RANKIN (With Optical Study by FRED E. WRIGHT). (*J. Ind. Eng. Chem.*, 1911, **3**, 211—227; *Zeitsch. anorg. Chem.*, 1911, **71**, 19—64).—The method chiefly used for determining the limits of the various fields in the ternary system was as follows: A small amount of material of the desired composition was placed in a furnace and kept at constant temperature until, on quenching, only one kind of crystal was present, the rest of the solution being cooled to a glass before it had time to crystallise. Temperatures could thus be found where the product was wholly glass or wholly crystalline.

In earlier work with mixtures of pure lime and silica, two compounds, the metasilicate, CaO,SiO_2, and the orthosilicate, $2CaO,SiO_2$, were definitely established, but no trace of the hitherto generally accepted tricalcium silicate could be found. The latter compound is formed immediately, however, in the ternary system on the addition of alumina to mixtures of appropriate lime-silica concentration, and the authors have been able to prepare it pure, except for a small excess (between 1 and 2%) of orthosilicate or lime or both. It appears to be unstable at its m. p., and so does not form from a melt of this composition. For the same reason, it does not form eutectics with the adjacent compounds, calcium orthosilicate and lime. Neither is there any evidence that it takes up calcium orthosilicate or lime in solid solution.

A new and probably unstable form of calcium orthosilicate has been obtained by cooling an old and hydrated sample of the orthosilicate rapidly from 1425°; it yields weakly birefracting and optically positive crystals.

In the ternary system nineteen quintuple points are indicated, and the location of the following five have been fixed:

CaO	59·5	58·5	52·8	49·2	48·5
Al_2O_3	32·5	33·0	40·5	44·0	42·0
SiO_2	8·0	8·5	6·7	6·8	9·5

If solid solutions are formed, they are very limited in extent, and are not sufficient to affect the optical properties either of the silicates, lime, or aluminates.

The diagram indicates that the constitution of slag cement will be seriously affected by relatively small differences of composition in the neighbourhood of the lime joining the compounds calcium orthosilicate and $2CaO,Al_2O_3,SiO_2$.

Ferric oxide appears not to form solid solutions with CaO, $3CaO,SiO_2$, Ca_2SiO_4, or $3CaO,Al_2O_3$. It appears to react in some way with $5CaO,3Al_2O_3$, but the nature of this reaction has not yet been studied.

Attention is called to the fact that ferric oxide dissociates at about 1400° with the formation of Fe_3O_4.

A full description is given of the optical properties of the many compounds which occur in the various binary systems and in the ternary system. T. S. P.

Artificial Crystallisation of Barium Sulphate. HERMON C. COOPER, T. S. FULLER, and A. A. KLEIN (*J. Amer. Chem. Soc.*, 1911, **33**, 845—847).—Barium sulphate crystals, 5 mm. long and 1 mm. wide, have been obtained by crystallisation from fused barium chloride and from fused sodium sulphate. They were orthorhombic, had n_D about 1·648, and agreed in these and other respects with the characters of natural barium sulphate (barite) as recorded by Groth.

Le Chatelier's statement (Abstr., 1897, ii, 135), with reference to the curve representing the m. p.'s of mixtures of sodium sulphate with increasing proportions of barium sulphate, could not be confirmed.

E. G.

Analysis of Aboriginal Copper Objects from Mexico and Yucatan. AUGUSTUS H. FISKE (*J. Amer. Chem. Soc.*, 1911, **33**, 1115—1116).—Analyses of four small copper bells are recorded which show that the original metal of the three objects from Yucatan must have been nearly pure copper. Traces of iron, silver, gold, and silica were found.

In the case of the bell from Mexico, 19·3% of lead was present.

H. M. D.

Formation of Double Salts. HARRY W. FOOTE and PERCY T. WALDEN (*J. Amer. Chem. Soc.*, 1911, **33**, 1032—1036).—From experiments in which varying proportions of cupric chloride, potassium chloride, and ethyl alcohol or acetone were shaken up at 25° until equilibrium was attained and the solution and residue analysed, it is found that the only double salt formed is $CuCl_2,KCl$. In both cases the cupric chloride combines with the solvent to form solid phases of the composition $CuCl_2,EtOH$ and $CuCl_2,C_3H_6O$ respectively. Similar determinations made with cupric chloride, ammonium chloride, and ethyl alcohol indicate the formation of solid $CuCl_2,NH_4Cl$ and $CuCl_2,EtOH$. H. M. D.

Vapour Pressures of Mercuric Chloride, Bromide, and Iodide. FREDERICK M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1911, 33, 777—781).—The values of the vapour pressures of mercuric chloride, bromide, and iodide which have been recorded previously show considerable disagreement, and determinations have therefore been made by the method employed for measuring the dissociation pressures of the ammonium halides (Abstr., 1908, ii, 157; 1909, ii, 23).

In the case of mercuric chloride, the vapour-pressure curve shows a decided break at 277°, corresponding with the m p. as found by Jonker (Abstr., 1910, ii, 127). The b. p. is 302·5°/760 mm.

The curve obtained for mercuric bromide shows the m. p. to be 236° and the b. p. 318°/760 mm.

The mercuric iodide curve does not show any decided change in the neighbourhood of the m. p. By extrapolation, the b. p. was found to be about 351°/760 mm. E. G.

The Stearate Separation of the Rare Earths. CHARLES W. STODDART and C. W. HILL (*J. Amer. Chem. Soc.*, 1911, 33, 1076—1090).—The fractionation of rare-earth mixtures can be conveniently effected by means of an alcoholic solution of potassium stearate which is added to a neutral solution of the earth nitrates in successive quantities sufficient for the precipitation of a portion of the earths present. To obtain good results, the hot alcoholic stearate solution should be added drop by drop to the cold dilute solution of the earth nitrates, the mixture being agitated by a glass stirrer driven at high speed by means of a small electric motor.

The method is applied to the fractionation of the yttrium earths from monazite, and it is shown that the separation of nearly pure yttrium can be effected by quite a small number of fractionations. As has been already found in the application of other methods, there is a slowing down in the progress of the fractionation at the portion which corresponds with an atomic weight of about 102. When applied to the yttrium earths from gadolinite, the stearate method affords a rapid separation without any pause at the fraction of atomic weight 102.

Experiments are also described which show that the gadolinium earths and the members of the cerium group may be separated by fractional precipitation as stearates.

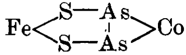
With a view to separating the rare earths of the yttrium series, these were treated with various organic liquids, but fractionation by this method was found to be impossible. H. M. D.

Solubility of Aluminium Hydroxide. WALTER HERZ (*Zeitsch. Elektrochem.*, 1911, **17**, 403—404).—Polemical against Slade (*ibid.*, 261). T. E.

The Crystallisation of White Cast Iron. CARL BENEDICKS (*Intern. Zeitsch. Metallographie*, 1911, **1**, 184—191).—The crystallisation of a eutectic mixture, such as that of white cast iron, takes place in such a way as to form "colonies" of definite orientation, having the external form and appearance of homogeneous crystals. The natural cleavage planes of white iron containing an excess of cementite exhibit forms due to the influence of surface tension. C. H. D.

A Fourth Recalescence in Steel. JOHN O. ARNOLD (*Intern. Zeitsch. Metallographie*, 1911, **1**, 192—203).—A thermal investigation of steels containing varying amounts of carbon, and a comparison with iron free from carbon, show that a development of heat occurs during the cooling of steel between the points Ar_3 and Ar_1. The maximum development of heat occurs in steels containing about 0·45% C, that is, consisting of equal parts of ferrite and pearlite. It is attributed to constitutional segregation of the solid solution to form microscopically distinct masses, which begins at Ar_3 and is complete at Ar_1. C. H. D.

The Cementation of Chromium Steels. FEDERICO GIOLITTI and F. CARNEVALI (*Atti R. Accad. Sci. Torino*, 1911, **46**, 558—568).—A chromium steel, containing 2·33% Cr, 0·41% C, 0·15% Si, and 1·02% Mn, is subjected to cementation in the manner employed for nickel steel (this vol., ii, 609). Cementation for five hours in ethylene at 950° and at 1050°, with carbon monoxide at the same temperatures, and with carbon and carbon dioxide in different proportions at 1000° and 1100°, show that the differences in the action of these cementing agents observed in the case of carbon steels (Abstr., 1910, ii, 616) also occur with chromium steel. In general, the presence of chromium tends to give rise to an increase in the maximum concentration of carbon in the cemented zone, as compared with that found in a carbon steel cemented under the same conditions. C. H. D.

Experiments with Glaucodote. A. BEUTELL (*Centr. Min.*, 1911, 411—415. Compare this vol., ii, 485).—Glaucodote, when heated in a cathode vacuum, yields a distillate containing 1·10% of sulphur and 5·43% of arsenic. When the material is alternately roasted and distilled in a vacuum, the yield is 4·38% of sulphur and 23·37% of arsenic. The effect of the roasting is to produce disulphide, which in the vacuum decomposes into monosulphide and sulphur. Less arsenic is distilled from glaucodote than from mispickel. The constitutional formula deduced from these experiments is  $Fe\begin{matrix}\diagup S-As \diagdown \\ \diagdown S-As \diagup\end{matrix}Co$, analogous to that arrived at for mispickel. The material, from Håkansboda, Sweden, used in the experiments gave analysis I; deducting copper with the corresponding amounts of iron and sulphur as copper-pyrites, the results under II are obtained.

	S.	As.	Fe.	Co.	Ni.	Cu.	Total.
I.	20·35	38·80	21·83	16·36	0·46	1·93	99·73
II.	19·56	41·22	21·39	17·37	0·46	—	100·00

L. J. S.

Ferroso-ferric Oxide and Ferrous Oxide. SIEGFRIED HILPERT and JOHANNES BEYER (*Ber.*, 1911, **44**, 1608—1619).—The reduction of ferric oxide at 500° by a mixture of hydrogen and steam shows a sharp break in the velocity of reaction when the composition Fe_3O_4 is attained. From this observation, the following method for preparing pure Fe_3O_4 has been worked out. Ferric oxide is reduced at 400° in a current of hydrogen which has previously passed through wash-bottles containing water at 30—50°. A reduced copper spiral should be inserted between the ferric oxide and the wash-bottles. If the concentration of the aqueous vapour, which at the temperature of the experiment gives a definite partial pressure of oxygen in the presence of the excess of hydrogen, is diminished, metal is produced and not oxides richer in ferrous oxide. At higher temperatures, however, and with increasing concentration of aqueous vapour, products richer in ferrous oxide are formed. Thus, at 700°, the oxide contained 85% FeO, and at 800°, 92% FeO, the concentration of the aqueous vapour being 38%. Further increase of temperature to 1100° did not, however, give pure ferrous oxide, the purest containing 1·5% Fe_2O_3.

Endeavours to prepare pure ferrous oxide by oxidation of iron with a mixture of hydrogen and steam were unsuccessful, and the various methods given in the literature for the preparation were found to be unsatisfactory.

Magnetic measurements on the various powdered ferroso-ferric oxides obtained indicate the existence of solid solutions. T. S. P.

The Oxidation of Ferrous Salts. CHARLES BASKERVILLE and RESTON STEVENSON (*J. Amer. Chem. Soc.*, 1911, **33**, 1104—1106).—When oxygen or air is passed through neutral or acid solutions of ferrous salts at the ordinary temperature, oxidation only takes place to a very small extent. The presence of salts of cobalt, chromium, copper, manganese, molybdenum, nickel, titanium, vanadium, and tungsten has no appreciable effect on the rate of oxidation. Dust particles, glass wool, and pumice stone behave similarly, but in presence of platinised asbestos oxidation occurs readily. At temperatures near the boiling point, the rate of oxidation is much greater in all cases.

In alkaline solution, ferrous iron is oxidised quite readily at the ordinary temperature.

From these observations, the conclusion is drawn that the expulsion of air during the reduction of iron solutions by zinc is unnecessary.

H. M. D.

Fluorides of Cobalt and Nickel. N. COSTACHESCU (*Ann. Sci. Univ. Jassy*, 1911, **7**, 5—13).—No matter in what way the experimental conditions were varied, the author has not succeeded in preparing the compounds $CoF_2,5HF,6H_2O$ and $NiF_2,5HF,6H_2O$, described by Böhm (Abstr., 1905, ii, 249).

Hexa-aquofluorides of cobalt and nickel do not exist, but the tetra-aquo-salts are readily obtained, the cobalt salt forming two isomerides, α and β. *α-Cobalt-hexa-aquofluoride*, $(H_2O)_4CoF_2$, is obtained in the form of large, garnet-red, rhombic octahedra by dissolving freshly-prepared cobalt hydroxide in 40% hydrofluoric acid, diluting the resulting solution with an equal volume of the acid, and allowing it to crystallise in a vacuum over strong sulphuric acid. The *β-salt* is produced when the above solution is precipitated with 96% alcohol; it forms small, rose-coloured crystals, and is isomorphous with the corresponding nickel salt. The β-salt is more soluble in water (the saturated solution at room temperature is 2·3203%, whilst that of the α-salt is 2·2328%) and hydrofluoric acid than the α-salt; it also loses water more readily, at 60° losing 37·10% H_2O, whilst the α-salt loses only 9·35%, and is more reactive than the α-salt. Both salts give identical solutions in water, as shown by measurement of the electrical conductivity. It is probable that the solids are stereoisomerides, in the α-form the fluorine atoms being situated at the opposite ends of one of the axes of the octahedron, whilst in the β-form they are at the opposite ends of one of the sides.

The *pyridine* derivative, $[(H_2O)_2CoPy_4]F_2,H_2O$, is obtained by dissolving either the α- or β-salt in warm pyridine, filtering the solution, and allowing it to crystallise. It forms brick-red, acicular crystals, which gradually lose pyridine on exposure to the air, leaving the compound $(H_2O)_4CoF_2$, the extra molecule of water being absorbed from the air. The same compound forms the residue obtained by evaporation of the solutions in alcohol or water.

Nickel hexa-aquofluoride, $(H_2O)_4NiF_2$, is prepared similarly to the cobalt compound, and forms very pale green crystals. By solution in pyridine, the *derivative*, $[(H_2O)_2NiPy_4]F_2,H_2O$, is obtained in the form of azure-blue crystals, which possess properties similar to those of the corresponding cobalt compound. T. S. P.

Metal–Nitroso-compounds. VOLKMAR KOHLSCHÜTTER and P. SAZANOFF (*Ber.*, 1911, **44**, 1423—1432).—The authors discuss the results hitherto obtained in the investigation of the absorption of nitrous oxide by solutions of ferrous and ferric salts (compare Abstr., 1910, ii, 956, 1055; this vol., ii, 272); at the same time they contribute some new results with respect to the optical behaviour of such solutions.

The absorption of nitric oxide by a 0·04*N*-solution of a ferrous salt causes the appearance of a broad absorption band in the yellow, extending from 605 to 565 μμ, and corresponding with the reversible reaction: $Fe^{\cdot\cdot} + NO \rightleftharpoons Fe(NO)^{\cdot\cdot}$. If increasing concentrations of hydrochloric, hydrobromic, or sulphuric acid are added to the solution of the ferrous salt, the absorption of nitric oxide increases, although it never exceeds 1 atom of nitric oxide to 1 atom of iron; at the same time the colour of the solution changes, and the absorption band in the yellow gradually disappears. The absorption of nitric oxide is now characterised by the formation of complex anions, which are more stable than the complex cations mentioned above, as, for example, shown by the equation :

$$(FeCl_{2+x})'^{x} + NO \rightleftarrows [FeCl_{2+x}(NO)]'^{x}.$$

Solutions of ferrous chloride in methyl and ethyl alcohol, acetone, ethyl acetate, etc., containing nitric oxide are optically similar to the solutions in concentrated hydrochloric acid, whereas the solutions in formic acid, pyridine, etc., show the characteristic absorption band of the aqueous solutions. Since ferrous chloride has practically a normal molecular weight in pyridine solution, it follows that simple electrolytic dissociation has practically no effect on the absorption spectrum.

In the case of cupric salts, the optical investigation, which is also confirmed by the direction of migration of the coloured ion, shows that nitric oxide forms part of a complex anion in concentrated aqueous and in alcoholic solutions, and in solutions strongly acidified with hydrochloric or sulphuric acid, whilst in solutions in formic and glacial acetic acid, it forms part of the cation.

The optical investigation affords no support to Raschig's view that in sulphuric acid solutions of copper and iron salts the absorption of nitric oxide is conditioned by the sulphuric acid residue, as in nitrosisulphonic acid. T. S. P.

Action of Carbon on Chromyl Chloride. José Rodriguez Mourelo and Antonio Garcià Banús (*Anal. Fis. Quim.*, 1910, **8**, 355—362).—It was thought possible that, on passing carefully dried vapours of chromyl chloride mixed with air over heated carbon, carbonyl chloride would be formed, thus: $4CrO_2Cl_2 + 4C + O_2 = 2Cr_2O_3 + 4COCl_2$. But instead of this action occurring, chromic oxide was formed in the first portion of the tube, and chromic chloride sublimed forward. Difficulty was experienced in obtaining dry wood-carbon free from hydrocarbons, and in the experiments described the carbon used was heated to redness for some time prior to passing the chromyl chloride ; even after this treatment, on passing dry chlorine, hydrogen chloride was formed from hydrocarbons retained by the carbon, and a certain amount of sublimate was produced.

On passing a mixture of dry chlorine and chromyl chloride over carbon heated to redness, the proportion of chromic chloride formed is greatly increased at the expense of the chromic oxide, the action $2CrCl_2O_2 + Cl_2 + 4C = 2CrCl_3 + 4CO$ apparently preponderating. This process affords a simple and rapid means of obtaining well crystallised chromic chloride. W. A. D.

Distillation of Tin in a Vacuum. Erich Tiede and Franz Fischer (*Ber.*, 1911, **44**, 1711—1717. Compare Schuller, Abstr., 1904, ii, 109 ; Moissan, Abstr., 1906, ii, 92 ; Greenwood, Abstr., 1910, ii, 390).—A quantitative separation of lead from tin in an alloy of these two metals was carried out by vacuum distillation in a quartz tube heated in a Heraeus furnace, the vacuum being obtained by an ordinary mercury pump. No trace of tin was carried over by the lead. Even when the temperature of the furnace was raised considerably above that necessary for the distillation of lead, tin could not be distilled, since air diffused through the quartz and spoiled the vacuum. The authors therefore designed an apparatus, the essential parts of which were as follows. The electric oven proper consisted of a porcelain or magnesia tube, wound round with platinum wire and properly insulated. It was contained in a jacketed glass tube, a stream of cold water flowing continuously through the jacket; the glass tube was connected with a Gaede pump and a tube cooled in liquid air for condensing mercury vapour, all connexions being made of glass with mercury seals. A cathode-light vacuum was maintained during the distillation, the porcelain tube being heated to a bright red heat. The metal to be distilled was placed in a boat in the porcelain tube.

Tin was readily distilled in the above apparatus, collecting on the ends of the porcelain tube. At the same time, with all the purest samples of commercial tin used, a deposit formed on the cold walls of the glass tube, which was at first brass-yellow in colour, finally becoming dark brown to black; it proved to be tin sulphide. Pure tin, prepared from Kahlbaum's stannic chloride, did not give this deposit; a short exposure to the atmosphere of the laboratory was sufficient, however, for some tin sulphide to be formed, as proved by a further distillation. T. S. P.

Preparation of Colloidal Vanadic Acid by a New Dispersion Method. ERICH MÜLLER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **8**, 302—303).—A colloidal solution of vanadic acid is obtained when the molten acid is poured into distilled water. If the solution is evaporated to dryness on the water-bath, the residue obtained is insoluble in water, but is much more reactive than the ordinary form of the acid. It is supposed that the production of the colloidal acid in the above manner is due to the rapidity with which the transition from the liquid to the solid state is effected. H. M. D.

Sodium-Gold Alloys. C. H. MATHEWSON (*Intern. Zeitsch. Metallographie*, 1911, **1**, 81—88).—Gold dissolves readily in sodium at low temperatures. The freezing point of sodium is lowered until a eutectic point is reached at 3·6 atomic % of gold and 81°; the freezing-point curve then rises to a maximum at 989°, corresponding with the compound Au_2Na, from which it falls to a second eutectic point at 83 atomic % Au and 876°. Solid solutions are not formed to any appreciable extent in any part of the series. The compound Au_2Na is stable in air, but is attacked by hot water, or more rapidly by acids.

Gold may be separated from its alloys with silver by dissolving in molten sodium and subsequently extracting with nitric acid. The residue contains a trace of silver. The alloys of gold and sodium are very rapidly attacked by a dilute solution of potassium cyanide containing hydrogen peroxide. Platinum, if present, remains almost completely undissolved. C. H. D.

Mineralogical Chemistry.

The Platiniferous Deposits of the Urals. LOUIS DUPARC (*Arch. Sci. phys. nat.*, 1911, [iv], **31**, 211—230, 322—345, 439—456, 516—533).—A detailed account is given of the geological relations of the platiniferous districts; and petrographical descriptions, with several analyses, are given of the rocks. The platinum occurs mostly in the dunites, less frequently in the pyroxenites, and it is often associated with chromite. Fifteen analyses by H. C. Holtz (published also in *Tsch. Min. Mitt.*, 1910 [1911], **29**, 498—504) are given of native platinum collected from the stream beds at various localities; the extreme values are:

Pt.	Ir,Os.	Pd.	Cu.	Rh,Ru,Ir.	Fe.
75·37—88·98	0·28—5·41	0·15—0·99	0·03—1·66	2·79—3·96	7·03—16·60

In most of the analyses, however, Pd, Cu, Rh, Ru, Ir are given together, the extreme values being 3·00—8·04. L. J. S.

Yttrofluorite, a New Mineral from Norway. THOROLF VOGT (*Centr. Min.*, 1911, 373—377).—The mineral forms a vein some metres in width in a pegmatite vein intersecting granite in northern Norway (exact locality not stated); associated minerals are fluorite (D 3·2006), orthite, gadolinite, fergusonite, euxenite (?), and xenotime. It is translucent to transparent, yellowish or brownish, and has a vitreous to greasy lustre. There is an imperfect octahedral cleavage, and the material is optically isotropic, belonging therefore to the cubic system. Hardness $4\frac{1}{2}$, D 3·5572, n_{Na} 1·4572 (of the material analysed); another sample gave D 3·5356, n_{Na} 1·4522. The composition is also variable; one sample gave the following results, agreeing with $20CaF_2,3YF_3$:

CaO.	Y_2O_3, etc.	Ce_2O_3, etc.	Alkalis.	F (calcd.)	Loss on ignition.	Hygrosc. water.	Total less O for F.
54·89	17·35	1·68	0·15	45·54	0·67	0·22	101·33

Spectroscopic examination showed the presence of several other rare earths. Although somewhat resembling fluorite in its characters, the mineral is more nearly related to yttrocerite, but differs from this in containing less cerium earths. These minerals are regarded as forming an isomorphous group with the formulæ: fluorite, CaF_2 or Ca_2F_6; yttrocerite, $(Ca_3,Ce_2,Y_2)F_6$; yttrofluorite, $(Ca_3,Y_2)F_6$. L. J. S.

Composition of Blende from Picos de Europa. RAMÓN LLORD Y GAMBOA (*Anal. Fis. Quim.*, 1910, **8**, 413—421).—Blende from Picos de Europa examined by the spectrographic method (compare Urbain, Abstr., 1909, ii, 1026) was found to contain indium (traces), gallium (relatively abundant), and germanium (approximately 1 in 1,000,000). Iron was present in very varying proportions in all the blendes from this locality which were examined, and it is probable that the orange and blood-red specimens owe their colour to this element. The colour is not homogeneously distributed in the crystals, but exists in zones. One nearly colourless specimen contained only 0·066% of ferrous sulphide. The colourless blendes do not contain manganese, but lead could be detected in these. Cadmium is always present. Calcium, potassium, sodium, and lithium can be detected in nearly all specimens spectroscopically; these are probably present as chlorides, and form the inclusions visible under the microscope. By powdering the mineral very finely and extracting with water, the filtered extract shows the presence of chlorine and the metals named. The aqueous extract from 100 grams also contains 0·007 gram of organic matter, which is volatile and has a turpentine-like smell. The powdered blende after extracting with water no longer showed the presence of calcium, potassium, sodium, or lithium when examined spectroscopically, showing that the metals are present exclusively as soluble chlorides. The extracted blende, however, shows the phenomenon of thermoluminescence, which, therefore, is not due to the presence of these impurities. W. A. D.

Muthmannite, a New Mineral. FERRUCCIO ZAMBONINI (*Zeitsch. Kryst. Min.*, 1911, **49**, 246—249).—Attention is called to the fact that the published analyses of krennerite fall into two groups: those containing but little silver and with the ditelluride formula [Au,(Ag)]Te_2; and those containing about 20% silver, which have the monotelluride formula (Ag,Au)Te. It is only those of the former group that were made on material of which the crystallographic identity with the orthorhombic krennerite had been determined. Those of the latter group are taken as representing a distinct species, for which the name *muthmannite* is proposed; the following new analysis of this also agrees with the formula (Ag,Au)Te.

Au.	Ag.	Pb.	Fe,Cu.	Te.	Total.
22·90	26·36	2·58	little.	46·44	98·28

The material analysed resembles krennerite in its external appearance; but the imperfect crystals are tabular and often elongated in one direction, parallel to which direction there is a perfect cleavage. The colour is very pale brass-yellow, but on a fresh cleavage greyish-white. The mineral occurs with quartz and iron-pyrites on crevices in dacite; its locality is not stated (but is presumably Nagyag, Transylvania). L. J. S.

Apatite and Spodiosite. FRANK K. CAMERON and W. J. MCCAUGHEY (*J. Physical Chem.*, 1911, **15**, 463—470).—When tricalcium phosphate is dissolved in fused calcium chloride a granular, crystalline substance which has the formula $Ca_3(PO_4)_2,CaCl_2$ results. This is the chlorine analogue of spodiosite and is termed *chlorspodiosite*. It is also produced by dissolving natural chlorapatite in fused calcium chloride. When excess of dicalcium phosphate is dissolved in calcium chloride, the product is chlorapatite, $Ca_3(PO_4)_2,\frac{1}{3}CaCl_2$. Artificial fluorapatite mixed with fluorite is obtained by dissolving calcium fluoride in fused disodium phosphate.

The apatites, which are more soluble than the spodiosites, are formed on heating the latter to redness, hence spodiosites rarely occur in nature. Apatite, which is widely distributed in rocks and soils, has apparently been formed when the molten magma was strongly acidic, and was one of the first minerals to crystallise out. Apatite crystallises in hexagonal prisms, chlorapatite having bipyramidal ends and fluorapatite usually basal pinacoid ends. Artificial fluorapatite sometimes exhibits the peculiarity of re-entrant pyramidal ends or phantom crystals. Spodiosite is orthorhombic, chlorspodiosite being much less developed along the *c* axis than fluorspodiosite. R. J. C.

New Mineral [from Brazil]. J. M. DE PADUA E CASTRO (*Revista Chim.*, 1910, **6**, 365—369).—This mineral, found in the State of Espirito Santo, Brazil, consisted for the larger part of material having D 4·511, and containing in addition to tantalic, niobic and titanic acids, and zirconia, about 30% of a metallic oxide (XO) of a yellow colour, which belonged to the group of the rare earths, but could not be identified with any of those known. Aluminium, glucinum, chromium, yttrium, cerium, lanthanum, didymium, and thorium were all excluded. The quantitative composition was found to be as follows:

Ta_2O_5,Cb_2O_5.	TiO_2.	ZrO_2.	Fe_2O_3.	XO.	H_2O.	Not estimated.*
39·5	20·0	1·0	3·0	30·0	3·2	3·3

* Quartz, alumina, graphite, and silica soluble in alkali.

The mineral is not entirely uniform, but showed at certain points yellow particles of a schistose character consisting of quartz (90%), combined silicic acid (1·5%), ferric oxide (7%), and alumina (0·8%). W. A. D.

Composition of Potash Felspars. PHILIPPE BARBIER (*Bull. Soc. franç. Min.*, 1911, **34**, 117—123. Compare Abstr., 1908, ii, 704).—A reply to Vernadsky and Révoutsky (this vol., ii, 122). L. J. S.

Formation of Kaolinite in Some Coal-measure Shales of Northumberland. R. COOKSEY BURTON (*Proc. Univ. Durham Phil. Soc.*, 1911, **4**, 24—29).—Kaolinite occurs as white patches in clay-ironstone at Whitley Bay (anal. I); as a material replacing the calcite of fossil shells in shale at West Wylam Colliery; and on the surfaces of fissures in shale at the Duke Colliery, Ashington (anal. II). Under the microscope, it is seen to consist of silvery-white scales, only rarely with hexagonal outlines, which possess a perfect basal cleavage and give a biaxial interference-figure; sp. gr. 2·58. Anal. III, of the portion insoluble in hydrochloric acid of the clay-ironstone from Whitley Bay, shows an approximation to the analyses of the kaolinite. The material has evidently been formed by the action of carbon dioxide in solution, which has removed the ferrous carbonate and more readily decomposed silicates, and caused the aluminium silicate to recrystallise :

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	H_2O.	Total.
I.	40·91	41·53	—	trace	trace	trace	16·83	99·27
II.	46·82	39·44	—	—	—	—	13·93	100·19
III.	47·24	21·72	3·39	0·08	0·70	4·42	22·56*	100·11

* Including organic matter.

L. J. S.

Metameric Natrolite. STANISLAUS J. THUGUTT (*Centr. Min.*, 1911, 405—411).—In weathered phonolite, occurring in contact with fresh basalt in a quarry between Satteles and Schömitz, near Carlsbad, Bohemia, the minerals found in the cavities are, in the order of their formation, phillipsite, thomsonite, natrolite, and calcite. The natrolite forms radiating bunches of needles on a base of thomsonite. The needles exhibit a distorted development of their faces, and the oblique optical extinction of 5—6° indicates monoclinic symmetry. Analysis of the material gave the following results, which, after deducting lime, etc., as due to the presence of admixed thomsonite (12·15%), agree with the natrolite ratios : $H_2O : SiO_2 : Al_2O_3 : Na_2O =$ 2·18 : 2·98 : 1·00 : 1·03 :

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
45·83	27·32	1·68	0·04	15·17	10·72	100·76	2·24

The fact that the material is a mixture is also indicated by the microchemical colouring reactions with methylene-blue and with silver chromate. The natrolite when partly dehydrated by heating over a flame for a few seconds gives an intense blue with methylene-blue, or an orange-red colour with silver chromate (10% silver nitrate with 20% potassium chromate). If the heating is continued for seven seconds these colour reactions are not obtained. On the other hand, with the natrolite from Leitmeritz (Abstr., 1909, ii, 1097) and some other localities the heating may be continued for a longer period of time, proving that the material is more stable. For the less stable form of natrolite from Schömitz, the name *epinatrolite* is suggested. This has also been detected in the phonolites of some other localities, and it is suggested that it owes its origin to the alteration of minerals of the sodalite group, whilst normal natrolite is a derivative of nephelite. In their morphological and optical characters, and in chemical composition, these two forms of natrolite exhibit no difference.

The suggestion of Brögger that natrolites with oblique optical extinction contain potash, does not apply in the material here analysed. L. J. S.

Optical Properties of Rose Beryl from Madagascar. ALFRED LACROIX and ETIENNE RENGADE (*Bull. Soc. franç. Min.*, 1911, **34**, 123—125).—The rose-coloured beryl, occurring in Madagascar as crystals of tabular habit, contains alkalis, more especially cæsium, replacing the glucinum. Corresponding with the higher atomic weights of the replacing elements, there is an increase in the sp. gr.

and refractive indices of the beryl. New analyses are given of material from : (I) Vohidahy, and (II) Maharitra :

	SiO_2.	Al_2O_3. GlO.	FeO.	MnO.	CaO.	Cs_2O.	Na_2O.	Li_2O.	Loss on ignition.	Total.
I.	62·70	30·30	1·04	trace	—	1·43	1·03	0·83	2·63	99·96
II.	60·39	29·05	0·26	trace	0·34	4·56	0·24	2·00	2·23	99·07

This material also gave the following results, which are compared with the results obtained by Duparc, Wunder, and Sabot (Abstr., 1910, ii, 312) and by Ford (Abstr., 1910, ii, 873) for rose beryl from Madagascar :

Locality.	Total alkalis.	Sp. gr.	ω.	ϵ.	$\omega-\epsilon$.
Tsilaisina (Duparc)	0·92	2·716	1·5822	1·5760	0·0062
Vohidahy	3·29	2·75	1·5860	1·5795	0·0065
Madagascar (Ford)	4·98	2·79	1·59500	(1·58691)	(0·00809)
Maharitra	6·80	2·81	1·5996	1·5811	(0·0085)

L. J. S.

A Variety of Riebeckite (Bababudanite) and Cummingtonite from Mysore. William Frederick Smeeth (*Records Mysore Geol. Dept.*, [1911 ?], 9 [for 1907—8], 85—94).—The quartz-magnetite-schists of the Bababudan Hills in the Kadur district contain beds of cummingtonite, with, here and there, black radiating prismatic aggregates of a soda-amphibole closely allied to riebeckite, for which the name bababudanite is proposed. The quartz-magnetite-schists appear to have been derived from the decomposition of the amphiboles. Analysis I. of the bababudanite gives the formula

$$2NaFe'''(SiO_3)_2,Fe''Mg_3(SiO_3)_4.$$

The mineral has a prismatic cleavage angle of 56° ; and it differs from riebeckite in having a slightly greater angle of extinction ($\mathfrak{a} : c' = 7—9°$), and in the character of the pleochroism ($\mathfrak{a}$ prussian-blue, $\mathfrak{b}$ purple tending to violet, $\mathfrak{c}$ yellow with tinge of green).

The cummingtonite is brown, due to ferruginous material along cracks, but when magnetite has been separated with a magnet and the material boiled with hydrochloric acid, it is perfectly colourless (anal. II.) :

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	54·48	2·10	15·79	5·02	0·08	1·04	12·11	0·32	6·34	0·40	98·31*	3·18
II.	56·48	0·51	—	20·55	2·90	0·85	18·68	—	—	—	99·97	3·191

* Insol. in HF and H_2SO_4, 0·63 ; P_2O_5, trace ; TiO_2, nil.

L. J. S.

Physiological Chemistry.

The Causes of Absorption of Oxygen by the Lungs in Man. C. Gordon Douglas and John S. Haldane (*Proc. Roy. Soc.*, 1911, *B*, **84**, 1—2).—During rest and under normal conditions, and provided the blood is not more than about 25% saturated with carbon monoxide (experimentally added to the inspired air), the tensions of oxygen in the arterial blood and in the alveolar air are practically identical. Under such conditions, therefore, oxygen absorption occurs by diffusion alone. But when the percentage of oxygen in the inspired air is lowered sufficiently (or the saturation of the blood with carbon monoxide is increased sufficiently), the tension of oxygen in the arterial blood is much higher than in the alveolar air. During muscular work, especially when the air is poor in oxygen, the same effect is produced. Under these conditions, therefore, active secretion of oxygen inwards is taking place. In muscular work, it is considered that the pulmonary epithelium is stimulated to secrete oxygen inwards by the products of metabolism. W. D. H.

Influence of Inhalation of Oxygen on the Lactic Acid Produced during Hard Work. ISRAEL FELDMAN and LEONARD E. HILL (*J. Physiol.*, 1911, **42**, 439—443).—Inhalation of oxygen markedly lessens the excretion of lactic acid in the urine after hard work. The increased production of the acid which occurs when air is breathed is considered to be due to want of oxygen. The observations were made on man. W. D. H.

The Action of Intravenous Infusions of Saline Solutions on the Respiratory Exchanges. FRITZ VERZÁR (*Biochem. Zeitsch.*, 1911, **34**, 41—51).—The method employed was the same as that used by Tangl. It was found that injection of even 0·75% sodium chloride caused an increase in the oxygen consumption when the kidneys were excluded from the circulation. This increase is less than the increase of carbon dioxide excretion; the injection of the saline solution causes, therefore, a diminution in the respiratory quotient. The experiments afford no explanation as to the mode of action of sodium chloride. S. B. S.

The Respiration of the Eggs of the Sea-urchin (Strongylocentrotus lividus) in Pure Sodium Chloride Solutions. OTTO MEYERHOF (*Biochem. Zeitsch.*, 1911, **33**, 291—302).—The amount of oxygen used up by the eggs was determined by Winkler's method. It was found that in sodium chloride solutions from somewhat less than two to more than four times as much oxygen was used up as in isotonic sea-water. S. B. S.

Action of Chloroform on Blood-Vessels. J. ARGYLL CAMPBELL (*Proc. physiol. Soc.*, 1911, xxxiii—xxxiv; *J. Physiol.*, **42**).—Schäfer and Scharlieb state that chloroform in oxygenated Ringer's fluid produces vaso-constriction, except in the kidney vessels. Embley and Martin, using the drug in oxygenated defibrinated blood, state that the main effect is vaso-dilatation. Both these results are confirmed. If the blood is not oxygenated, constriction occurs. Oxygenation makes no difference to the effect obtained when Ringer's fluid is employed. W. D. H.

Effect of Increased Temperature of the Carotid Blood. V. H. K. MOORHOUSE (*Amer. J. Physiol.*, 1911, **28**, 223—234).—Dogs were anæsthetised with urethane or morphine, and the carotid arteries enclosed in heaters through which a stream of hot water was kept flowing. The vertebral arteries were tied. The results of thus warming the brain are: (1) an increase in the heart's rate preceded by a primary decrease due to an increased vagus tone; (2) increase of blood in the periphery due to vaso-motor response, and (3) an increase in respiratory ventilation, which is usually due to an increased rate of breathing; but increase of depth may occur in respiration without increase, or even with decrease, in the rate. These differences are probably due to difference in activity of the sensory side of the respiratory mechanism. W. D. H.

The Influence of Intravenous Blood Transfusion on the Metabolism of Matter and Energy. PAUL HÁRI (*Biochem. Zeitsch.*, 1911, **34**, 111—146).—The effect of directly transfusing the blood from one dog into another was investigated, the respiratory exchanges, nitrogen and carbon output in the urine and fæces (the latter estimated by the Brunner-Messinger-Scholz dichromate method) being measured. Direct measurements of the heat developed by the animals were also made at the same time as that of the respiratory exchanges with the employment of a Rubner respiration calorimeter. The caloric values of the egesta were also measured in a Berthelot-Mahler calorimeter. It was found that the transfusion of blood into an animal caused an increased destruction of protein and apparently also a limitation of the fat consumption. In starving animals, when the amount of water ingested is the same before and after transfusion, there is a diminution of the water excreted after the transfusion; this is not the case with fed animals. There is a small increase in heat production after transfusion, due to the increased work of the heart. S. B. S.

Deamidation in the Blood of Normal Animals, and in Those Deprived of the Thyroid. AN. K. MEDVEDEFF (*Zeitsch. physiol. Chem.*, 1911, **72**, 410—448).—The course of the development and disappearance of ammonia in the blood in (1) normal animals; (2) animals in the state of inanition, and (3) after removal of the thyroid, is expressed by the equation $dx/dt = (k_d - k_s)(a - x)$, where k_d and k_s are the respective coefficients of velocity of the deamidation and synthetic processes. In the circulating blood of the animals of the first category, $k_d = k_s$ and $k_s =|= 0$; in those of the second category, $k_d < k_s$ and $k_s =|= 0$; in those of the third category, $k_s = 0$ and $k_d =|= 0$. In the blood of animals of the first two categories, after bleeding, deamidase diffuses into the blood-plasma from the corpuscles; in those of the third category this does not occur, the amount of deamidase in it remaining constant. W. D. H.

Anti-coagulants on Frog's Blood. HAROLD PRINGLE and JOHN TAIT (*Proc. physiol. Soc.*, 1911, xxxviii—xxxix; *J. Physiol.*, **42**).—Most anti-coagulants of frog's blood (viperine venom, peptone, novocaine, potassium oxalate and fluoride, neutral salts, and hirudin) preserve the shape of the spindle cells or thrombocytes, and prevent rosetting of red-corpuscles around them. If calcium chloride is subsequently added, cytolysis of the thrombocytes and rosetting of red-corpuscles begins in a few minutes. It is inferred that calcium is necessary for cytolysis of these cells. W. D. H.

The Scission of Esters in the Blood. PETER RONA (*Biochem. Zeitsch.*, 1911, 33, 413—422).—The scission of tributyrin by blood was investigated by the method of surface-tension measurements already described by the author. The reaction was found to be unimolecular when carried out in a neutral solution (1 part monohydrogen and 7 parts dihydrogen sodium phosphate). The reaction rate was directly proportional to the quantity of ferment present. The optimum of the reaction was in the presence of the hydrogen ion concentration of the blood, and the rate diminished if this concentration be increased by using acetate mixtures, or mixtures containing larger quantities of the mono-hydrogen phosphate. Increase of alkalinity to a certain point also diminished the rate, but in this case accurate results were not obtainable, owing to the direct hydrolysing action of the hydroxyl ions. S. B. S.

The Blood of Ascidians. I. Vanadium Compound in the Blood-corpuscles. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1911, 72, 494—501).—*Phallusia* was the principal ascidian worked with, but similar results were obtained with the blood of *Ascidia mentula*. The plasma contains only 0·2% of protein; it has $\Delta - 2{\cdot}12$, whilst that of sea-water is 2·07. The blood-corpuscles are extremely acid to litmus; the acid being volatile with steam in part, and probably organic. On exposure to air the corpuscles turn yellowish-green to blue; the chromogen of the pigment is dissolved out of them by distilled water (it is also soluble in acetone), and in time turns brown. This is probably not due to oxidation; on incineration it yields about 15% of vanadic acid (V_2O_5). W. D. H.

The Permeability of Blood-corpuscles in Physiological Conditions, Especially to Alkali and Alkali-earth Metals. G. GRYNS (*Proc. K. Acad. Wetensch. Amsterdam*, 1911, 14, 122—123). —Polemical. A further discussion on Hamburger's results, especially on the way in which the calculations should be made. W. D. H.

Do the Individual Red-Blood Corpuscles of a Suspension of the Same Show Measurable Individual Differences? LUDWIG DIENES (*Biochem. Zeitsch.*, 1911, 33, 268—274).—The method of investigation consisted in treating a suspension of the corpuscles with an amount of hypotonic salt solution insufficient to cause complete hæmolysis. The total solids and hæmoglobin content were estimated in the centrifuged residue, and the ratio of these two factors compared with the ratio in centrifuged untreated corpuscles. The two ratios were found to be the same, and the author gives the reasons for drawing the conclusion from these results that there are individual differences in the blood-corpuscles, the chief reason being that it is unlikely that the hæmoglobin and other constituents are dissolved from the corpuscles in the same proportions. S. B. S.

The Proteins of Serum. FERDINAND BREINL (*Arch. exp. Path. Pharm.*, 1911, **65**, 309—314).—The relationships of the albumin and globulin of the blood-serum constitute a puzzling physiological problem. Cervello found that the administration of antipyrine increases the globulin and diminishes the albumin. This is confirmed. It is further shown that *in vitro* admixture of antipyrine with serum leads to the same result. The proteins were estimated by the "salting out" method. If the transformation is a real one, it is further assumed that it must be accompanied with a change of a part of the cystine of the albumin into glycine, since globulin contains glycine and albumin does not, and globulin contains less cystine than albumin. W. D. H.

The Chemical and Physical Changes in the Blood-Serum Taking Place During Starvation. MICHAEL POLÁNYI (*Biochem. Zeitsch.*, 1911, **34**, 192—204).—During starvation there is a diminution in the following factors: protein content, total solids, viscosity, and specific gravity. The surface tension increases. The content in ash increases during starvation, as does also the chlorine content (measured directly, and indirectly by Wassmuth's calculations from the conductivity). The osmotic pressure also rises The amount of fat shows no regular variations. The concentration of the hydrogen ions increases. S. B. S.

Formation of Dental "Tartar" by Dissociation of the Carbophosphates of Saliva. A. BARILLÉ (*J. Pharm. Chim.*, 1911, [vii], **3**, 582—585).—Nespoulous has recently extended the views expressed by the author (Abstr., 1904, ii, 27; 1910, ii, 74, 523) as to the origin of bones and calculi by dissociation of carbophosphates, to explain the formation of dental tartar, and the present paper gives confirmatory experimental data. Saliva leaves 5 or 6 grams per litre of mineral matter, consisting of magnesium and calcium carbonates and phosphates, and gives a precipitate of these constituents when made alkaline or exposed to air, due to removal of carbon dioxide from dissolved carbophosphates in either case. Salivary calculi always contain calcium phosphate and carbonate. The mineral matter of dental tartar includes 70% of tricalcium phosphate and 8% of calcium carbonate, the presence of the former being due to the fact that decomposition of carbophosphates in the mouth usually occurs in presence of alkali. T. A. H.

Influence of Intake of Food on Gaseous Metabolism and Energy Production. ALFRED GIGON (*Pflüger's Archiv*, 1911, **140**, 509—592).—The organism carries on its fundamental metabolic processes independently of the moments when food is taken. The work of digestion has, however, a certain effect, and even in fasting the activity of digestive organs is a small factor. In ordinary conditions of nutrition the taking of carbohydrate or protein produces intermediate effects. Sugar is in part changed into fat. Protein food also leads to the laying on of fat. Each constituent of the diet has a specific action both in the direction of energy production as well as in its metabolic effects. This specific action manifests itself whether the substances are given alone or mixed together.

W. D. H.

The Action of Certain Sulphur Compounds on Metabolism and Excretion. CHARLES O. JONES (*Bio.-Chem. J.*, 1911, 5, 427—441).—In rabbits, sulphates in large amount lessen oxidative changes in the cells, by preventing exchange between them and the blood-stream. As the sulphate is reduced this disappears, and a stage of stimulation accompanied by diuresis follows. There is a marked irritant action on the kidney cells. Purgation is not common. Thiosulphates which are quickly reduced in the body to sulphates act in the same way; so also do sulphites and sulphides if oxidising enzymes are abundant. If there is a deficiency of these enzymes, sulphites appear to unite with and neutralise the action of tissue enzymes; and sulphides appear to unite with some constituent of the cell itself, and to interfere with and ultimately stop all metabolic changes.

W. D. H.

Fat Digestion. STEFAN VON PESTHY (*Biochem. Zeitsch.*, 1911, 34, 147—169).—The hydrolysis of fats (emulsions of olive oil with gum arabic and water, and of egg-yoke with water) by means of the lipases of stomach (from dog and man) and pancreas was investigated by estimating, not only the fatty acids, but the glycerol formed in the process. The latter was determined by precipitation of the digestion mixture with phototungstic acid, removal of the excess of the latter by barium salt, removal of the excess of barium by carbon dioxide, and of the chlorine by silver hydroxide. In the filtrate from the various precipitates, the glycerol was estimated by the Zeisel-Fanto method. The same methods were employed for estimating the glycerol and fatty acids in the contents of the small intestine. It was found that the glycerol estimations yielded more trustworthy values than the fatty acids determinations, as the latter, for some unknown reason, showed irregularities in the case of egg-yolk. With pure fats, however, both factors gave fairly accurate numbers. The conclusion was drawn from the results obtained that the stomach contains a true lipase secreted from the mucous membrane, and that the scission of fat is not due to regurgitated enzymes from the intestine, as these lose their activity in the acid gastric contents; furthermore, in cases where regurgitation is known to take place, as in achylia gastrica and carcinoma, no scission of fat by the gastric contents was observed. In the intestine, both fat and glycerol were present, but not in the proportions corresponding with the chemical formula of fats.

S. B. S.

The Influence of the Melting Point of Fats on their Rate of Disappearance from the Stomach FRANZ TANGL and ALEXANDER ERDÉLYI (*Biochem. Zeitsch.*, 1911, 34, 94—110).—The fats, linseed oil, olive oil, lard, and beef fat, were made into emulsions, in as nearly as possible the same way, by means of water and gum arabic, and introduced by a stomach-tube into the stomachs of dogs. In different animals, after various intervals, the content of the stomach in fat was estimated. This was done by administering to the animals at the desired intervals after ingestion of the fat, *apo*morphine, which causes the stomach contents to be vomited quantitatively. As the result of numerous experiments carried out in this manner, the conclusion was drawn that the rate of disappearance of emulsions of fats from the stomach is a function of their melting points and viscosities; the higher the melting point and the greater the viscosity, the more slowly they disappear from the stomach. S. B. S.

The Diastases. IX. The Influence of Serum, Lymph, and the Expressed Juices of Organs on Diastatic Action. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1911, 33, 303—314).—Serum accelerates the action of diastase to a much greater extent than can be accounted for by its content in sodium chloride. The accelerating action is not increased by allowing the serum to act on the diastase for a prolonged period, and it appears, therefore, that the diastase does not enter into combination with the accelerating substance, but that the latter forms a substrate for the action in the same way that sodium chloride does. The accelerating action can be detected when only very small quantities of serum are added, and serum obtained from all parts of the body of the same animal has an equal accelerating effect. Serum taken from an animal after a meal has a slightly greater effect than that taken from the animal before. The strongest activating effect is obtained by the sera from the dog, sheep, and rabbit; then follow the sera from man, rat, horse, ox, and goat. The diastase from all organs is activated by serum. The lymph and expressed juice from other organs also exert an accelerating effect. The accelerating substance is in all cases heat-stable and soluble in alcohol. The comparative accelerating effect of the expressed juices of several organs was investigated. S. B. S.

Carbohydrate Metabolism. FELIX REACH (*Biochem. Zeitsch.*, 1911, 33, 436—448).—Raw meat increases the sugar output in a dog from which the greater part of the pancreas has been removed. This increase cannot be explained by assuming that with raw meat there is a greater utilisation of the food-stuff. The observation of Hédon was confirmed that phloridzin decreases the blood-sugar content in dogs with pancreatic diabetes. By this means the amount of blood-sugar can be reduced to the normal. It does not appear, therefore, that the diminution of the blood-sugar content in diabetes can be regarded as a favourable alteration in the metabolism disturbances. The influence of muscular work on the blood-sugar content was also investigated. There was found in nearly all cases an increase when the muscles passed from a condition of rest to one of activity, and in most cases a diminution when the muscles passed from a state of activity to one of rest. S. B. S.

The Metabolism of Starch when Introduced Parenterally. Fritz Verzár (*Biochem. Zeitsch.*, 1911, **34**, 66—85).—If starch solutions be injected rapidly, starch will appear in the urine; the kidneys are therefore permeable to starch. With slow injections, on the other hand, no starch will appear in the urine. Both dogs and rabbits behave in this respect in a similar way. If the starch is injected slowly, it disappears rapidly from the blood. The intravenously injected starch is, in this case, entirely oxidised, a fact determined by the measurement of the respiratory exchanges. The same result was obtained whether the starch was injected into the jugular or portal vein. With dogs made diabetic with uranium nitrate, the injection of starch causes an increased output of sugar in the urine; this increase corresponds with the amount of starch injected. Starch appears, therefore, when injected, to be first hydrolysed to a sugar, which is then burnt. After partial extirpation of the pancreas, dogs will tolerate the injection of quantities of starch which are fatal to normal animals. This fact can be explained by the presence of larger quantities of diastase in the blood of those animals in which the pancreas has been partly removed. S. B. S.

The Resorption and Excretion of Starch Granules. Fritz Verzár (*Biochem. Zeitsch.*, 1911, **34**, 86—93).—Experiments were carried out on human beings, dogs, rabbits, and rats. Starch granules, in the form of paste, were ingested. At intervals afterwards, the urine was collected, with stringent precautions to guard against any contamination, and centrifuged. The deposit was examined histologically, and found to contain starch granules, from which result the conclusion was drawn that the granules can pass from the intestine into the blood-stream, and then be excreted by the kidneys. These observations confirm those of Hirsch. S. B. S.

Creatine and Creatinine Metabolism in Dogs with Eck Fistula. Nellis B. Foster and Henry L. Fisher (*J. Biol. Chem.*, 1911, **9**, 359—362).—In dogs with Eck fistula, ingestion of creatinine was followed by a rise in creatinine excretion, and in one case by an increase of creatine excretion. This, however, was probably accidental. After ingestion of creatine, there is no rise in creatine output, and the rise in creatinine excretion was too small to be convincing. W. D. H.

Action of Gastro-Intestinal Juices on Nucleic Acids. Phœbus A. Levene and Florentin Medigreceanu (*J. Biol. Chem.*, 1911, **9**, 375—387).—The nucleic acids are mono- or poly-nucleotides, that is, compounds of phosphoric acid conjugated with a complex composed of carbohydrate and a base. During metabolism they undergo complete disintegration; how far this occurs in the process of digestion is uncertain, although London and Schittenhelm regard it as proved that in the intestine (but not in the stomach) decomposition occurs, which, if complete, liberates purine bases, and if incomplete leads to the formation of nucleosides. In the present experiments the substances employed (given in order of increasing complexity) were inosin, cytidin, guanylic acid, pyrimidine nucleotides, yeast-nucleic acid, and thymus-nucleic acid. The juices used were active, and were supplied by Pawloff. Inosin, guanosin, and cytidin were unchanged by gastric, pancreatic, and intestinal juices alone or in combination. Guanylic acid was changed by intestinal juice only, and the change was a detachment of the phosphoric acid from guanosine, the latter substance being precipitated in crystalline form. Pyrimidine-nucleotides underwent the same change under the influence of the same juice, but to a less degree. The nucleic acids from yeast and thymus were also attacked by intestinal juice only, and of the two that from yeast was most decomposed. It became soluble in glacial acetic acid; this is possibly due to cleavage into mono-nucleotides; phosphoric acid was also liberated. W. D. H.

Digestion and Absorption of Nucleic Acid in the Gastro-Intestinal Canal. II. E. S. London, Alfred Schittenhelm, and Karl Wiener (*Zeitsch. physiol. Chem.*, 1911, **72**, 459—462).—The authors agree with Levene and Jacobs that the final splitting of nucleic acids occurs in the organs and tissues. If, however, guanylic acid is given to dogs, the chyme in the ileum contains guanosine; this was isolated and identified with certainty. It also was found after feeding on thymus-nucleic acid. W. D. H.

The Presence of Secretin During Fœtal Life. Harold Pringle (*Proc. physiol. Soc.*, 1911, xl; *J. Physiol*, **42**).—Active secretin can be prepared from new-born kittens and some fœtuses. The date of its appearance in fœtal life is still undetermined.
W. D. H.

Autolysis of the Brain. Friedrich Simon (*Zeitsch. physiol. Chem.*, 1911, **72**, 463—483).—Previous attempts to determine whether proteolytic, phosphatide-splitting or other enzymes are present in brain tissue have yielded uncertain and contradictory results. Calves' brain was employed in the present investigation, and chloroform used as an antiseptic; distinct evidence was found of the presence of auto-digestive enzymes; proteolytic products occur; the main question investigated, however, relates to phosphorised constituents; phosphorus is split off from organic union, and the amount of inorganic phosphates rises correspondingly; this is true for the brain constituents which are soluble as well as for those which are insoluble in alcohol and ether. W. D. H.

Carbohydrate Tolerance and the Posterior Lobe of the Hypophysis Cerebri. Emil Goetsch, Harvey Cushing, and Conrad Jacobson (*Bull. Johns Hopkins Hospital*, 1911, **22**, 165—190).—From experimental studies on animals, and clinical observations on man, the following conclusions are drawn. The secretion of the posterior lobe of the pituitary body is discharged into the third ventricle, and enters the blood-stream by way of the dural sinuses. The infundibulum and its stalk hold a reserve deposit of this secretion, and when this part is interfered with, a transient hyperglycæmia and glycosuria occurs; the fleeting glycosuria which often accompanies fractures of the base of the skull is probably produced in this way. A short period follows in which the assimilation limit for ingested carbohydrates is lessened, and alimentary glycosuria is readily produced. This is succeeded by an enduring augmentation of tolerance for sugars, which is lowered by injection of posterior lobe extract. The sugar tolerance of normal animals is also lowered by such injections. The increased tolerance is accompanied by adiposity, and a subnormal temperature which indicates conversion of sugar into fat and a lessened power of oxidation. Injections of the posterior lobe extract conversely cause emaciation. Adiposity is not due therefore solely to deficiency in the secretion of the anterior lobe. W. D. H.

The Chemistry of Hydrocephalic Liquid. MICHAEL POLÁNYI (*Biochem. Zeitsch.*, 1911, **34**, 205—210).—The following factors were determined from four cases of hydrocephalons: specific gravity, freezing point, electrolytic conductivity, hydrogen ion concentration, refractive index, viscosity, surface tension, total solids, protein, fat (by different methods), cholesterol, ash, water-soluble and water-insoluble constituents of ash, and sodium chloride. From the results, which are tabulated, the author draws the conclusion that the hydrocephalic liquid is probably lymph. S. B. S.

Iodine in the Human Pituitary. W. DENIS (*J. Biol. Chem.*, 1911, **9**, 363—364).—Twenty-six human pituitaries were investigated, and in five of these cases iodide had been administered before death. In no case was even a trace of iodine obtainable. W. D. H.

The Amino-acids in the Mature Human Placenta. ARTHUR H. KOELKER and J. MORRIS SLEMONS (*J. Biol. Chem.*, 1911, **9**, 471—489).—Approximately one-half of the fresh placenta is blood; the dried placental material is about 7% of the fresh weight. The hydrolytic products (amino-acids and ammonia, the results of estimation of which are given in detail) represent 31% of the organic matter. Placental tissue free from water and ash contains 14·9% of nitrogen. W. D. H.

The Magnitude of the Work of the Liver. FRITZ VERZÁR (*Biochem. Zeitsch.*, 1911, **34**, 52—62).—Tangl's method was also employed in these experiments, in which the respiratory exchanges in curarised dogs before and after exclusion of the liver from the circulation, were measured. In this case it was not possible to exclude the liver entirely, Queirolo's operation being carried out, which consists in joining the vena cava with the portal vein. From the results, the conclusion is drawn that the liver utilises 12% of the total energy of the organism when muscular work is excluded by curare. There is also an increase in the respiratory quotient. S. B. S.

Is the Activity of the Liver Indispensable for the Combustion of Sugar? FRITZ VERZÁR (*Biochem. Zeitsch.*, 1911, **34**, 63—65).—The respiratory exchanges were measured in curarised animals with the liver excluded from circulation by the method described in the previous paper, before and after injection of starch and dextrose solution. From the measurement of the increased oxygen consumption and carbon dioxide excretion, the conclusion was drawn that the injected substances were entirely oxidised, and that for the utilisation of carbohydrates it is not essential that they should be first converted into glycogen in the liver. S. B. S.

Influence and Rôle of Fatty Matters in the Catalytic Activity of Hepatic Extracts. EUGÈNE CHOAY (*J. Pharm. Chim.*, 1911, [vii], 3, 525—534, 574—580).—Pigs' liver after extraction by chloroform is much more active, and after extraction by acetone slightly more active, than the crude liver towards hydrogen peroxide. The chloroform and acetone extracts are inactive. The increase of activity is not proportional to the quantity of inert matter removed, being greater for chloroform and less for acetone. It is suggested that chloroform removes the enveloping fats and lipoids from the ferments in the liver and thus renders the ferments more readily soluble, and that acetone removes only the more liquid fatty matters, leaving the solid ones surrounding the ferments, so that the latter pass less easily into solution in water.

In the second paper the effects of extraction by chloroform and light petroleum are compared. Extraction by chloroform again produced an increase in activity, whilst extraction with light petroleum caused a greater diminution in activity than extraction by acetone.

The activity of all these materials towards hydrogen peroxide varies with the acidity of the peroxide solution, and consequently the latter should be neutralised by barium hydroxide and a definite quantity of sulphuric acid then added. T. A. H.

The Independence of the Diastatic Action on the Lipoids. EMIL STARKENSTEIN (*Biochem. Zeitsch.*, 1911, 33, 423—435).—No appreciable difference could be detected between the diastatic action of the liver when the material contained lipoids and when it had been extracted in a dried form by toluene, ether, or alcohol and toluene. The divergence of this result from that obtained by other authors may be perhaps due to the fact that the lipoids decolorise the iodine used in Wohlgemuth's method of estimation of the diastases. Egg-yolk extract and commercial lecithin, however, inhibit the diastatic action, and this result is probably due to the acid character of the preparations. The authors also quote experiments which negative Bang's conclusions as to the increase of diastatic action of the organs in puncture diabetes, and in other cases of experimental glycosuria. He draws the conclusion that diastatic action generally is independent of the presence of lipoids. S. B. S.

Uric Acid Metabolism in Rabbits. H. ACKROYD (*Bio.-Chem. J.*, 1911, 5, 442—444).—The excised rabbit's liver perfused with Ringer's solution produces a small quantity of allantoin. Sodium urate added to the solution is converted quantitatively into allantoin. None of the allantoin so produced is further destroyed. W. D. H.

Pnein. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1911, 33, 315—339).—Pnein is a substance of unknown nature which accelerates the primary respiration processes of tissues, as this respiratory process weakens after the death of the animal. It can best be studied on the liver of the dog, the kidneys of ox, and the muscles of horse or ox, which on washing with water can be deprived of the pnein contained in them. It appears to be necessary for the primary respiration, as tissues freed from pnein by washing, lose the greatest part of the respiratory power. The primary respiration is due, therefore, to the concomitant action of pnein and a very labile substance. The greater the weakening of this process, the larger the quantity of pnein necessary to restore it. It appears to exist in all tissues, and is in especially large quantities in the muscles of ox and horse. Certain tissues contain *antipnein*, which can be separated from pnein by dialysis, or by precipitation of the nucleoproteins by acids. Milk, blood, bile, and urine do not contain pnein. It is not destroyed by the respiration of the tissues, and does not appear therefore to be an oxidisable substance. It is easily soluble in water, acids, and alkalis, is dialysable, and not destroyed on boiling. For its destruction, the liquid containing it must be heated at 200°. It is not altered by pepsin or trypsin, or by hydrogen peroxide or ferric chloride, although it is destroyed by the combined action of the last two substances. It is slightly soluble in alcohol, but insoluble in benzene and ether. It can be partly purified by repeated precipitation by alcohol. It has no influence on secondary respiratory processes, or on the oxidation of uric acid by alcohol, or succinic acid by animal tissues. By itself, it exerts no oxidative action, neither does it increase the oxidative capacity of hydrogen peroxide. S. B. S.

Extractive Material of Ox Kidneys. K. BEBESCHIN (*Zeitsch. physiol. Chem.*, 1911, 72, 380—386).—The following substances have been previously isolated from kidneys: purine bases, uric acid, carbamide, creatine, leucine, tyrosine, glycogen, and inositol. The author has succeeded in isolating betaine in the form of the *compound*, $C_5H_{12}O_2NCl,6HgCl_2$, m. p. 246—250°. The base was also identified by means of its chloride, aurichloride, and picrate, m. p. 183° (Tonani gives 180—181°).

The betaine was isolated from the fraction from which Gulewitsch and Krimberg obtained carnitine.

Carnosine, methylguanidine, and carnitine do not appear to be present in kidney extract. J. J. S.

The Work of the Kidneys and the "Specific-dynamic action" of Food-Stuffs. FRANZ TANGL (*Biochem. Zeitsch.*, 1911, 34, 1—40).—The method of investigation consisted in determining the respiratory exchange of dogs before and after the exclusion of the kidneys from the circulation, and from the differences of the carbon dioxide output and oxygen consumption when the kidneys are in action and when they are thrown out of action, calculating the work done by these organs. The respiratory exchanges were measured by a modification of the Zunz-Geppert method, and the animals were curarised so as to exclude as much as possible muscular work. They were kept at constant temperature in specially devised thermostats, or when too large, on electrically heated tables. Artificial respiration was employed in all cases. It was found by this method that 8·7% of the oxygen utilisation and 5·1% of the carbon dioxide excretion were due to the kidneys, numbers which agree well with the determinations of Barcroft and Brodie. From these numbers it was calculated that 7·9% of the energy metabolism of the whole organism was due to the kidneys. It has been found by Zuntz that certain substances, such as urea, sodium chloride, and proteins, cause, after ingestion, an increase in the energy exchanges of the organisms. Experiments were performed to determine how far this "specific-dynamic" action is due to the kidneys. The energy exchanges of the animals after exclusion of the kidneys from the circulation were measured both before and after the administration of such substances. It was found that even after exclusion of the kidneys, the administration caused an increase of the respiratory exchanges, from which the conclusion was drawn that the "specific-dynamic" action of such substances was not due directly to their stimulating action on the kidneys. S. B. S.

Reflux from Intestine to Stomach. E. Provan Cathcart (*J. Physiol.*, 1911, **42**, 433—438).—That bile is frequently found in the stomach has been known since Beamont's days; several recent workers have pointed out that the administration of fat provokes an increased reflux of the intestinal contents. In the present research regurgitation in dogs was produced by sodium oleate and hydrochloric acid (0·2—0·4%), which are both substances that lead to formation of secretin; water, dextrose, and urea (one experiment) produced no such effect; sodium carbonate, peptone, and Liebig's extract produced the effect in one experiment and not in the other. The stronger the acid used, the earlier does the reflux occur. The regurgitated fluid, as a rule, only enters the antrum pylori, owing to the activity of the prepyloric sphincter. W. D. H.

The Chemistry of the Contents of the Intestine. Rudolf Boehm (*Biochem. Zeitsch.*, 1911, **33**, 474—479).—A part of the ileum with two blind ends, due to an operation for hernia fourteen years before the death of the patient, was removed in a *post-mortem* examination, and was found to be filled with solid contents which were not of fæcal character. This contained in addition to nucleoprotein, a portion soluble in ether and light petroleum which was about 33% of the total solids, and was obtained in crystalline form. The melting point and polarisation indicated that this substance was dihydrocholesterol. S. B. S.

The Action of Sulphur on the Intestine. Theodor Frankl (*Arch. exp. Path. Pharm.*, 1911, **65**, 303—308).—The change of sulphur into hydrogen sulphide was not found to occur in the intestine; but it is partly oxidised into sulphurous acid, which stimulates the intestinal wall, and in some cases produces hyperæmia, the outcome being increase of peristalsis. W. D. H.

The Relation of Stimulation and Conduction in Irritable Tissues to Changes in the Permeability of the Limiting Membranes. RALPH S. LILLIE (*Amer. J. Physiol.*, 1911, 28, 197—222).—A rapid increase in surface permeability is the critical change in stimulation. This implies that the stimulus (for instance, an electric current) alters permeability directly or indirectly. The stimulating current produces a depolarisation at the seat of stimulation, which at the break is at the cathode. This decrease of an already existing polarisation is probably the really critical change in stimulation, and the increase of permeability is secondary to it.

W. D. H.

Estimation of the Indophenol Oxydase of Animal Tissues. HORACE M. VERNON (*J. Physiol.*, 1911, 42, 402—427).—When the chopped tissues of rat and rabbit are mixed with α-naphthol, *p*-phenylenediamine, and sodium carbonate, the velocity of indophenol formation is in direct linear proportion to the time, although this slows down after the first two hours. When the substrate contains $M/100$-naphthol and diamine, the amount of indophenol formed is proportional to the square of the quantity of enzyme; with $M/150$-substrate, it is proportional to the quantity of enzyme; and with $M/400$, to the square root of the quantity of enzyme. The tissues of the rat are richer in oxydase than those of the rabbit; heart muscle is richest of all, then follow tongue muscles and diaphragm, renal cortex, and cerebral grey matter. The oxydasic power of the tissues runs parallel with their degree of oxygen saturation. W. D. H

Lactic Acid and Cardiac Muscle. W. BURRIDGE (*Proc. physiol. Soc.*, 1911, xli; *J. Physiol.*, 42).—The diastolic stoppage of the frog's heart produced by lactic acid is considered to be due to a displacement of calcium and potassium salts. Such a heart recovers in Ringer's solution, or by suitable doses of potassium and calcium salts.

W. D. H.

Nicotine and Curarised Muscles. W. BURRIDGE (*Proc. physiol. Soc.*, 1911, xlii; *J. Physiol.*, 42).—Langley showed that nicotine produces a larger initial shortening in curarised than in non-curarised muscles. The tracings obtained by the author suggest that this is due to a fusion of two effects, a quick one followed by another of a variable rate of development. W. D. H.

The Significance of Imbibition Phenomena on the Onset and Passing Off of rigor mortis. OTTO VON FURTH and EMIL LENK (*Biochem. Zeitsch.*, 1911, 33, 341—380).—It has been shown that acids when not above certain concentrations greatly accelerate the imbibition capacity of gelatin and other proteins for water. The same is true for muscular and other tissue, and the first stage of the post-mortem changes of muscular tissue is therefore apparently an imbibition phenomenon. After a time, the muscular tissue, as the authors' experiments show, loses water, the maximum increase of weight taking place between twenty and thirty hours after death.

This loss is not due to the increase in acid, as this increase is shown not to exceed that amount of acid above which loss of water occurs instead of imbibition. These results were arrived at by the investigation of the imbibition phenomena both in lactic acid and phosphoric acid solutions. With the loss of water by the tissues, the *rigor mortis* passes off, and this change, as the experiments show, is not due to mere loss of water by unchanged tissues, as the increase of acidity is not sufficient for this explanation. The second stage is due rather to a gradual coagulation of the proteins, the coagulated proteins possessing, as the experiments show, a smaller imbibition capacity for water than do the natural proteins. There are therefore two distinct post-mortem changes, namely, the imbibition of water, due to setting free of lactic acid, which change is a reversible one, and later a coagulation, resulting in the formation of a protein with smaller imbibition capacity. The latter change is irreversible. By a study of the action of salts and other substances, two distinct actions could be discriminated, either the substances could act on the cells and accelerate lactic acid formation, and consequently the imbibition rigor, or they could coagulate the proteins and produce a coagulation rigor, corresponding with the second stage of normal post-mortem change. S. B. S.

Utilisation of Ammonium Acetate and Asparagin for Maintenance and for Production of Milk. August Morgen, Carl Beyer, and F. Westhausser (*Landw. Versuchs-Stat.*, 1911, **75**, 265—320. Compare Abstr., 1907, ii, 294).—The results of further experiments with sheep confirmed those previously obtained, indicating that with rations deficient in protein, but containing sufficient starch values, ammonium acetate and asparagine may be utilised, not only for maintenance, but for milk production.

When ammonium acetate or asparagine was given instead of protein, the yield of milk was reduced by about 20—25%, whilst with carbohydrate in the place of protein, the reduction in the yield was about 10—15% more.

As regards the effect of the different foods on the live weight, the weights increased on the whole throughout the whole experimental period.

The average proportion of the nitrogen in the forms of ammonium acetate and asparagine utilised for maintenance and milk production amounted to 32·2%.

The amounts of products of metabolism were normal with foods containing protein and with ammonium acetate and asparagine, whilst they were somewhat higher when carbohydrates were substituted for protein. N. H. J. M.

An Animal Alkaloid from Sterilised Milk kept under Specific Conditions. N. D. Awerkieff (*Zeitsch. physiol. Chem.*, 1911, **72**, 347—362).—Milk sterilised at 102° has been subjected to the following different treatments: (1) Exposure to light and air, the mouth of the vessel being protected by a cotton-wool plug. (2) Exposed to air, but protected from light. (3) Exposed to light, but protected from air by sealing the neck of the vessel. (4) Protected from both light and air.

The following determinations were made of the original sterilised milk and of a specimen kept for three years under the first three sets of conditions: reaction, sp. gr., fat, casein, albumin, lactose, ash, dry residue. After exposure to the conditions 1, 2, and 3, the milk had a sharp, unpleasant smell, the fat had diminished some 85%, and a solid layer had formed on the surface. From each of the three samples an *alkaloid*, $C_{36}H_{69}O_6N$, was isolated. From 2 litres of milk under conditions 1, 0·562 gram; under conditions 2, 0·280 gram; and under conditions 3, 0·173 gram were isolated. The alkaloid was not formed under conditions 4. The alkaloid forms an amorphous powder, m. p. 38°, and begins to volatilise at 52°. It dissolves in most organic solvents with the exception of benzene, is charred by concentrated sulphuric acid, and gives an intense red coloration with hydrochloric acid. It yields precipitates with solutions of mercuric iodide, potassium iodide and iodine, mercuric chloride, potassium cadmium iodide; oxalic acid or picric acid in ether; tannic acid and platinic chloride. When injected in the form of an emulsion into guinea-pigs, it acts as a strong poison. Specimens of sterilised milk kept for four years and eleven months protected from air and light (conditions 4) contained no alkaloid, and had no poisonous properties. J. J. S.

Sex and Metabolism. R. A. KRAUSE and WILHELM CRAMER (*Proc. physiol. Soc.*, 1911, xxxiv—xxxv; *J. Physiol.*, **42**).—The urine of women differs qualitatively and quantitatively from that of men; details will be published later. The point here emphasised is a tendency to creatinuria and a high ammonia excretion. Creatine occurs in the urine of normal women (on a creatine and creatinine-free diet) during and for some months after pregnancy, and also in the menstrual period. W. D. H.

Process of Acid Excretion. LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1911, **9**, 403—424).—Like temperature and osmotic pressure, the normal neutrality or alkalinity $[(OH')_{38^0} = 7 \times 10^{-7}N)]$ is adjusted and kept constant by a mechanism within the body. The acid end-products of metabolism take up alkali from blood and protoplasm; this tends to disturb the normal protective equilibrium between bases and acids, but is held in check by the kidney, which in urine formation acts in the reverse way and restores the alkali to the blood which had served as a carrier of acid. The quantity of acid excreted is measured by the amount of alkali which must be added to the urine in order to obtain the reaction of blood plus the urinary ammonia, and the method used for this purpose is described in full. The elaboration of ammonia and the presence of phosphoric acid as an end-product of metabolism make possible the excretion of acid; regulation of ammonia production and of the ratio of the acid to the alkaline phosphates of the urine are the means of regulating the acid excretion. W. D. H.

Glycosuria and Sucrosuria in a Healthy Man, following the Ingestion of 100 Grams of Sucrose. J. LE GOFF (*Compt. rend.*, 1911, **152**, 1785—1787).—The author holds the view that diabetes is increasing in France, and that this is due to an increase in the consumption of sucrose. This opinion is supposed to receive support from experiments carried out on twenty-two subjects in whom there was no previous history of glycosuria. Each was given 100 grams of sucrose in the morning, and the urine examined after four hours. Dextrose was present in twenty instances (0·4—5·27 grams per litre), and sucrose was detected in every case (0·09—7·9 grams per litre). W. O. W.

The Influence of Phenylcinchonic Acid (Atophan) on Purine Metabolism. EMIL STARKENSTEIN (*Arch. exp. Path. Pharm.*, 1911, **65**, 177—196).—This drug has been recommended for use in the uric acid diathesis. It increases the amount of uric acid excreted. In animals this is accompanied by a corresponding fall in the excretion of allantoin, and it probably acts by lessening oxidative processes that lead to allantoin formation. In man, however, this explanation does not hold; it is the endogenous uric acid which is increased, and the drug probably exerts an influence on the catabolism of nucleo-protein. W. D. H.

The Effects of Potassium Salts on the Circulation and on Plain Muscle. G. C. MATHISON (*J. Physiol.*, 1911, **42**, 471—494)—Intravenous injection of potassium salts causes a fall of arterial pressure, followed if the dose is not too large by a rise. The fall is due to action on the heart, and recovery is facilitated by washing it out with normal saline solution. Intra-arterial injection of potassium chloride causes in decerebrate and spinal amimals, and in animals with the spinal cord destroyed, an immediate rise of pressure, which is due in part to excitation of vaso-motor centres, and in part to a direct effect on the muscular coat of the arteries, since it occurs when the nerve-endings are paralysed with ergotoxine. Skeletal muscle centres in the spinal cord are first excited, then depressed, and plain muscle in uterus and œsophagus is markedly contracted. W. D. H.

Chloroform and Reversal of Reflex Effects. CHARLES S. SHERRINGTON and (Miss) S. C. M. SOWTON (*J. Physiol.*, 1911, **42**, 383—388).—Reversal of reflexes under chloroform has been hitherto mainly studied in reference to blood-pressure effects. It is now shown that the same thing may occur in reflexes carried out by skeletal muscles. W. D. H.

Action of Methyl Alcohol in the Organism. ADOLF FORSTER (*Bied. Zentr.*, 1911, **40**, 431; from *Zeitsch. Spiritusind*, 1910, **33**, 2).—The stronger physiological action of methyl alcohol as compared with ethyl alcohol is perhaps due to impurities hitherto not detected. N. H. J. M.

The Toxic Action of Methyl Alcohol. LOUIS LEWIN (*Chem. Zentr.*, 1911, i, 672; from *Apoth. Zeit.*, 1911, **26**, 54—55).—The author gives many instances of the extraordinary toxicity of methyl alcohol which follows both inhalation and ingestion through the stomach. Of sixty-three hens' eggs, after injection of ethyl alcohol, 11·11% did not develop at all, 34·93% developed monstrosities; after injection of methyl alcohol, 11·11% did not develop, whereas 65·09% gave rise to monstrosities. S. B. S.

[Physiological] Action of Tetramethylammonium Chloride. CHARLES R. MARSHALL (*Proc. physiol. Soc.*, 1911, xxxvii—xxxviii; *J. Physiol.*, 42).—This substance temporarily inhibits respiration, mainly owing to its paralysing action on the nerve-endings in the respiratory muscles. W. D. H.

Inactivation of Adrenaline in vitro and in vivo. WILHELM CRAMER (*Proc. physiol. Soc.*, 1911, xxxvi; *J. Physiol.*, 42).—Adrenaline is completely inactivated by a few minutes' contact with dilute formaldehyde, and this is probably due to an amino-group in the adrenaline molecule. Epinine (3 : 4-dihydroxyphenylethylmethylamine) is similarly affected. Pituitrine is not, and is therefore not a primary or secondary amine. Tissue extracts which lower blood-pressure are also unaffected by formaldehyde. It is suggested that the disappearance of adrenaline *in vivo* is due to a similar reaction with metabolic products. W. D. H.

The Mechanism of the Action of Adrenaline. L. LICHTWITZ (*Arch. exp. Path. Pharm.*, 1911, 65, 214—224).—Adrenaline is known to act as a stimulus of the sympathetic system. Reasons are advanced for believing that the secretion of the suprarenal is not distributed by the blood, but by the nerves themselves, the secretion being poured into the sympathetic portion of the suprarenal bodies. Among the experiments adduced in favour of this view, the following may be mentioned. If the drug is injected into a frog's leg which is in connexion with the rest of the body by the sciatic nerve only, general effects on the rest of the body (the pupil, for instance) are observable. W. D. H.

The Pharmacological Action of Some Halogen Substitution Products of Iminazoles [Glyoxalines]. KARL GUNDERMANN (*Arch. exp. Path. Pharm.*, 1911, 65, 259—283).—The great physiological importance of the halogens really dates from the discovery that iodine may be an integral part of organic compounds in the organism (as in thyreo-globulin), and from what has been found later, namely, that in iodised proteins the iodine is found united in certain of the merged cleavage products, such as tyrosine and tryptophan. It is now shown by experiments on bacteria, moulds, and animals that bromine-substitution products of glyoxaline (iminazole) are more toxic than the corresponding iodine compounds; 0·2 gram of 2 : 4 : 5-tribromoglyoxaline given by the mouth killed a dog weighing 6·5 kilos. in two hours. The most poisonous of the numerous iodine products examined is 4-iodo-5-methylglyoxaline; then follows 4 : 5-di-iodo-2-methylglyoxaline, whilst 2 : 4 : 5-tri-iodoglyoxaline is relatively non-toxic. 1 : 2 : 4 : 5-Tetraiodoglyoxaline and tetraiodohistidine anhydride have little or no action, but it is difficult to ascertain how much of these are absorbed in the intestine. It is hoped that a continuation of this work may throw light on the way iodine is combined in the thyroid. W. D. H.

The Action of Morphine on the Heart. A. A. J. van Egmond (*Arch. exp. Path. Pharm.*, 1911, **65**, 197—213).—Text-book statements as to the effect of morphine on the heart are brief and contradictory. In dogs, 0·04 mg. per kilo. of body-weight slows the heart, and this effect is more marked with larger doses. If, as sometimes occurs, this is preceded by quickening of the pulse, this is due to nausea, not to the drug. The slowing of the pulse is accompanied by fall of blood-pressure. The effect is excited on the vagus centre, and can be counteracted by division of the vagi, or by atropine. In cats, sometimes the heart is quickened, sometimes slowed; this is attributed to action on the vagus centre. In rabbits there is no certain effect on the heart at all. On the isolated cat's heart the contractions are strengthened by morphine. W. D. H.

The Pharmacology of Certain Organic Mercury Compounds. The Action of Metallic Poisons. Franz Müller, Walter Schoeller, and Walther Schrauth (*Biochem. Zeitsch.*, 1911, **33**, 381—412).—As the result of the investigation of the action of a large number of mercury compounds on cats and dogs, including several in which the mercury is directly combined with the carbon atom, the authors draw the conclusion that intoxication is not due directly to the mercury ion itself, as such an ion is not capable of existence in a medium containing protein. Of the metallic organic compounds, the sodium salts of the mercury dicarboxylic acids (with the metal directly combined with carbon) exert no toxic action when intravenously injected. The corresponding mercury hydroxyl compounds, on the other hand, exert a distinct toxic action, which is to be regarded as the action of the whole molecule and not of the ion alone. Death follows in these cases, as in all other cases of poisoning by mercury compounds after a typical paralysis of the vessels, or heart, or both. If, however, sub-toxic doses be given intravenously, the molecular action of the compound is first exerted, causing distinct symptoms of central origin; these rapidly disappear, and are followed by a third stage with the ordinary phenomena of chronic mercury poisoning (nephritis, enteritis, etc.). The chronic poisoning is a resultant of the rate of elimination and the rate of destruction of the compounds in the body (that is, the rate at which the mercury is set free from combination with the carbon in the compound). The latter factor runs parallel with the rate of formation of mercuric sulphide by ammonium sulphide. In the decomposition of these mercury carbon compounds an organic chloromercury compound is formed as an intermediate product. S. B. S.

The Antagonism of Acids by Salts. Jacques Loeb and Hardolph Wasteneys (*Biochem. Zeitsch.*, 1911, **33**, 489—502).—The toxic action of acids on *Fundulus* can be antagonised by neutral salts. The coefficient of antagonism NaCl/acids is the same for hydrochloric and nitric acids, namely, 1/166; for butyric acid it is 1/100, and for acetic acid 1/33. For different concentrations of butyric acid the coefficient salt/acid is nearly constant. For different concentrations of nitric acid there are larger variations, due possibly to the fact that the concentration intervals of the salt were not sufficiently small. The antagonistic action of calcium chloride is eight to eleven times as large as that of sodium chloride. S. B. S.

The Antagonistic Action of Sodium to Potassium Chloride.

JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, **33**, 480—488).—Whereas, in the case of *Fundulus*, it is possible fully to antagonise potassium chloride in the concentration in which it occurs in sea-water by sodium chloride, it is not possible completely to antagonise the sodium salt in the concentration in which it occurs in sea-water by the potassium salt; this can only be completely accomplished by calcium chloride. Sodium chloride solutions of greater concentration than 5/8 *m* cannot be antagonised by potassium chloride, and when the concentration is greater than 7/8 *m*, complete antagonism cannot be brought about by calcium chloride. The coefficient of antagonism NaCl/KCl is about 125 to 250, whereas the coefficient of antagonism KCl/NaCl is 1/15 to 1/17. If the concentration of sodium salt exceeds the latter limits the fish will die from sodium poisoning; if the concentration of the potassium salt exceeds the former limits, it will die from potassium poisoning. S. B. S.

The Toxicity of the Fatty Acids and other Decomposition Products of the Fats.

THOMAS BOKORNY (*Chem. Zeit.*, 1911, **35**, 630—632).—The toxic action of decomposed fats can be ascribed to the formation of the free fatty acids and other products of decomposition, glycerol, of course, forming an exception. From butyric acid upwards all the fatty acids are poisonous, in so far as they are soluble in water. The aldehydes are also poisonous, in some cases very markedly so, whereas the ketones are not so poisonous.

The poisonous action of a fat may not always be ascribed to the presence of decomposition products, since it is possible that it may be mixed with a poisonous substance which belongs neither to the fatty acids nor to the aldehydes. T. S. P.

Toxicity of Two New Nitriles and the Antitoxic Action of Sodium Thiosulphate towards One of Them.

ALEXANDRE DESGREZ (*Compt. rend.*, 1911, **152**, 1707—1709).—From experiments on rabbits the toxic doses of Moreu and Bongrand's cyanoacetylene (this vol., i, 22) and dicyanoacetylene (Abstr., 1910, i, 159) are found to be 180 and 37 times as great as that of acetonitrile. It requires 2·65 grams of acetonitrile per kilogram of body-weight to produce death in ten minutes. Sodium thiosulphate in doses of 2 grams per kilogram has a protective influence in the case of dicyanoacetylene, but not in that of cyanoacetylene. W. O. W.

The Influence of Poisons on the Catalase and the So-called ψ-Peroxydase Content of the Blood.

F. DUNCKER and ALF. JODLBAUER (*Biochem. Zeitsch.*, 1911, **33**, 253—267).—The catalase was estimated by determining the amount of hydrogen peroxide decomposed by a given quantity of blood in a given time. The ψ-peroxydase content was determined by estimating the amount of carbon dioxide evolved when a given solution of pyrogallol was treated with a given amount of blood in a current of oxygen. The hæmoglobin content was also estimated. To rabbits were administered various poisons, and the examinations of the blood were made before, and at stated times after, the administration of the poison. Hydrocyanic acid caused a small diminution of the catalase content. Arsenic in non-toxic doses in ill-nourished animals can cause an increased catalase content of 22%. In well-nourished animals no change was observed. Arsenic in toxic doses had hardly any effect on the catalase content, although it caused a diminution of the hæmoglobin and ψ-peroxydase. Hydrogen arsenide caused a large diminution of catalase, hæmoglobin, and ψ-peroxydase. Phosphorus and chloral hydrate both cause a diminution of the catalase content; the other two factors are not appreciably altered. The alterations of the catalase content are independent of the alterations in the hæmoglobin; the alterations in the amounts of ψ-peroxydase run parallel with the changes in the hæmoglobin content. S. B. S.

Experiments Serving to Explain the Parallelism between the Glycogenic Function and the Antitoxic Function of the Liver. ENRIQUE IGLESIAS (*Anal. Fis. Quim.*, 1910, 8, 421—426).—The experiments were made by injecting into the peripheral vein of a rabbit known weights of different poisons mixed with glycogen; the weights of the poison taken had been found to prove fatal in rabbits of the same body-weight when injected in the absence of glycogen. The substances experimented with were ammonium chloride, ammonium carbonate, morphine hydrochloride, cocaine citrate, and antipyrine, in solutions varying from 1% to 10% concentration. In nearly all cases, the rabbits showed marked symptoms of poisoning, but in most cases recovered. It is suggested that the glycogen acts as an antitoxin by combining with the poison in the blood, thus rendering it less diffusible and preventing it from permeating the walls of the cells so rapidly as to disturb the existing equilibrium therein. Glycogen may also act as a source of energy which enables endothermic degradation changes to occur within the cell more rapidly than usual, so that the partly killed cell receives help in eliminating the poison.
W. A. D.

Chemistry of Vegetable Physiology and Agriculture.

β-Alanine as a Bacterial Aporrhegma. D. ACKERMANN (*Zeitsch. Biol.*, 1911, **56**, 87—90).—So far the only known aporrhegma (that is, a substance split off by biological action) of aspartic acid is succinic acid. This originates from aspartic acid by the action of putrefactive bacteria. It is probable that malic acid is split off from aspartic acid in plant life, but this is at present only a hypothesis. The experiments now recorded show that, accompanying the succinic acid in putrefying aspartic acid, β-alanine is also present. W. D. H.

Rôle of Mineral Substances in the Formation of the Anthrax Protease. Jean Bielecki (*Compt. rend.*, 1911, **152**, 1875—1877).—The proteolytic activity of anthrax bacteria depends to a considerable extent on the mineral constituents of the medium in which the organism has been cultivated. A culture taken from an asparagine solution containing calcium salts liquefies gelatin more rapidly than one from which these are absent, whilst salts of potassium, sodium, ammonium, and magnesium have an inhibitory effect on the subsequent activity. In experiments on the liquefaction of coagulated egg-albumin, the salts showed precisely the contrary effect, those of the alkalis favouring proteolysis, those of calcium hindering it. The salts are not effective in either case if they have been added to the culture already well developed in a pure medium. W. O. W.

The Biological Stimulative Action of Natural Humus. Theodor Remy and Georg Rösing (*Centr. Bakt. Par.*, 1911, ii, **30**, 349—384).—Earlier results obtained by Krzemieniewski (Abstr., 1909, ii, 335) were confirmed, and the relation between soil or soil humus and the power of nitrogen fixation by *Azotobacter chroococcum* was investigated. The stimulative action possessed by these substances was shown to be due, not to the humus itself, but to the small amounts of iron and silicates contained therein. The value of the iron depends largely on the form in which it is supplied. Ferric hydroxide held in solution by sucrose is very effective, whilst ferric silicate is also good. This accounts satisfactorily for the favourable action of basic slag on the nitrogen-fixing power of *Azotobacter*.

The optimum amount of iron was found to be 15 mg. Fe_2O_3 for each gram of mannitol supplied; of this, only about 1 mg. is actually assimilated by the organism.

This distinct difference between optimum requirements and assimilated iron suggests a possible action of iron compounds in increasing the amount of oxygen in the cultures, and thus leading to increased assimilation of nitrogen. H. B. H.

Biochemical Study of Proteus vulgaris, Hauser. Christian A. Herter and Carl Ten Broeck (*J. Biol. Chem.*, 1911, **9**, 491—511).—In cultures, *Proteus vulgaris* ferments dextrose and sucrose, but not lactose; it destroys some native proteins, producing ammonia, primary amines, hydrogen sulphide, fatty acids of high molecular weight, aromatic hydroxy-acids, indole, and indoleacetic acid; it does not produce phenol, scatole, mercaptan, alcohols, aldehydes or ketones. If given to animals, the effects vary greatly, depending on the virulence of the organisms and the nature of the diet. The bodies of the organisms precipitated by alcohol contain a toxic material which is thermostable. W. D. H.

Assimilability of Different Carbohydrates by Different Yeasts. P. Lindner and K. Saito (*Bied. Zentr.*, 1911, **40**, 418—420; from *Woch. Brauerei*, 1910, **27**, 509; *Zeitsch. ges. Brauw.*, 1910, **33**, 626).—Maltose is the most readily assimilated sugar, and very rarely fails to be utilised. Lactose, on the other hand, is only assimilated in isolated cases. Dextrin is frequently assimilated, but only to a small extent. Sucrose is of less importance in assimilation than glucose and lævulose. Raffinose and arabinose occasionally give moderate growth. Dextrose and lævulose are usually only moderately assimilated, if at all; in some cases when dextrose is assimilated, lævulose is not, and vice versa.

Schizosaccharomyces octosporus was the only yeast which failed to assimilate any of the sugars employed, in presence of asparagine. *Saccharomyces Ludwigii* ferments dextrose, lævulose, and sucrose vigorously, but does not assimilate them. N. H. J. M.

Influence of Humates on Micro-organisms. E. KAYSER (*Compt. rend.*, 1911, **152**, 1871—1873. Compare this vol., ii, 648).—It is possible that the disease affecting ciders known as greasiness is due to insufficient washing of the apples from earthy material. It has been found that soluble humates from soil favour the development of the ferment to which the disease is due, probably by acting as an aliment for the organism, and not merely as a stimulant to its activity. W. O. W.

Utilisation of Aucubin by Aspergillus niger. HENRI HERISSEY and C. LEBAS (*J. Pharm. Chim.*, 1911, [vii], **3**, 521—525. Compare Abstr., 1894, ii, 109; 1896, ii, 321; 1902, i, 634, and Puriewitsch, Abstr., 1899, ii, 683).—It is shown that the glucoside aucubin may be utilised by a mould, such as *Aspergillus niger*, but only when hydrolysis of the glucoside is effected by acids simultaneously present, or when there is enough mould tissue present to secrete hydrolytic enzymes in some quantity. Thus *Aspergillus niger* continues to grow in aqueous solutions of aucubin, and conidia of the mould develop and grow in acid nutrient media containing aucubin as the source of carbohydrate, but in neutral nutrient media containing aucubin, development of the conidia takes place very slowly. The dextrose produced from the glucoside is used by the mould, but it is doubtful whether the aucubigenin is so used. T. A. H.

Assimilation of Atmospheric Nitrogen by Higher Plants. EVA MAMELI and GINO POLLACCI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 680—687. Compare Abstr., 1910, ii, 645).—The authors have grown sterilised seeds of *Acer negundo, Solanum nigrum, Cucurbita pepo, Raphanus sativus*, and *Polygonum fagopyrum* in sterile nutrient media either free from nitrogen or containing a known amount of this element, and covered with bell-jars containing sterilised air exempt from ammoniacal, nitrous, nitric, and organic nitrogen. Determination of the weights of the plants obtained and estimation of the amounts of nitrogen in them and in the media employed show that, in all cases, atmospheric nitrogen is assimilated by these plants. In those experiments where large amounts of nitrogen were supplied in the media, little free nitrogen was taken up from the air; whilst, where the media contained but little nitrogen, which was all, or nearly all, utilised by the plants, larger amounts of atmospheric nitrogen were assimilated. The results indicate that all plants, from the algæ to the phanerogams, are able to assimilate atmospheric nitrogen.

T. H. P.

[Assimilation of Carbon by Plants.] LÉON MAQUENNE (*Compt. rend.*, 1911, **152**, 1818—1819).—*Aspidistra*, which, according to Cailletet (this vol., ii, 642), are plants deriving most of their carbon from organic substances in the soil, are found to decompose regularly 0·03 c.c. of atmospheric carbon dioxide per hour per sq. cm. of surface during cloudy weather. This is slightly above the normal amount for herbaceous plants under like conditions. It follows that plants, such as ferns, which flourish in subdued light do not differ essentially from those which require sunlight for the satisfactory assimilation of carbon.

W. O. W.

The Fermentative Oxidation of Oxalic Acid. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1911, **33**, 449—455).—Wheat seeds contain a ferment or catalyst, in the presence of which oxalic acid is oxidised to carbon dioxide. The reaction proceeds best with 1% solutions; in 3% solutions of the acid, the action ceases. Seeds previously heated or treated with methyl alcohol lose the oxidative action. The process does not, however, depend on the living condition of the seeds, as those treated with ether are also active. Finely-powdered pea seeds and wheat embryos do not exert the same action, and the authors call attention to the differences in the respiratory processes between these and the wheat seeds.

S. B. S.

The Law of the Minimum and the Conclusions to be Drawn from It. EILHARD A. MITSCHERLICH (*Landw. Versuchs.-Stat.*, 1911, **75**, 231—263).—The law of minimum (*Landw. Jahrb.*, 1909, **38**, 537) is a logarithmic function. It requires new, exact vegetation experiments similar to Hellriegel's sand cultures.

N. H. J. M.

Chemical Differentiation of Species. MURIEL WHELDALE (*Bio.-Chem. J.*, 1911, **5**, 445—456).—This is a preliminary attempt to co-ordinate the organic compounds occurring in plants with a view to the chemical differentiation of species. Many chemical compounds, for instance, certain alkaloids, are peculiar to certain species of plants. Lists are given of the principal groups of chemical compounds and of the plants in which they occur.

W. D. H.

Diffusion of Saline Substances through Certain Vegetable Organs. GUSTAVE ANDRÉ (*Compt. rend.*, 1911, **152**, 1857–1860).—Potatoes immersed in sodium chloride containing formaldehyde as a preservative take up the salt in considerable amount, but this is slowly eliminated by exosmosis when the tubers are placed in distilled water. Untreated potatoes similarly lose about 40% of their naturally-occurring sodium chloride under the same conditions. All the chloride would probably be lost after a sufficiently long immersion in water.

W. O. W.

Genesis of the Alkaloids in Plants. GIACOMO L. CIAMICIAN and CIRO RAVENNA (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 614—624. Compare Abstr., 1908, ii, 773; 1909, ii, 604; 1910, ii, 234).—The authors have investigated the effect on the formation of alkaloids in *Datura* and the tobacco plant of inoculation, by the method previously described, with pyridine, piperidine, and pyrrolecarboxylic acid, and, in the case of tobacco, also with asparagine, ammonia, and certain non-nitrogenous compounds, such as dextrose and phthalic acid.

Pyridine has no specific influence in increasing the amount of alkaloid formed; in the tobacco plant, ammonia produces the same effect as pyridine. When asparagine is employed, the greatest yield of alkaloid is obtained. The amount of nicotine in the tobacco plant is also increased by making an aperture in the outer skin similar to that by means of which inoculation is effected and then closing it with paraffin wax. Dextrose also determines a considerable increase in the formation of nicotine. With phthalic acid, the increase is so small that, allowing for the effect of merely making an aperture, this compound actually seems to diminish the quantity of nicotine produced.

The results support the view that the vegetable alkaloids have their origin in amino-acids, and also Winterstein and Trier's supposition (Die Alkaloide, Berlin, 1910), that the bases, such as lysine and ornithine, formed from amino-acids are utilised by plants for the synthesis of alkaloids. T. H. P.

The Chemical Composition of the Root of Asclepias vincetoxicum. GEORGES MASSON (*Chem. Zentr.*, 1911, i, 1065; from *Bull. Sci. Pharm.*, 1911, **18**, 85—89).—After extracting the fat and a resin with light petroleum, a saponoid together with sugar can be obtained from the dried root by extraction with 60% alcohol. This is an acid which is insoluble in water, and can be obtained from its sodium salt by dialysing against acidified water. The free *asclepiac acid* is an optically inactive, amorphous, yellow powder, m. p. 90—91°, which on hydrolysis with 0·5% alcoholic sulphuric acid undergoes scission into a reducing sugar, or a bright red, amorphous powder, insoluble in water. S. B. S.

Action of Cold, of Chloroform and Ether on Eupatorium triplinerve. EDOUARD HECKEL (*Compt. rend.*, 1911, **152**, 1825—1827. Compare Pougnet, Abstr., 1910, ii, 993; this vol., ii, 528).—This plant does not contain a preformed odorous substance, but the odour becomes perceptible on drying the leaves or submitting them to cold by the evaporation of ethyl chloride. Exposure to the vapour of chloroform or ether acts in the same way. The odour resembles that given by *Melilotis officinalis* under the same conditions (Abstr., 1910, ii, 63) and is probably due to the same substance. W. O. W.

Sensitiveness of Lupins towards Lime. Behaviour of Some Other Plants Towards Alkaline and Acid Media. THEODORE PFEIFFER and E. BLANCK (*Bied. Zentr.*, 1911, **40**, 394—401; from *Mitt. landw. Inst. Univ. Breslau*, **6**, 273).—The results of past experiments with *Lupinus luteus* showed that 0·1% of calcium carbonate was without appreciable effect, whilst the yield was reduced by 0·3% and still more by 0·6%. The results with calcium sulphate were conflicting, small amounts being more injurious than corresponding amounts of calcium carbonate, whilst with the larger amounts the results were reversed. Calcium phosphate also proved to be injurious, probably in part owing to the amount of phosphoric acid being excessive. With calcium nitrate the injury was also greater than with carbonate.

The conclusion is drawn that lupins are especially sensitive towards alkali, and that the injurious action of calcium salts is in part due to neutralisation of the root acids. The acidity of lupin roots, which enables the plants to thrive in certain soils better than many other plants, cannot be checked without injury to the plant.

Potatoes and beet were not affected by the amounts of alkali which are injurious to lupins. N. H. J. M.

Philippine Firewood. ALVIN J. COX (*Philippine J. Sci.*, 1911, **6**, 1—22).—The chief woods used in the Philippines as fuel are the *Rhizophoraceae*, composing the thick mangrove swamps of the coast.

Wood dried at 103—105° will absorb from the air an amount of moisture somewhat less than that which the air-dried wood will retain of the original moisture of the green stick; the best seasoned wood retains 12·5—13% of moisture, calculated on the weight of the dry wood, which is the only constant basis on which to compute the percentages of moisture and ash. Tables are given of the determination of the calorific values of some Philippine woods and barks, of analyses of wood ash, of the determination of the specific gravities of some Philippine woods, and of the approximate fuel value of North American and Philippine firewoods. The available heating value of the combustible matter of wood, that is, wood − (water + ash), is practically constant, and is equal to 4418 calories. From this number the available heating value of a wood, of known moisture and ash content, is given by the expression, $4418 \times (100 - \%\ \text{water} - \%\ \text{ash})/100 - 6 \times \%\ \text{water}$. The percentage of moisture and of ash, and the specific gravity are the three most important factors controlling the fuel value of a wood. The volatile constituents of a mangrove ash are large, and may condense as clinker on the walls of a furnace, or glaze any surface with which they come in contact. C. S.

Fruit of Solanum dulcamara. BENTON R. ANDERSON (*Chem. News*, 1911, **104**, 2—3. Compare Wells and Reeder, Abstr., 1908, i, 58).—The fruits lost 46·05% of their weight on extraction, first with alcohol and then with water. They contained (*a*) 31·55% of sugars in which lævulose was observed; (*b*) 9·15% of oil having D 0·9603 and saponification equivalent 306, and yielding ricinoleic acid on hydrolysis; (*c*) 0·934% nitrogen; (*d*) 0·15% of alkaloid; (*e*) ash, containing the usual mineral constituents found in plants. The fruits also contained citric, tartaric, and acetic acids; the last probably as the result of fermentation. T. A. H.

The Influence of Light on the Composition of the Sugar-Beet. Friedrich Strohmer, Hermann Briem, and Ottokar Fallada (*Chem. Zentr.*, 1911, i, 1065—1067; from *Österr.-ung. Zeitsch. Zuckerind.*, **40**, 11—28).—Comparative experiments on the growth of plants from the same seeds and at the same place, under as nearly comparable conditions as possible, were carried out, one portion being grown in the light, and the other under the shade of trees. With insufficient light, the leaves develop at the expense of the roots, which contain a smaller percentage of dried substance, this being accounted for mainly (74%) by the diminished sugar production. The content in nitrogenous substances was, on the other hand, higher in the roots of the plants grown in the shade. These contained a greater proportion of non-protein nitrogenous substances. The difference in the proportion of protein to non-protein nitrogen was specially marked in the leaves. The leaves of the shaded plants contained also appreciably larger quantities of oxalic acid. Tables are given showing the composition of the ash. S. B. S.

Occurrence of Starch in Sugar-Beet Roots. Javoslaw Peklo (*Bied. Zentr.*, 1911, **40**, 386—387; from *Österr.-ung. Zeitsch. Zuckerind. Landw.*, **38**, Pt. 2).—The condensation of soluble carbohydrates to starch in the cells of sugar-beet is not merely a chemical process, but is connected with the presence of leucoplasts in the cells. Starch production can be readily noticed in roots with high percentages of sugar. N. H. J. M.

Discrepancy between the Results Obtained by Manuring, etc., in Pots and in the Field. Lionel Cohen (*Proc. Roy. Soc. N.S. Wales*, 1909, **43**, 117—122).—Divergences between the results of pot and field experiments are probably mainly due to the more variable amounts of water present in field experiments, and consequently varying concentration of soil solutions.

It is suggested that the wilting of plants observed by Sachs in clay soils containing 12% of water was due to excessive concentration of the dissolved salts. Tobacco plants in sandy soil remained turgid, when only 1·5% of water was present. N. H. J. M.

Absorption of Ammonia from the Atmosphere. Alfred D. Hall and Norman H. J. Miller (*J. Agric. Sci.*, 1911, **4**, 56—68. Compare Bineau, *Ann. Chim. Phys.* 1854, [iii], **42**, 428; Müller, *J. pr. Chem.*, 1866, **96**, 339; Heinrich, Abstr., 1882, 789; *Kellner. Landw. Jahrb.*, 1886, **15**, 701).—Monthly estimations, for two years, of the amounts of atmospheric ammonia absorbed by dilute sulphuric acid in dishes 26·5 cm. in diameter.

The highest results were obtained with dishes kept at a height of about 115 cm. above the ground in front of the Rothamsted laboratory, near the outside of the town, the nitrogen absorbed amounting to 1·48 lb. per acre per annum. In dishes in the same situation, but only 5 cm. above the ground, the amount absorbed was only 0·85 lb.

Dishes placed in the experimental grass plots showed somewhat higher results in the upper dish (0·78 lb.) than in the lower one (0·70 lb.). In the experimental wheat field the absorption in the upper dishes was 1·14 lb., and in the lower dishes 1·53 lb. The higher results obtained in the wheat field as compared with the grass plots is mainly due to considerable amounts of ammonia given off by the soil for some weeks following the application of ammonium salts to some of the wheat plots. In April, 1909, the absorption in the upper and lower dishes in the wheat field was 0·29 and 0·61 lb. respectively. During the ten months not affected by the manures, the average absorption in the wheat field was higher in the upper than in the lower dishes. N. H. J. M.

Action of Alumina and Silicic Acid on the Utilisation of the Phosphoric Acid in Soils by Plants. THEODOR PFEIFFER and E. BLANCK (*Bied Zentr.*, 1911, **40**, 381—383; from *Mitt. landw. Inst. Univ. Breslau*, **6**, 315).—Pot experiments in which lupins were grown in sand, manured with potassium phosphate, alone and in conjunction with alumina and gelatinous silica. Some of the pots were subjected to the action of cold and heat respectively, and some received calcium chloride in addition to the other substances.

The results failed to give indications of the production of adsorption compounds. Addition of alumina and gelatinous silicic acid merely gives rise to the chemical combination of the phosphoric acid. It is, however, possible that under other conditions—omission of silica and the employment of less alumina in relation to the phosphoric acid—different indications might be obtained. N. H. J. M.

Utilisation of Sewage Waters in Agriculture. ACHILLE MÜNTZ and E. LAINÉ (*Compt. rend.*, 1911, **152**, 1814—1818. Compare this vol., ii, 421; Petit, *ibid.*, ii, 649).—The sewage of Paris does not lose phosphates during the treatment by bacterial beds, but as a fertilising material it is deficient in these salts, and, consequently, to obtain the best results in agriculture, phosphates must be added. W. O. W.

Importance of Phonolite as Potassium Manure. THEODOR PFEIFFER, E. BLANCK, and M. FLÜGEL (*Bied. Zentr.*, 1911, **40**, 375—380; from *Mitt. landw. Inst. Univ. Breslau*, **6**, 233).—The results of pot experiments in which oats, grown in sand and a mixture of sand and loam, were manured with phonolite (potassium silicate) showed that the manure is only utilised to a slight extent. Similar results were obtained when calcium nitrate and "humus silicate" respectively were applied along with the phonolite. N. H. J. M.

Action of Carbon Dioxide on Bordeaux Mixture. CONRAD T. GIMINGHAM (*J. Agric. Sci.*, 1911, **4**, 69—75. Compare Pickering, Trans., 1907, **91**, 1988).—The conclusion is drawn that the fungicidal action of Bordeaux mixture cannot be due to copper sulphate liberated by atmospheric carbon dioxide, and that only minute amounts of copper carbonate, if any at all, are likely to be dissolved in the rain or dew on the surfaces of the leaves. Probably the actual contact between the fungus and the particles of the insoluble copper compound is the chief means by which further growth is prevented.

N. H. J. M.

Analytical Chemistry.

Tests for Purity, and the Washing of Precipitates in Relation to Adsorption. K. Scheringa (*Pharm. Weekblad*, 1911, 48, 674—675. Compare *Chem. Weekblad*, 1911, 8, 11).—From his experimental results the author draws the conclusions: (1) Tests for purity are rendered more delicate by washing a substance insoluble in water with a salt solution. (2) The washing of precipitates can often be accelerated or improved by employing a solution of a volatile organic or inorganic substance instead of water. (3) The method is applicable to washing photographs. (4) In cases of acute poisoning, the stomach should be washed out with a salt solution. A. J. W.

Modified Colorimeter and Some Tests of its Accuracy. Edward D. Campbell and William B. Hurley (*J. Amer. Chem. Soc.*, 1911, 33, 1112—1115).—A simple form of colorimeter is described in which the solution to be examined is contained in one of a pair of cylindrical tubes, the second containing the standard solution, the level of which can be raised or lowered by means of a glass plunger working in an attached reservoir. The light passing upwards through the tubes impinges on two mirrors at an angle of 45° to the vertical. One of these mirrors is cut vertically and cemented in such a position as to reflect one half of the circular field of light coming through one of the tubes. One half of the circular beam from the second tube and mirror is cut off by the first mirror, and in this way two juxtaposed images, separated by a vertical dividing line, are to be seen through the observing tube. This is lined with black felt, and is provided with a diaphragm which allows only the light from the bottoms of the two comparison tubes to reach the eye-piece.

Data showing the efficiency of the apparatus are recorded for titanium solutions colloured yellow by the action of hydrogen peroxide. H. M. D.

Determination of the Constants of the Differential Blood-gas Apparatus. Joseph Barcroft and H. L. Higgins (*J. Physiol.*, 1911, 42, 512—518).—Important data are given for the use of the instrument. W. D. H.

Estimation of Chlorides in [Commercial] Bromides. H. Rabe (*Pharm. Zeit.*, 1911, 56, 505).—One gram of the bromide to be tested is dissolved in 100 c.c. of water and titrated with *N*/10-silver nitrate. The amount of chloride is then found from the equation $y = mx + b$, in which x represents the number of c.c. of silver used, whereas m and b are constants. For ammonium bromide, $m = 20/17$ and $b - 120$; for potassium bromide, $m = 2$ and $b - 168$; for sodium bromide, $m = 50/37$ and $b - 4850/37$. L. de K.

Phenomenon of Occlusion in Precipitates of Barium Sulphate, and its Relation to the Exact Estimation of Sulphates. John Johnston and L. H. Adams (*J. Amer. Chem. Soc.*, 1911, **33**, 829—845). —It has been pointed out by Allen and Johnston (Abstr., 1910, ii, 650) that in the estimation of sulphates by the usual method an error of 1% or even more may be occasioned by the occlusion of foreign substances, especially alkali sulphates, by the precipitated barium sulphate.

It has now been found that the amount of impurity occluded depends on the concentration of the salts in the original solution and on the fineness of the precipitate, the latter factor being controlled by the rate of precipitation, the solubility of the barium sulphate in the supernatant liquid, and the interval which is allowed to elapse between precipitation and filtration. It is shown that the occlusion is probably a phenomenon of absorption at the surface of the grains of the precipitate.

The following method, based on these results, is recommended for the exact estimation of sulphates. To 30 c.c. of the solution, which should be of such a concentration as to yield a precipitate weighing about 2 grams, 50 c.c. of concentrated hydrochloric acid are added. The mixture is heated until it boils, and a 10% solution of barium chloride is added drop by drop until precipitation is complete; the latter operation should take about four minutes. The whole is evaporated to dryness on the water-bath, and the residue treated with hot water; the barium sulphate is collected, washed until free from chlorides, ignited carefully in such a way as to obviate reduction, and heated with the bunsen burner until of constant weight. The correction to be applied is determined by making a solution of alkali sulphate of nearly the same composition as the solution under examination, and estimating the sulphate in it in exactly the same manner. The difference between the calculated amount of barium sulphate and that actually found is the correction required.

This method is easier and more rapid than Allen and Johnston's (*loc. cit.*), but is not so generally applicable. When, however, the approximate composition of the solution containing the sulphate is known, the new method will give results within ± 0·05% of the total sulphate present. E. G.

Analysis of Nitrous Oxide. Warren R. Smith and E. D. Leman (*J. Amer. Chem. Soc.*, 1911, **33**, 1116—1117).—The composition of the gas drawn off from cylinders containing liquid nitrous oxide depends on the rate at which the gas is removed, the length of time elapsing between the withdrawal of samples and various other factors. To avoid the uncertainties which are thus caused by the greater volatility of the admixed nitrogen and oxygen, the authors recommend the expedient of inverting the cylinder, and drawing a sample from the bottom of the liquid. This is shown to give a fair sample.

H. M. D.

Detection of Nitrates with Diphenylamine. HUBERT CARON (*Ann. Chim. anal.*, 1911, **16**, 211—215).—Minute traces of nitrates may be detected, as is well known, by the diphenylamine test. According to the author the reagent is best prepared by dissolving 2 mg. of diphenylamine in 100 c.c. of pure sulphuric acid; $2\frac{1}{2}$ volumes of this are then added to 1 vol. of the nitrate solution. The ring test does not seem to be more delicate. If, however, the reagent is intended for a colorimetric estimation, and when the liquid under examination also contains chlorides, it is best prepared by dissolving 3 mg. of diphenylamine in 100 c.c. of sulphuric acid mixed with 40 c.c. of water and 2 or 3 c.c. of *N*/10-hydrochloric acid; 5 c.c. of this are then added to $\frac{1}{2}$ c.c. of the nitrate solution, and the mixture is gently heated. Among the substances which interfere with the reaction may be mentioned methyl and ethyl alcohols, glycerol, ethyl ether, acetone, and hydrocarbons.

L. DE K.

Estimation of Nitric Acid. GYSBERT ROMYN (*Pharm. Weekblad.*, 1911, **48**, 753—757; *Zeitsch. anal. Chem.*, 1911, **50**, 566—570).—One hundred grams of ammonium sulphate and 100 c.c. of ammonia (D 0·96) are dissolved and made up to 500 c.c. Five c.c. of this reagent are placed in a 100 c.c. flask, which is then filled with the nitrate solution to be tested; this should be free from iron and not contain more than 0·4 gram of nitrogen pentoxide per litre. The liquid is transferred to a dry flask, 0·2 gram of zinc dust mixture is added, and after closing the flask the contents are well shaken; after about five minutes, 95% of the nitrate is converted into nitrite. (The zinc mixture is prepared by intimately mixing zinc dust, "extra fine," with an equal weight of kieselguhr.) After pouring through a dry filter, 50 c.c. of the clear filtrate are placed in a dry stoppered flask, and 10 c.c of *N*/10-permanganate followed by 5 c.c. of dilute sulphuric acid are added. After waiting for half an hour, 5 c.c. of 10% potassium iodide solution are added, and the iodine liberated is titrated with *N*/10-thiosulphate.

L. DE K.

Detection and Estimation of Nitric and Nitrous Acid in Waters. J. TILLMANNS and W. SUTTHOFF (*Zeitsch. anal. Chem.*, 1911, **50**, 473—493).—A lengthy article on the detection and colorimetric estimation of nitric and nitrous acid, or both, in waters. The following are the most important points. For the detection of nitric acid (+ nitrous acid), the following reagent is used: 0·085 gram of diphenylamine is covered in a 500 c.c. flask with 190 c.c. of dilute sulphuric acid (1 : 3), and sufficient strong acid is then added to heat the liquid and cause the diphenylamine to dissolve; more sulphuric acid is then added nearly up to the mark, and when cold the volume is exactly made up. When testing a water, 100 c.c. are mixed with 2 c.c. of brine, so as to promote the reaction, 1 c.c. of the water is taken with a delicate pipette, and 4 c.c. of the reagent are added. The blue coloration is observed and matched after one hour. It gradually begins to fade and discolour after that time.

For the detection and colorimetric estimation of nitrous acid alone, a slightly different reagent is used [0·06 gram of dimethylamine, 325 c.c. of dilute sulphuric acid (1 : 3), sulphuric acid up to 500 c.c.]. Five c.c. of the water, to which no brine need be added, are mixed with 5 c.c. of the reagent, and the mixture is at once cooled. The blue colour due to nitrous acid alone reaches its maximum in about twenty minutes, and then soon fades. If it is desired to make a direct estimation of the nitric acid also, the water may be freed from nitrite by boiling, for instance, with a little ammonium chloride.

L. DE K.

Titration of Phosphates. WILHELM STRECKER and PAUL SCHIFFER (*Zeitsch. anal. Chem.*, 1911, **50**, 495—499).—Aliquot portions of a solution of sodium hydrogen phosphate were tested (1) by evaporation and heating and weighing as sodium pyrophosphate, (2) by weighing as phosphomolybdic anhydride according to Woy's method, (3) by titration with uranyl acetate, and (4) by precipitation with standard silver nitrate in acetic acid solution and determining the excess of silver by Volhard's process, a method proposed originally by Perrot in 1881, but since taken up by Holleman and others.

The results obtained by these four methods were quite concordant.

L. DE K.

Volumetric Estimation of Phosphoric Acid. J. ROSIN (*J. Amer. Chem. Soc.*, 1911, **33**, 1099—1104).—The reaction between silver nitrate and disodium hydrogen phosphate in aqueous solution corresponds with the equation: $3Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 6NaNO_3 + H_3PO_4$. The filtered solution contains from 35 to 38% of the original phosphoric acid; this is greater than the 33·3% required by the equation, but the excess is probably due to the solvent action of the liberated phosphoric acid on the silver phosphate. The observed reaction is made the basis of a volumetric method for the estimation of phosphoric acid. The phosphoric acid solution is made neutral to phenolphthalein by addition of sodium hydroxide, an excess of 0·1*N*-silver nitrate being then added, and the mixture well shaken. Zinc oxide is then added little by little until the acid reaction towards litmus paper disappears. The solution is now made up to a known volume with water, the precipitate allowed to settle, and the solution filtered. The excess of silver is then determined in an aliquot portion of the filtrate by Volhard's method. The method yields satisfactory results if the excess of silver nitrate added does not fall below 30% of that which is required for precipitation of the phosphoric acid, and if, after addition of the zinc oxide, the mixture is not left too long before filtering. The method can be used in presence of sulphates, nitrates, chlorides, and calcium, but cannot be used for the estimation of the total phosphoric acid in presence of more than traces of iron and aluminium.

The reaction between zinc phosphate and silver nitrate, on which the process depends, is also found in the case of other insoluble phosphates. In general, those phosphates which are soluble in acetic acid are reacted on in this way by silver nitrate, while those which are insoluble in acetic acid are inactive. H. M. D.

Estimation of Arsenic and of Iron Salts in Mineral Waters. F. AGENO and N. GUICCIARDINI (*Gazzetta*, 1911, **41**, i, 473—478).—For the analysis of the water of Roncegno (compare Abstr., 1910, ii, 222), which contains arsenites, arsenates, ferrous and ferric salts, and organic matter, the following methods were employed.

Titration in acid solution with permanganate gives the amount of the latter corresponding with the ferrous salts, arsenites, and organic substances. Separate determinations are made of the total iron and of the total arsenic. The latter is estimated by the method of Andrews and Farr (Abstr., 1909, ii, 437), the arsenic being precipitated in the metallic state by adding 2—5 volumes of a solution containing 10 grams of crystalline stannous chloride and 40 grams of tartaric acid per litre of 40% hydrochloric acid; the arsenic is then dissolved in excess of standard iodine solution containing sodium hydrogen carbonate: $As + 5I + 7NaHCO_3 = Na_2HAsO_4 + 5NaI + 7CO_2 + 3H_2O$, the excess of iodine being determined by titration with arsenious anhydride. For the separate estimation of the arsenites, the iron salts are eliminated by precipitation with boiling sodium or potassium hydroxide and carbonate; the filtered liquid is treated with carbon dioxide to convert the hydroxides into carbonates, and titrated with iodine solution. The ferrous salts are estimated after elimination of the sulphuric acid under conditions which do not admit of the ferrous salts being oxidised, thus: the sulphuric acid is precipitated in solution slightly acidified with hydrochloric acid in a fairly large flask fitted with a three-holed stopper, through which pass the end of the barium chloride burette and a carbon dioxide delivery tube dipping below the surface of the liquid, the third hole allowing the gas to escape; the ferric and ferrous salts are then separated by the method given by Fresenius. The amounts of the separate constituents can then be calculated.

T. H. P.

Sodium Thiosulphate as the Standard Substance in Alkalimetry. WALTER FELD (*Zeitsch. angew. Chem.*, 1911, **24**, 1161—1163).—With excess of mercuric chloride, sodium thiosulphate reacts according to the equation: $Na_2S_2O_3 + 2HgCl_2 + H_2O = Hg_2Cl_2 + Na_2SO_4 + 2HCl + S$, 2 mols. of acid being liberated for every molecule of sodium thiosulphate (compare this vol., ii, 289). Since sodium thiosulphate can be obtained in a very pure state from Merck, the author recommends that the above reaction should be used to standardise solutions of alkali, the acid liberated being titrated by the alkali to be standardised. For the estimation, a cold saturated solution of mercuric chloride and a 4*N*-solution of ammonium chloride are used. The thiosulphate solution is added to excess of the mercuric chloride solution, and when the reaction is complete, either in the cold or on warming, an excess of ammonium chloride solution is added, and then the acid titrated with alkali, using methyl-orange as indicator. The ammonium chloride is necessary to prevent yellow mercuric oxide being precipitated by the action of the alkali on the excess of mercuric chloride; it must never be added before the reaction between the thiosulphate and mercuric chloride is complete, otherwise it hinders the reaction.

Excess of mercuric chloride is necessary, otherwise mercuric sulphide is formed according to the equation: $Na_2S_2O_3 + HgCl_2 + H_2O = HgS + Na_2SO_4 + 2HCl$, and masks the colour change of the indicator.

The author finds that Merck's sodium thiosulphate (solid) keeps well, at least for a year, in a corked bottle. T. S. P.

Rapid Estimation of Silver and Cadmium by means of the Gauze Cathode and Stationary Anode.

Raymond C. Benner and William H. Ross (*J. Amer. Chem. Soc.*, 1911, **33**, 1106—1112).—Experiments have been made to determine the best conditions for the electro-deposition of silver and cadmium. In both cases the best results are obtained with cyanide solutions to which alkali hydroxide has been added.

The deposition of silver, in quantities from 0·15 to 0·3 gram, can be carried out with currents up to 5 amperes, and the strength of the current appears to have little influence on the character of the deposit. The rate of deposition diminishes as the concentration of the potassium cyanide is increased, but the amount of silver which can be deposited in an adherent form may be correspondingly increased. For quantities of silver weighing less than 0·3 gram, the most satisfactory results were obtained when about 8 grams of potassium cyanide were added to 60 c.c. of solution.

The concentration of cyanide has much less effect on the character of the deposit in the case of cadmium. When deposited from solutions containing no hydroxide, the solution became coloured, and slightly higher results were obtained. This effect is not observed, however, when potassium hydroxide is added to the solutions. The addition of 2 grams of potassium hydroxide and 6 grams of potassium cyanide to 75 c.c. of solution is recommended. H. M. D.

Method for the Separation of the Metals of the Ammonium Carbonate Group (Calcium, Barium, and Strontium).

Erich Birnbräuer (*Chem. Zeit.*, 1911, **35**, 755).—The precipitate of mixed carbonates is dissolved in dilute nitric acid, and the solution evaporated to dryness on the water-bath. Calcium nitrate, if present, is extracted from the residue by repeated treatment with a 1 : 1 mixture of alcohol and ether; the solution so obtained is evaporated to dryness, the calcium nitrate dissolved in water, and the calcium precipitated as oxalate.

The residue of barium and strontium nitrates is dissolved in a small quantity of hot water, acetic acid and ammonium acetate or ammonia added to the solution, which should smell of acetic acid, and the barium precipitated as chromate by the addition of ammonium dichromate and boiling. Strontium is precipitated as sulphate from the filtrate by the addition of 1 : 2 ammonium sulphate solution. T. S. P.

The Volumetric Estimation of Lead Peroxide.

Julius F. Sacher (*Chem. Zeit.*, 1911, **35**, 731).—The author has observed that lead peroxide is somewhat soluble in nitric acid, and this causes errors in the estimation of the lead peroxide-content according to Lux's method (Abstr., 1880, 585). The error is avoided if the oxalic acid is added before the treatment with nitric acid. Before the titration with permanganate, the lead may be precipitated as sulphate with sulphuric acid; it is not necessary to filter off the lead sulphate before titrating.

Forestier's method (*Zeitsch. angew. Chem.*, 1898, 11, 176) is inaccurate. T. S. P.

Galvanic Estimation of Copper in Preserves. K. LAKUS (*Zeitsch. Nahr. Genussm.*, 1911, 21, 662—664).—Around an amalgamated zinc rod, 4 to 5 cm. in length, is twisted in two or three windings a copper wire. The solution to be tested (obtained by treating the ash with sulphuric acid) is placed into a perfectly clean and polished platinum dish. The about 5 cm. long end of the wire is laid over the edge of the dish in such a manner that the rod dips, in the middle of the dish, about 1 cm. deep into the liquid. As in this way the zinc does not come into direct contact with the platinum, and owing to the amalgamation, no hydrogen is evolved, and the copper forms a firmly-adhering deposit of a normal colour. L. DE K.

Analysis of Materials Containing Copper, Nickel, and Cobalt. HARALD PEDERSON (*Metallurgie*, 1911, 8, 335).—The finely-powdered material is attacked by fuming nitric acid, and is then twice evaporated with sulphuric acid. The iron is twice precipitated from the solution by ammonia, and after acidifying the filtrate with sulphuric acid, the copper is estimated electrolytically. Only traces of nickel and cobalt are deposited on the cathode. The solution is then rendered ammoniacal, and nickel and cobalt are deposited electrolytically. The deposit is dissolved in hot concentrated nitric acid, evaporated with addition of hydrochloric acid to remove nitric acid, diluted, and mixed with a 1% alcoholic solution of dimethylglyoxime, a small excess of ammonia being then added. The nickel precipitate is collected on a Gooch filter, washed with hot water, and dried at 110—120°. C. H. D.

Qualitative Detection of Mercury by Klein's Method. WILLIAM C. MOORE (*J. Amer. Chem. Soc.*, 1911, 33, 1117—1119).—The use of a solution containing potassium iodide, sodium hydroxide, and ammonia is recommended for the detection of mercury. By a comparison test with a standard solution of mercury, it is possible to estimate roughly the quantity of mercury present in a given solution. H. M. D.

Detection of Mercury in Urine. ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, 72, 387—401. Compare Hofmeister, *Arch. exp. Path. Pharm.*, 1884, 25, 225; Siebert, Abstr., 1910, ii, 656).—The urine is made distinctly acid by the addition of hydrochloric acid, and is evaporated first over the free flame and finally on the water-bath until salt begins to separate. The addition of 2 c.c. of

25% hydrochloric acid to each 500 c.c. of urine is usually sufficient. The mixture is then oxidised with hydrochloric and chloric acids and evaporated, and the residue extracted with alcohol. The alcoholic extract is evaporated, again oxidised, evaporated, and extracted with 40 c.c. of absolute alcohol; 60 c.c. of ether are added to precipitate most of the salts and the whole filtered. The alcoholic ethereal solution is evaporated, and the residue extracted by 10 c.c. of water by strongly shaking. After filtration through a stout filter-paper, five drops of a solution of stannous chloride and hydrochloric acid are added. If a turbidity or precipitate is formed, more hydrochloric acid is added. If the reaction is negative, the first alcoholic residue can be extracted with aqueous hydrochloric acid, filtered, evaporated, oxidised, and the same test again applied. J. J. S.

Colorimetric Estimation of Mercury in Urine. ALFRED HEINZELMANN (*Chem. Zeit.*, 1911, **35**, 721—722).—The method given by Schumacher and Jung (Abstr., 1903, ii, 44) for the estimation of mercury in urine is unsatisfactory. Errors are caused by the chlorine liberated when potassium chlorate is added to accelerate the solution of the zinc amalgam, and by the precipitating effect of the hydrochloric acid present on the colloidal mercuric sulphide. The following method is recommended by the author: 500 c.c. of urine are heated in a litre flask with 5 grams of potassium chlorate and 50 c.c. of hydrochloric acid (D = 1·12). When the mixture has become limpid and light yellow in colour, it is cooled to 70°, 10 grams of pure rasped zinc added, and left overnight. The urine is then poured off from the zinc, which is washed several times with water and then dissolved in 50 c.c. of hydrochloric acid (D = 1·18). Twenty grams of potassium acetate are added, the solution transferred to a Hehner cylinder and made up to 90 c.c. with water, and then to 100 c.c. with hydrogen sulphide water. The colour is then compared with that of a standard prepared at the same time from mercuric chloride. The comparison of colour should be made after about five minutes; the solutions obtained after the addition of the hydrogen sulphide water are stable only for about twenty minutes. T. S. P.

Analysis of Aluminium and its Alloys. GEORG KLEIST (*Chem. Zeit.*, 1911, **73**, 668—669).—The silicon in "pure" aluminium is determined as by Smith (*Chem. Zeit. Repert*, 1911, **45**, 188), but without special addition of sulphuric acid. For iron, 2—5 grams are heated in an Erlenmeyer flask with 100 c.c. of dilute sodium hydroxide until dissolved. The solution is strongly acidified with sulphuric acid, filtered, diluted to about 600 c.c., and titrated with permanganate. For copper and tin, the filtrate from the estimation of silicon is saturated with hydrogen sulphide, filtered, and the precipitate washed with cold water, ignited, and weighed as cupric and stannic oxides. If tin is present, as shown by insolubility in nitric acid, it is estimated as described later. The filtrate is concentrated to about 100 c.c., the iron thrown out with sodium hydroxide, then boiled, and filtered. Traces of zinc are precipitated from the filtrate by hydrogen sulphide, collected, ignited, and weighed as zinc oxide. In the case of alloys, the silicon and iron are determined in like manner, and the copper and tin in the filtrate are precipitated together as before. The tin is separately found by heating 1—2 grams of the alloy in an Erlenmeyer flask, provided with a bored rubber cork, with 150 c.c. of hydrochloric acid (D 1·19) until dissolved. The boiling liquid is titrated with ferric chloride solution, which has stood over pure tin, the end being marked by a yellow tinge. Otherwise, the weighed precipitate of cupric and stannic oxides may be dissolved in nitric acid, filtered, and the copper found by electrolysis or titration with potassium cyanide may be resorted to. The filtrate from the copper and tin is concentrated to 100 c.c., ammonia added, and just enough sulphuric acid to redissolve the alumina. After dilution to 400—500 c.c., hydrogen sulphide is passed in to saturation, and the zinc sulphide collected and washed with very dilute sulphuric acid containing some ammonium sulphate and hydrogen sulphide. The precipitate is dissolved from the filter with hot dilute hydrochloric acid, made slightly ammoniacal, boiled, and filtered. The filtrate is very slightly acidified with sulphuric acid, and the zinc re-precipitated by hydrogen sulphide. J. D. K.

Separation of Aluminium and Glucinum. M. Wunder and (Mlle.) Nina Chéladzé (*Ann. Chim. anal.*, 1911, **16**, 205—209).—The separation of glucinum from aluminium by taking advantage of the solubility of glucinum hydroxide in concentrated ammonium carbonate gives utterly untrustworthy results. The separation by means of potassium or sodium hydroxide which dissolves both hydroxides, but deposits the glucinum hydroxide only when the solution is sufficiently diluted and boiled for an hour (taking care to replace the water evaporated), seems, however, quite satisfactory. The aluminium is then recovered from the filtrate by acidifying with hydrochloric acid and reprecipitating with ammonia. L. de K.

Estimation of Chromium in Chrome Iron Ore. Otto Nydegger (*Zeitsch. angew. Chem.*, 1911, **24**, 1163—1164).—0·5 Gram of the powdered ore (not necessarily finely powdered) is heated with 5 grams of borax fusion mixture (made by fusing two parts of anhydrous sodium carbonate with one part of borax glass) in a platinum crucible over a good bunsen flame for one to two hours, or until all the ore has been taken up. The fused mass is dissolved from the cooled crucible with 300—400 c.c. of water containing 4 c.c. of concentrated sulphuric acid, and any chromium remaining unoxidised is transformed into chromate by the addition of 0·2 gram of potassium persulphate, which at the same time precipitates any manganese present as peroxide. The excess of persulphate is destroyed by boiling for thirty to forty minutes, the solution filtered from the manganese peroxide, and the filtrate titrated with standard ferrous ammonium sulphate solution, using potassium ferricyanide as indicator. T. S. P.

A Reaction for Uranium Salts. J. A. Siemssen (*Chem. Zeit.*, 1911, **35**, 742).—A weighed quantity of the uranium salt is dissolved in water and a 10% solution of ethylenediamine added drop by drop until a precipitate no longer forms (compare this vol., ii, 230). The precipitate, which is insoluble in water and the usual organic solvents, is washed with water, collected, dried, and ignited to the oxide, U_3O_8. The results are quantitative.

A solution of ethylenediamine more dilute than 10% should not be used, otherwise a gelatinous precipitate is formed. The precipitate is insoluble in excess of the precipitant (*loc. cit.*), but soluble in excess of the uranium salt. T. S. P.

Behaviour of Zirconium Oxide Towards Hydrofluoric Acid. EDGAR WEDEKIND (*Ber.*, 1911, **44**, 1753—1755. Compare Weiss and Neumann, Abstr., 1910, ii, 217).—When zirconium silicides, or zirconium metal containing silicon, or mixtures of the oxides of zirconium and silicon, are treated with a mixture of sulphuric and hydrofluoric acids to remove the silicon, some of the zirconium is often volatilised. This can be prevented by the addition of sufficient sulphuric acid, the zirconium material being treated with a mixture of twenty times its amount of concentrated sulphuric acid with forty-five times its amount of hydrofluoric acid; the zirconium is weighed as oxide, ZrO_2, formed from the sulphate by ignition.

Attempts to determine the combined silica in zirconium silicate (hyacinth) by the above method were unsuccessful. T. S. P.

Quantitative Chemical Analysis of Mixtures by means of Differences in Density. MICHAEL A. RAKUSIN (*Ber.*, 1911, **44**, 1676).—The author points out that the centrifugal method used by Friedenthal (this vol., ii, 555), even with 3000 revolutions per minute, causes considerable alterations in the optical and other properties of the earth-oils investigated. In one case the density diminished by 0·002—0·003, whilst the carbonisation constant rose about 30%. T. S. P.

Estimation of Camphor in Smokeless Powders. MARQUEYROL (*Ann. Chim. anal.*, 1911, **16**, 209—210).—Ten grams of the powder are extracted with ether in a Soxhlet tube for ten hours. The ether is poured into a beaker of 65—70 mm. in diameter and 35—40 mm. in height, which is then placed in a desiccator over sulphuric acid, and when the volume of the ether is reduced to a few c.c., the beaker is covered with a glass disk and rapidly weighed. The beaker is replaced in the desiccator, and the weighings are repeated, say, every ten minutes. Finally the camphor is expelled by heating at 30—35° and another weighing is taken. L. DE K.

Estimation of Glycerol in Fats and Soaps. ADOLF BEYTHIEN, H. HEMPEL, P. SIMMICH, W. SCHWERDT and C. WIESEMANN (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 673—675).—In the absence of soluble fatty acids (butyric, for instance), the original process of Benedikt and Zsigmondy (oxidation with alkaline permanganate and estimation of the oxalic acid formed) gives very satisfactory results.

In the presence of compounds acted on by permanganate, the acetin process should be employed. The dichromate process much used in soap works also gives good results provided the leys have been properly defecated with basic lead acetate. L. DE K.

Determination of the Rotatory Power of Some Organic Substances in Presence of Lead Reagents; Inconvenience of Distilled Water Containing Carbon Dioxide. HENRI PELLET (*Ann. Chim. anal.*, 1911, 16, 215—218).—Contrary to Sellier's statement that a solution of glutamine yields a gradually increasing precipitate with basic lead acetate, the author states that with pure glutamine no precipitate is obtained provided the water is absolutely free from carbon dioxide. No trouble is experienced in the polarisation.

Glutamic acid, asparagine, aspartic acid, raffinose, invert sugar, dextrose, and lævulose are also unaffected by basic lead acetate.

L. DE K.

Estimation of Gum in Syrups. XAVIER ROCQUES and G. SELLIER (*Ann. Chim. anal.*, 1911, 16, 218—220).—A process recently published by Chauvin (*Mon. Sci.*, 1911, May), but which has been already employed by one of the authors for some years.

Twenty-five grams of the syrup are mixed with 80 c.c. of alcohol (90° French), slowly at first, 2 c.c. of a saturated alcoholic solution of lead acetate are added, and the precipitate is allowed to settle for twenty minutes. It is then collected on a tared filter, and washed with alcohol (75°). After drying, the precipitate is weighed, and, after allowing for the lead oxide it contains (calcination with nitric acid), the result equals pure gum, which multiplied by 1·18 represents ordinary gum arabic.

If it is desired to know the weight of gum per litre of syrup, 20 c.c. are diluted with 10 c.c. of water, 2 c.c. of alcoholic lead acetate are added, and then 90 c.c. of alcohol (95°). The precipitate is then treated as before. L. DE K.

Estimation of Salicylic Acid in Fruit Juices. P. VIERHOUT (*Zeitsch. Nahr. Genussm.*, 1911, 21, 664—666).—Fifty c.c. of the juice are placed in a spacious separating funnel, 15 drops of sulphuric acid are added, and the mixture shaken with 50 c.c. of light petroleum, b. p. 40—60°.

In order to destroy the thick emulsion, 25 c.c. of 96% alcohol are added, and the whole again shaken. After siphoning off the supernatant liquid into a measure, the remainder is again shaken with 50 c.c. of light petroleum, and then with 25 c.c. of alcohol. The whole of the contents of the funnel are now poured into the measure, and the liquid is made up to 200 c.c. by adding a mixture of 5 vols. of light petroleum and $2\frac{1}{2}$ vols. of alcohol. The whole is shaken for a moment, and 50 c.c. of the supernatant liquid (12·5 c.c. of the sample) are pipetted off into a small flask containing a few grams of dry sodium sulphate, and, after closing the flask, the whole is allowed to remain for two hours. The solution is then filtered through a dry filter into an Erlenmeyer flask containing 50 c.c. of *N*/10-sodium hydroxide, the sodium sulphate is washed with a few more c.c. of the alcohol-petroleum mixture, and the light petroleum is distilled off. The excess of alkali is then titrated with *N*/10-acid, and the percentage of salicylic acid found by an easy calculation. L. DE K.

Iodometric Estimation of Uric Acid in Urine. DIOSCORIDE VITALI (*Boll. Chim. Farm.*, 1911, **50**, 365—366).—The author has already described (Abstr., 1899, i, 117) the reaction which Pizzorno (this vol., ii, 667) proposes to apply for the above purpose, but he did not propose it as a method of estimation, because there may well be other substances in urine which will consume iodine. R. V. S.

Estimation of Formaldehyde by the Ammonia Process. ADOLF BEYTHIEN, H. HEMPEL, P. SIMMICH, W. SCHWERDT, and C. WIESEMANN (*Zeitsch. Nahr. Genussm.*, 1911, **21**, 671—673).—Smith's modification of the ammonia process is recommended (2 grams of ammonium chloride are dissolved in 25 c.c. of water, 2·5 c.c. of the formalin are added, and then 25 c.c. of *N*-sodium hydroxide. After remaining for half an hour in a closed flask, the excess of ammonia is titrated with *N*-acid, using rosolic acid as indicator.

Other indicators, such as cochineal and methyl-orange, are less suitable, and litmus, phenolphthalein, and Congo-red must be rejected altogether. L. DE K.

Assay of Paraldehyde. R. RICHTER (*Pharm. Zeit.*, 1910, **56**, 536—538).—The author states that as the "D.A.-B.V." seems to insist on the presence of 4% of aldehyde in the drug paraldehyde, the density of the sample at 15° may be as low as 0·993, instead of 0·998—1·000. About one-half may pass over on distillation before the temperature of 123° is reached. When observing the solidifying point, it must be remembered that besides aldehyde, metaldehyde is also formed, which elevates the solidifying point. The amount of metaldehyde is found with fair accuracy by evaporating 10 grams of the sample at 50° and weighing the residue.

In the author's opinion the presence of aldehyde in the drug renders it less suitable for medicinal purposes, and an article as follows should be prescribed: $D^{15} = 0·998—1·000$, b. p. 124·7—125·2°, solidifying point 10—12°; metaldehyde to be estimated as directed. Aldehyde may be tested for by the colour given on warming at 50—60° with an equal volume of 5% potassium hydroxide. L. DE K.

Estimation of Acetone in Animal Liquids. H. SCOTT-WILSON (*J. Physiol.*, 1911, **42**, 444—470).—A new method based on that of Marsh and Struther's mercuric cyanide process (Trans., 1905, **87**, 1878) is described. Urine contains some substance which, after exposure to alkali, yields on distillation with acid an additional amount of acetone. The average daily excretion of free and combined acetone in human urine is 2—4 mg. The amount runs parallel to the nitrogen. W. D. H.

Detection and Estimation of Cyanamide in the Presence of other Fertilisers. L. VUAFLART (*Ann. Falsif.*, 1911, **4**, 321—324). —Cyanamide may be recognised, even in the presence of other manures, by its peculiar odour, due to the action of moisture on traces of calcium carbide. When moistened with sulphuric acid, a heavy fine powder is left, whilst organic manures (blood, for instance) leave a swollen, brown mass. Contrary to expectation, cyanamide yields all its nitrogen as ammonia by soda-lime combustion. The assay of commercial samples is as follows:

One gram of the sample is shaken in a closed vessel with 250 c.c. of water for a few hours. Of the filtrate, 100 c.c. are mixed with 20 c.c. of 5% silver nitrate solution and then 20 c.c. of ammonia. The precipitate is washed with cold water, and then re-dissolved in dilute nitric acid (1 : 2). The silver is then estimated by the thiocyanate method: 108 parts of silver = 14 parts of nitrogen. On an average, 87·3% of the total nitrogen exists as cyanamide. Dicyanodiamide, which is present in old samples, may be estimated jointly with cyanamide by mixing 100 c.c. of the solution (this time of double strength) with silver solution, but adding, instead of ammonia, 20 c.c. of 10% potassium hydroxide. After washing the precipitate the nitrogen is determined by the Kjeldhal process. L. DE K.

Analysis of Calcium Cyanamide. ALBERT STUTZER (*Chem. Zeit.*, 1911, **35**, 694).—It is pointed out that the unsatisfactory results obtained by Monnier (this vol., ii, 668) in the estimation of calcium cyanamide by precipitation as the silver salt and determination of the silver in the precipitate by means of ammonium thiocyanate, confirm the experiments of the author and Söll (Abstr., 1910, ii, 1009) and of Caro (this vol., i, 118), who, at the same time, give an satisfactory method of analysis. Also, in contradistinction to Monnier, the author finds that the Kjeldahl method for the determination of the total nitrogen is quite satisfactory; furthermore, he does not agree with Monnier's results as to the amount of nitrogen present which has for its source the coal used in the manufacture of the calcium carbide.

T. S. P.

A Delicate Test for Acetanilide. G. N. WATSON (*Amer. J. Pharm.*, 1911, **83**, 269—270).—By heating a mixture of acetanilide and boric acid over the bare flame until the boric acid melts, a yellow residue is obtained, having a peculiar fragrant odour resembling sweet clover or arbutus. The yellow colour is, however, also given by phenacetin. Antipyrin gives a pink colour and an odour of naphthalene. Phenacetin gives an odour characteristic of itself, but very faint. With mixtures of the three, the fragrant odour produced by the acetanilide is sufficient to give the characteristic odour, which is intensified by moistening the residue with water.

Reversely, acetanilide may, perhaps, be used as a test for boric acid. L. DE K.

Reactions of Pyramidone. A. MOULIN (*Ann. Chim. anal.*, 1911, **16**, 220—221)—If pyramidone in powder is treated with a drop of nitric acid, decomposition takes place with evolution of nitrous fumes, and the spot first turns yellow with a bluish-black zone, but gradually becomes a pale blue.

Solutions of pyramidone are not coloured blue by nitric acid unless nitrous vapours are present. Nitrates which are easily decomposable, such as mercury or silver nitrate, also cause the coloration to appear.

L. DE K.

Alkaloid Reactions. Arecoline. C. REICHARD (*Pharm. Zentr.-h.*, 1911, **52**, 711—716).—A large number of colour reactions given by arecoline with reagents are described. The following are the most characteristic. On adding arecoline hydrobromide to cold sulphuric acid, a colourless solution with a few minute crystals is formed. On warming, a cloudiness appears near the crystals, then spreads through the liquid, and finally disappears. Nitric acid behaves similarly. With potassium dichromate and a drop of water, a green tint is produced as the mixture dries, and becomes more pronounced on adding hydrochloric acid, but is never very intense. Ammonium molybdate behaves similarly, giving a pale blue coloration. With potassium ferrocyanide, the alkaloid gives after some hours a bluish coloration changing slowly to green, and with potassium ferricyanide a bright green with characteristic crystalline forms. The ferrocyanide residue becomes blue on adding hydrochloric acid, whilst the ferricyanide residue becomes darker green with bluish tones. These and other reactions are described in detail in the original. T. A. H.

The Crystalline Deposit of a Certain Fluid Extract of Cinchona Bark. The Estimation of the Quinine Alkaloids and Quininine Silicotungstate. MAURICE JAVILLIER and B. GUÉRITHAULT (*Chem. Zentr.*, 1911, i, 1065; from *Bull. Sci. Pharm.*, 1911, **18**, 85—89).—The crystalline deposit from a percolate of cinchona bark with a mixture of glycerol, alcohol, and water consists exclusively of calcium quinate, and is free from alkaloids. Yvon's method for estimating the alkaloids by silicotungstic acid gives good results, the quinine salt having the formula

$$SiO_2,12WO_3,2H_2O,2C_{20}H_{24}O_2N_2 + 7H_2O,$$

a light, yellow powder, which loses 6 mols. of water of crystallisation at 120°, and the composition of which remains constant under most diverse methods of precipitation. S. B. S.

Estimation of Nicotine in the Presence of Pyridine Bases. LÉON SURRE (*Ann. Falsif.*, 1911, **4**, 331—334).—The nicotine extract is, if necessary, diluted to about 10% strength of nicotine. Twenty-five to fifty c.c. of the solution (this depends whether the sample is alkaline or acid) are then distilled with addition of 1—2 grams of magnesia and 2—4 grams of powdered pumice in a special apparatus until 25 c.c. have passed over; water is now added continually to keep up the volume of the liquid, and the distillation is continued until exactly 150 c.c. of distillate has been collected; the receiver is then changed and another 150 c.c. is distilled off.

The first distillate contains all the pyridine with the bulk of the nicotine, which is then determined polarimetrically, pyridine being quite inactive. The second portion of the distillate contains the remainder of the nicotine, which is then titrated with standard acid, using luteol as indicator. L. DE K.

Estimation of Tannin in Wines. PHILIPPE MALVEZIN (*Bull. Soc. Chim.*, 1911, [iv], **9**, 620—621; *Ann. Chim. anal.*, 1911, **16**, 221—222).—The method consists in precipitating the tannin as its zinc derivative, dissolving this in dilute sulphuric acid, and titrating with *N*/10-permanganate.

The zinc solution is made by dissolving 10 grams of zinc oxide in sufficient acetic acid, adding 80 c.c. of ammonia, and making up to 1 litre with distilled water. Ten c.c. of wine are mixed with 10 c.c. of the zinc solution; the mixture is boiled during five minutes, cooled, and 25 c.c. of boiling distilled water added. The precipitate is collected, washed with 100 c.c. of boiling distilled water, dissolved in dilute sulphuric acid (2·5 c.c. in 100 c.c. of distilled water), and titrated with *N*/10-permanganate at 60—70°, each c.c. of which is equal to 0·116 gram of gallotannic acid per litre of wine.

T. A. H.

Lecithin. ROBERT COHN (*Zeitsch. öffentl. Chem.*, 1911, **17**, 203—217).—The fact that all the lecithin cannot be extracted with ether from commercial preparations of lecithin and yolk of egg may be attributed to an adsorption of this substance by the albumin. The whole of the adsorbed lecithin may be extracted with cold ethyl alcohol; it is not necessary to employ hot alcohol, as subsequent treatment with this liquid only removes traces of other phosphatides.

If the original preparation has been heated, it is not always possible to extract the whole of the lecithin with ether and alcohol or other liquids.

Lecithin may be estimated in preparations which contain added phosphoric or glycerophosphoric acids by extraction first with ether and then with alcohol. The alcoholic product contains some of the added acids, and must be re-extracted with chloroform to remove the soluble lecithin from these substances. W. J. Y.

Estimation of Aliphatic Amino-groups. Applications to the Study of Proteolysis and Proteolytic Products. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1911, **9**, 185—204).—Full details of the apparatus and method previously described (Abstr., 1910, ii, 751) are given. The nitric oxide is produced by the action of a feeble acid, for example, acetic acid, on sodium nitrite solution. The results are summarised as follows: Every known amino-acid obtained from proteins by acid hydrolysis reacts quantitatively with one and only one nitrogen atom, except lysine, which reacts with two, and proline and oxyproline, which do not react at all. All the amino-acids react with the whole of their nitrogen, except tryptophan, which reacts with half, histidine with one-third, arginine with one-fourth, and proline and oxyproline with none.

The dipeptides leucyl-leucine and leucylglycine, react with only their free amino-groups, the nitrogen in $-CO \cdot NH-$ groups does not react. Glycyl anhydride does not give off nitrogen when treated with nitrous acid. The proteins egg-albumin and edestin evolve but little nitrogen. The proportion of free amino-nitrogen is twice as great in the primary albumoses, and still greater in the deutero-albumoses.

Purine and pyrimidine derivatives react normally with the exception of guanosine, which gives 1·25 instead of 1 mol. of nitrogen, probably owing to the rupture of the purine ring.

Glycine and nitrous acid yield, not only nitrogen, but also carbon dioxide, and this is not absorbed by the permanganate. The abnormal results obtained with glycine and glycylpeptides are most probably due to the fact that the intermediary diazo-compound does not decompose entirely in the normal manner, yielding glycollic acid, but that a part is completely decomposed, yielding carbon dioxide and other products, and the disintegration of the group at the end of the peptide chain severs the peptide linking and exposes to attack the nitrogen of the next amino-group.

Lysine reacts abnormally in requiring a longer time in order to react completely with the nitrous acid. This is probably due to the fact that one of the two amino-groups is not in the α-position.

The method of amino-nitrogen determination has been used for measuring the rate of hydrolysis, using the ordinary equation for a unimolecular reaction. The method can also be used for determining the relative digestibility of proteins, for quantitative determination of proteolytic enzymes, for the analysis of amino-acids, for the determination of the complexity and structure of peptides and proteolytic products, and for the characterisation of proteins.

J. J. S.

Estimation of Proline Obtained by the Ester Method in Protein Hydrolysis. Proline Content of Casein. Donald D. van Slyke (*J. Biol. Chem.*, 1911, **9**, 205—207).—The usual method of estimating proline, namely, by the alcoholic extraction of the amino-acids, the esters of which boil below 90° under pressure of less than 1 mm. and calculating as proline all the soluble acids, gives too high results, as other soluble acids are also present. If, on the other hand, the proline is racemised and recrystallised as the *dl*-copper salt, only a portion of this can be separated from the mixture.

As proline does not give up its nitrogen when treated with nitrous acid, whereas the acids the esters of which distil over with proline do react with nitrous acid (compare preceding abstract), the following is a simple and accurate method for the determination of proline: the total nitrogen content of the mixture soluble in alcohol is determined, and this minus the amino-nitrogen as determined by nitrous acid gives the amount of nitrogen in the form of proline.

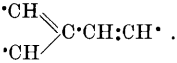
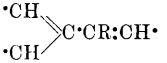
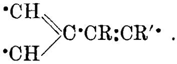
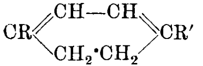
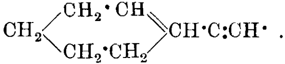
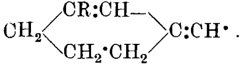
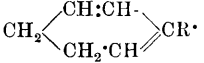
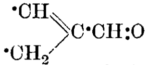
A specimen of casein examined by this method gave 6·7% of proline, a value about twice that given by Abderhalden. The amino-determination is the most delicate test for ascertaining the purity of proline isolated from mixtures of amino-acids. J. J. S.

General and Physical Chemistry.

Index of Refraction of Binary Mixtures. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 752—758).—In a detailed criticism of the work of Schwers (Abstr., 1910, ii, 913, 1039), the author points out that some of the regularities deduced by that writer are more apparent than real, inasmuch as they are in part necessary consequences of the mode of mathematical reduction employed.

R. V. S.

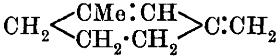
Spectro-chemical Investigations. II. The Refraction and Dispersion of Substances Containing One Pair of Conjugate Double Linkings. KARL AUWERS and FRITZ EISENLOHR (*J. pr. Chem.*, 1911, [ii], 84, 1—36).—The values of the specific refractions and dispersions of the compounds previously discussed (compare Abstr., 1910, ii, 365, 367, 561) have been re-calculated with the aid of Eisenlohr's recent values for the refractivities and dispersions of the various elements (this vol., ii, 81). With the aid of these and also of some additional data the following table is drawn up :

Compound.	Conjugate System.	$E\Sigma$ Ref.	$E\Sigma$ Disp., %
Aliphatic hydrocarbons	$\cdot CH{:}CH\cdot CH{:}CH\cdot$	1·90	50
	$\cdot CH{:}CH\cdot CR{:}CH\cdot$	1·10	50
Styrenes	 $\begin{matrix}\cdot CH \\ \cdot CH\end{matrix}\!>C\cdot CH{:}CH\cdot$	1·10	45
	 $\begin{matrix}\cdot CH \\ \cdot CH\end{matrix}\!>C\cdot CR{:}CH\cdot$	0·70	30
	 $\begin{matrix}\cdot CH \\ \cdot CH\end{matrix}\!>C\cdot CR{:}CR'\cdot$	0·45	20
Hydroaromatic hydrocarbons		0·8 –1·2	40 —
			
			
		0·25	20
Aldehydes	$\cdot CH{:}CH\cdot CH{:}O$	1·80	50
	$\cdot CH{:}CR\cdot CH{:}O$ $\cdot CH{:}CR\cdot CH{:}O$	1·25	45
Cyclic aldehydes	 $\begin{matrix}\cdot CH \\ \cdot CH_2\end{matrix}\!>C\cdot CH{:}O$	1·00	45
Ketones	$\cdot CH{:}CH\cdot CR{:}O$	0·90	30—40
	$\cdot CR'{:}CH\cdot CR{:}O$	0·85	
	$\cdot CH{:}CR'\cdot CR{:}O$	0·50	—
Acids	$\cdot CH{:}CH\cdot C(OH){:}O$	1·10	40
	$\cdot CH{:}CR\cdot C(OH){:}O$	0·80	—
Esters	$\cdot CH{:}CH\cdot C(OR){:}O$	0·80	30
	$\cdot CH{:}CR'\cdot C(OR){:}O$	0·50	20

As the value $E\Sigma_{\alpha}$ and $E\Sigma_{\mathrm{D}}$ differ but little from one another, the mean value is given in the table, and similarly for $E\Sigma_{\gamma-\alpha}$ and $E\Sigma_{\beta-\alpha}$, where $E\Sigma$ is the exaltation of Σ (Abstr., 1910, ii, 365).

The following new experimental data are given:

$\alpha\delta$-Diphenyl-Δ^{α}-hexene (Rupe and Burgin, Abstr., 1910, i, 161) has b. p. 190—191°/11 mm., $D_4^{21\cdot8}$ 0·9892, n_{α} 1·58083, n_{D} 1·58749, n_{β} 1·60490, and n_{γ} 1·62049 at 22·8°.

1-*Methyl-3-methenyl*-1-cyclo*hexene*,  $\mathrm{CH_2}{<}\begin{matrix}\mathrm{CMe{:}CH}\\ \mathrm{CH_2{\cdot}CH_2}\end{matrix}{>}\mathrm{C{:}CH_2}$, has b. p. 134—138°, $D_4^{18\cdot8}$ 0·8389, n_{α} 1·48274, n_{D} 1·48723, n_{β} 1·49872, and n_{γ} 1·50910 at 17·0°.

The ethyl ether of methyl*iso*phoronecarboxylic acid (Merling and Welde, Abstr., 1909, i, 480) has b. p. 150—151°/14 mm., D_4^{19} 1·0248, n_{α} 1·47760, n_{D} 1·48181, n_{β} 1·49023, and n_{γ} 1·49776 at 19°, and the ethyl ether of ethyl *iso*phoronecarboxylate has b. p. 163—166°/19 mm., D_4^{19} 1·0109, n_{α} 1·47936, n_{D} 1·48288, n_{β} 1·49148, and n_{γ} 1·49921 at 19°.

Crotonaldehyde has b. p. 103—104°, $D_4^{16\cdot7}$ 0·8537, $D_4^{23\cdot1}$ 0·8486, n_{α} 1·43064, n_{D} 1·43478, n_{β} 1·44550, and n_{γ} 1·45491 at 23·1°.

Citral has b. p. 114·6—115·6°/15·5 mm., $D_4^{16\cdot95}$ 0·8897, n_{α} 1·48506, n_{D} 1·48945, n_{β} 1·50073, and n_{γ} 1·51081 at 17·05°.

*cyclo*Citral (Tiemann and Schmidt, Abstr., 1901, i, 158) has b. p. 112—114°/29 mm., $D_4^{15\cdot25}$ 0·9566, n_{α} 1·49341, n_{D} 1·49707, n_{β} 1·50689, and n_{γ} 1·51575 at 13·3°. α-Ionone has b. p. 146·5—147·5°/28 mm., $D_4^{21\cdot2}$ 0·9298, n_{α} 1·49452, n_{D} 1·49842, n_{β} 1·50834, and n_{γ} 1·51735 at 22·3°.

1-Methyl-Δ^1-*cyclo*hexen-1-one (Knoevenagel, Abstr., 1895, i, 51) has b. p. 94·5—95·5°/22 mm., $D_4^{18\cdot8}$ 0·9707, n_{α} 1·49137, n_{D} 1·49547, n_{β} 1·50624, and n_{γ} 1·51573 at 18·7°.

Carvenone has b. p. 117—117·5°/19 mm., $D_4^{15\cdot4}$ 0·9302, n_{α} 1·48099, n_{D} 1·48457, n_{β} 1·49361, and n_{γ} 1·50175 at 16·25°.

Ethyl *iso*phoronecarboxylate has b. p. 142—143°/10 mm., $D_4^{15\cdot5}$ 1·0332, n_{α} 1·47711, n_{D} 1·48054, n_{β} 1·48905, and n_{γ} 1·49635 at 16·9°. Acetophenone has b. p. 83·5°/12 mm., $D_4^{16\cdot2}$ 1·0301, n_{α} 1·52945, n_{D} 1·53503, n_{β} 1·54925, and n_{γ} 1·56201 at 17·15°.

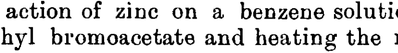
Geranic acid has b. p. 158°/14 mm., $D_4^{19\cdot4}$ 0·9518, n_{α} 1·48284, n_{D} 1·48695, n_{β} 1·49758, and n_{γ} 1·50690 at 20·2°.

Pure methyl benzoate free from chlorine has b. p. 83°/11 mm., D_4^{16} 1·0905, n_{α} 1·51309, n_{D} 1·51810, n_{β} 1·53060, and n_{γ} 1·54157 at 16°. Methyl geranate has b. p. 117°/14 mm., D_4^{20} 0·9220, n_{α} 1·46770, n_{D} 1·47143, n_{β} 1·48106, and n_{γ} 1·48929 at 19·1°. Ethyl itaconate has b. p. 111°/13 mm., $D_4^{16\cdot3}$ 1·0500, n_{α} 1·43833, n_{D} 1·44114, n_{β} 1·44765, and n_{γ} 1·45334 at 15·4°.

The high value for $E\Sigma_{\mathrm{D}}$ obtained for *dl*-$\Delta^{2\ 8(9)}$-*m*-menthadiene (Haworth, Perkin, and Wallach, Trans., 1911, **99**, 123) is probably due to the compound examined containing a certain amount of an isomeride with a semicyclic double linking (compare Auwers and Peters, Abstr., 1910, i, 826, 841). J. J. S.

Spectro-chemical Investigations. III. The Refraction and Dispersion of Hydrocarbons, Aldehydes, Ketones, Acids, and Esters containing Several Related Conjugations. KARL AUWERS and FRITZ EISENLOHR (*J. pr. Chem.*, 1911, [ii], **84**, 37—121. Compare preceding abstract).—The theoretical values have been calculated with the aid of Eisenlohr's recent numbers (this vol., ii, 81). Straight chains of conjugate linkings are termed "grouped conjugations," and systems of the types $-C{:}C{<}\begin{smallmatrix}C{:}C-\\C{:}C-\end{smallmatrix}$ and $-C{:}C{<}\begin{smallmatrix}C{:}C-\\C{:}O\end{smallmatrix}$ are termed "crossed conjugations." Difficulties are involved in the investigation of many of these compounds, as they are unstable and readily form additive compounds. Many of the examples given are taken from chemical literature. The following data are new: *allo*Ocimene, $CHMe_2{\cdot}CH{:}CH{\cdot}CH{:}CMe{\cdot}CH{:}CH_2$, has $D_4^{15\cdot6}$ 0·8119, n_α 1·54403, n_D 1·54558, n_β 1·57682, and n_γ 1·60086. Its exaltation for $\Sigma_{\gamma-\alpha}$ is 178%, and it cannot possibly be stereoisomeric with ocimene, as suggested by Enklaar. Pure α-phenyl-δ-methyl-$\Delta^{\alpha\gamma}$-pentadiene, after removal of all unaltered ketone, has b. p. 123—124°/14 mm., $D_4^{16\cdot2}$ 0·9512, n_α 1·5409, n_D 1·5474, n_β 1·5651, n_γ 1·5923 at 16·2°. Di-α-phenyl-Δ^α-heptylene (Klages and Heilmann, Abstr., 1904, i, 487) has D_4^{18} 0·9673 and n_D 1·5648 at 18°. Methylethylfulvene (Abstr., 1907, i, 639) has b. p. 87·4—87·9°/40 mm., $D_4^{20\cdot9}$ 0·8772 n_α 1·52988, n_D 1·53702 at 20·9°; diethylfulvene has b. p. 96·8—97·2°/40 mm., $D_4^{16\cdot4}$ 0·8812, n_α 1·52339, n_D 1·52997 at 16·4°; crotonylideneacetone (Meerwein, Abstr., 1908, i, 90) has b. p. 88°/28—29 mm., $D_4^{18\cdot7}$ 0·8946, n_α 1·50924, n_D 1·51767, n_β 1·53858 at 18·9°; styryl phenyl ketone, $D_4^{62\cdot4}$ 1·0712, n_α 1·63422, n_D 1·64578, n_β 1·68161 at 62·3°; styryl methyl ketone, b. p. 126—128°/9 mm., $D_4^{47\cdot3}$ 1·0076, n_α 1·57301, n_D 1·58241, n_β 1·60621 at 47·3°; α-methylstyryl ethyl ketone, b. p. 124·5—125°/10 mm., $D_4^{40\cdot2}$ 1·0072, n_α 1·56445, n_D 1·57202, n_β 1·59406 at 40·2°; benzylideneacetylacetone (Knoevenagel, Abstr., 1895, i, 50), b. p. 172—173·5°/12 mm., $D_4^{17\cdot3}$ 1·0928, n_α 1·5762, n_D 1·58464, n_β 1·6083 at 17·3°; β-ionone, b. p. 150—151°/24 mm., $D_4^{19\cdot6}$ 0·9445, n_α 1·51443, n_D 1·51977, n_β 1·53396, n_γ 1·54783 at 18·9°. The two modifications of benzophenone have much the same values (compare Eykman, *Rec. trav. chim.*, 1895, **14**, 189).

Ethyl α-methylcinnamate has b. p. 162—163°/30 mm., $D_4^{20\cdot6}$ 1·0321, n_α 1·54074, n_D 1·54753, n_β 1·565, n_γ 1·58162 at 20·6°; ethyl β-methyl cinnamate, b. p. 138—138·5°/9 mm., $D_4^{16\cdot6}$ 1·0392, n_α 1·5393, n_D 1·54558, n_β 1·56165, n_γ 1·57654 at 16·6°; *ethyl α-benzylcinnamate*, m. p. 38—39°, b. p. 227—229°/30 mm., D_4^{20} 1·0831, n_α 1·58163, n_D 1·5885, n_β 1·60717 at 16·1°; ethyl α-phenylcinnamate, m. p. 28°, b. p. 214—215°/28 mm., $D_4^{18\cdot2}$ 1·0971, n_α 1·58973, n 1·59723, n_β 1·61959 at 18·55°; ethyl benzylidenemalonate, b. p. 189—190°/14 mm., D_4^{20} 1·1045, n_α 1·53242, n_D 1·53894, n_β 1·55697, n_γ 1·57444 at 20·4°. *Ethyl* 1-*methyl*-Δ^1-cyclo*hexenylidene acetate*,



$$CH_2{<}\begin{matrix}CMe{=}CH\\CH_2{\cdot}CH_2\end{matrix}{>}C{:}CH{\cdot}CO_2Et,$$

obtained by the action of zinc on a benzene solution of methyl*cyclo*hexenone and ethyl bromoacetate and heating the resulting hydroxy-ester with potassium hydrogen sulphate (compare Auwers and Peters, Abstr., 1910, i, 841), has, after purification by conversion into the acid and subsequent esterification, b. p. 133·5—135°/15 mm., $D_4^{18\cdot9}$ 0·9987, n_α 1·52646, n_D 1·53312, n_β 1·55148, and n_γ 1·5694 at 17·3°.

Ethyl atropate, $CH_2{:}CPh{\cdot}CO_2Et$, prepared from the silver salt, has b. p. 124—124·4°/16 mm., or 120·2—120·4°/14 mm., $D_4^{16\cdot1}$ 1·0508, n_α 1·52151,

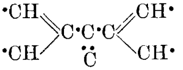
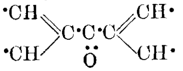
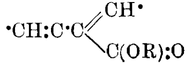
n_D 1·52605, n 1·53871, and n_γ 1·54996 at 16·1°. iso*Propyl cinnamylideneacetate*, $CHPh{:}CH{\cdot}CH{:}CH{\cdot}CO_2{\cdot}C_3H_7$, is a yellow oil, with b. p. 169°/9 mm., D_4^{18} 1·0256, n_β 1·59449, n_D 1·60663, n_β 1·64244 at 13·7°.

Amyl cinnamylidenemalonate, $CHPh{:}CH{\cdot}CH{:}C(CO_2{\cdot}C_5H_{11})_2$, has b. p. 212—214°/12 mm., $D_4^{19\cdot8}$ 1·087, n_α 1·60221, n_D 1·61599, n_β 1·65914 at 19·8°. Ethyl cinnamylideneacetoacetate (Knoevenagel, Abstr., 1898, i, 406) has b. p. 217—220°/18 mm., $D_4^{17\cdot4}$ 1·0823, n_α 1·60433, n_D 1·6155, n_β 1·66216 at 17·4°. *Ethyl sorbate*, $CHMe{:}CH{\cdot}CH{:}CH{\cdot}CO_2Et$, has b. p. 76°/14 mm., $D_4^{20\cdot15}$ 0·956, n_α 1·49554, n_D 1·50227, n_β 1·52001, n_γ 1·53664 at 20·15°.

Ethyl βδ-dimethylsorbate (compare Rupe and Lotz, Abstr., 1903, i, 229) has b. p. 105·5—107°/30 mm., $D_4^{16\cdot1}$ 0·9281, n_α 1·46165, n_D 1·46548, n_β 1·47513, n_γ 1·48385 at 16·7°. Ethyl fumarate has $D_4^{16\cdot6}$ 1·0537, n_α 1·43828, n_D 1·44150, n_β 1·44933, n_γ 1·45623 at 15·4° (compare Knops, Abstr., 1888, 938; 1889, 198). Methyl citraconate has b. p. 94—95°/11 mm., $D_4^{16\cdot8}$ 1·1248, n_α 1·44788, n_D 1·45107, n_β 1·459, n_γ 1·46583 at 17·2°. Ethyl citraconate has b. p. 107·5—108°/11 mm., $D_4^{17\cdot2}$ 1·0444, n_α 1·44326, n_D 1·44630, n_β 1·45351, n_γ 1·45967 at 41·9°. Knop's value for D is incorrect; the new value gives results for the exaltation of refraction and dispersion which agree with those for the methyl ester. Ethyl *iso*propylideneacetoacetate has b. p. 104—105·5°/15 mm. or 97—98·5°/13 mm., $D_4^{17\cdot6}$ 0·9959, n_α 1·44915, n_D 1·45223, n_β 1·46024, n_γ 1·46729 at 19·9°. Ethyl ethylidenemalonate, prepared by condensing ethyl malonate and acetaldehyde with acetic anhydride and zinc chloride, has b. p. 117—118°/17·5 mm., $D_4^{16\cdot5}$ 1·0426, n_α 1·43798, n_D 1·44084, n_β 1·44785, n_γ 1·45393 at 16·1°. Ethyl *iso*propylidenemalonate has b. p. 110·5—111·5°/9 mm., $D_4^{16\cdot4}$ 1·0284, n_α 1·44562, n_D 1·44857, n_β 1·45602, n_γ 1·46233 at 17°.

Compounds with grouped conjugations show a much greater exaltation than those with crossed conjugations, and the introduction of substituents tends to reduce the exaltations.

The following table gives a list of the mean values for the exaltations of refraction and dispersion for some of the more important groups.

	Grouping.	*E*Σ Ref.	*E*Σ Disp., %
Hydrocarbons	$\cdot CH{:}CR{\cdot}CH{:}CH{\cdot}CH{:}CH\cdot$	3·4	130
,, Phenylstyrene group	 $\begin{matrix}\cdot CH & & CH\cdot \\ & {>}C{\cdot}\underset{\ddot{C}}{C}{\cdot}C{<} & \\ \cdot CH & & CH\cdot\end{matrix}$	1·0	40
Aldehyde	$\cdot CH{:}CR{\cdot}CH{:}CH{\cdot}CH{:}O$	3·3	150
Ketones	$\cdot CH{:}CH{\cdot}CH{:}CH{\cdot}CR{:}O$	3·3	145
	$\cdot CH{:}CR{\cdot}CH{:}CH{\cdot}CR{:}O$	2·7	110
	$\cdot CH{:}CR{\cdot}CH{:}CR{\cdot}CR{:}O$	2·1	95
,, (benzophenone group)	 $\begin{matrix}\cdot CH & & CH\cdot \\ & {>}C{\cdot}\underset{\ddot{O}}{C}{\cdot}C{<} & \\ \cdot CH & & CH\cdot\end{matrix}$	1·0	45
Esters	$\cdot CH{:}CH{\cdot}CH{:}CH{\cdot}C(OR){:}O$	2·4	120
	$\cdot CH{:}CR{\cdot}CH{:}CH{\cdot}C(OR){:}O$	2 0	100
	$\cdot CH{:}CR{\cdot}CH{:}CR{\cdot}C(OR){:}O$	1·5	75
	 $\cdot CH{:}C{\cdot}C{<}\begin{matrix}CH\cdot \\ C(OR){:}O\end{matrix}$	0·5	25

The esters of cinnamylidene-acetic, -malonic, and -acetoacetic acids have especially high exaltations. That for the refractions Σ_D varies from 3·52 to 4·18, and for the dispersion $\Sigma_\beta - \Sigma_\alpha$ from 210 to 313%.

Several examples are quoted from chemical literature which appear to be exceptions to some of the generalisations. In most cases the authors suggest that the abnormal values may be due to impurity or to the fact that the compound has not the structural formula usually accepted. Among the examples discussed are: hexatriene, tropilidene (Willstätter, Abstr., 1901, i, 223), and phenyl propenyl ketone (Kohler, Abstr., 1909, i, 940), which are presumably impure; β-ionone and eucarvone, both of which give much smaller exaltations than expected: this may be due to the presence of the CMe_2 group; 1-methyl-1-dichloromethyl*cyclo*-$\Delta^{3,5}$-hexadien-2-one (Auwers and Heyden, Abstr., 1909, i, 592), which gives exceptionally low exaltations, probably due to the $\cdot CMe\cdot CHCl_2$ group; phorone, which gives high exaltations, a result probably due to the presence of certain amounts of the unsymmetrical isomeride $CH_3\cdot CO\cdot CH\dot{:}CMe\cdot CH\dot{:}CMe_2$. J. J. S.

Applications of the Doctrine of Finite Increments of Energy to Physico-chemical Questions. JOHANNES STARK (*Zeitsch. Elektrochem.*, 1911, **17**, 420—421).—The author calls attention to his earlier papers (Abstr., 1908, ii, 138; 1909, ii, 106, 109).

T. E.

[Spectroscopy of Oxygen.] HEINRICH KAYSER (*Ann. Physik*, 1911, [iv], **35**, 608—612).—Polemical in reply to Steubing (this vol., ii, 558) and Stark (this vol., ii, 558). H. M. D.

The Absorption of Light by Inorganic Salts. I. Aqueous Solutions of Cobalt Salts in the Infra-Red. ROBERT A. HOUSTOUN (*Proc. Roy. Soc. Edin.*, 1911, **31**, 521—529).—The absorption of infra-red rays emitted by a Nernst filament has been measured for solutions of cobalt fluoride, chloride, bromide, iodide, nitrate, and sulphate. An increase of either the concentration or the temperature causes an increase of the extinction-coefficient at each end of the region examined, intermediate values being almost unchanged. The sulphate is an exception, absorbing slightly less in more concentrated solutions.

C. H. D.

The Absorption of Light by Inorganic Salts. II. Aqueous Solutions of Cobalt Salts in the Visible Spectrum. ROBERT A. HOUSTOUN and ALEXANDER R. BROWN (*Proc. Roy. Soc. Edin.*, 1911, **31**, 530—537).—The absorption of solutions of cobalt salts in the visible spectrum is increased by rise of concentration or of temperature, as in the infra-red (compare preceding abstract). C. H. D.

The Absorption of Light by Inorganic Salts. III. Aqueous Solutions of Nickel Salts in the Visible Spectrum and the Infra-Red. ROBERT A. HOUSTOUN (*Proc. Roy. Soc. Edin*, 1911, **31**, 538—546). The absorption of aqueous solutions of nickel fluoride, chloride, bromide, iodide, nitrate, and sulphate has been measured throughout the visible and infra-red spectrum. In the case of the chloride and bromide, a great increase of absorption takes place in the violet when either the temperature or the concentration is increased.

C. H. D.

The Absorption of Light by Inorganic Salts. IV. Aqueous Solutions of Nickel and Cobalt Salts in the Ultra-violet.

ROBERT A. HOUSTOUN and JOHN S. ANDERSON (*Proc. Roy. Soc. Edin.*, 1911, **31**, 547—558).—A special form of quartz photometer is described for the photographic measurement of extinction-coefficients in the ultra-violet, using an iron arc as source of light.

The curves obtained by the thermopile, spectrophotometer, and photographic photometer join together well, completing the spectrum. The molecular extinction-coefficient is, to a first approximation, an additive quantity in the salts examined. The absorption bands in the infra-red must be due to the metal. The sulphates do not show bands due to the acid radicle, but bands appear in the ultra-violet region in the halides, and the nitrates and iodides show well-marked bands.

C. H. D.

Absorption Spectrum of Aniline in the Ultra-violet.

HERMANN KOCH (*Zeitsch. wiss. Photochem.*, 1911, **9**, 401—414).—The ultra-violet absorption spectrum of aniline vapour has been examined at temperatures between 15° and 80°. The spectrum, which exhibits a series of well-developed bands, extends further towards the red than the spectra of other benzene derivatives. The heads of the bands are on the violet side, and all of them are shaded off towards the red end. Changes of temperature, pressure, and thickness of the absorbing layer of vapour are without influence on the character of the band spectrum. Analysis of the wave-length measurements indicates that there are three distinct series of bands.

The absorption spectra obtained in the investigation of differently concentrated solutions of aniline in ethyl alcohol are also described.

H. M. D.

Dynamic Isomerism.

HENRY E. ARMSTRONG, THOMAS M. LOWRY, SYDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Brit. Assoc. Reports*, 1910, 80—81).—This report deals with the absorption spectra of camphor and its derivatives, in particular with the effect of the introduction of unsaturated groups ($\cdot CO$, $:CH_2$, $:CHPh$, $:CX\cdot OR$) on the frequency and penetrating power of the absorption band.

T. S. P.

Application of a Valency Hypothesis to Fluorescence.

JOHANNES STARK (*Zeitsch. Elektrochem.*, 1911, **17**, 514—517).—A theoretical paper in which the author's hypothesis of the nature of valency (Abstr., 1908, ii, 574) is applied to explain fluorescence. An atom is regarded as a positively charged body, on the surface of which there are one or more negative electrons. When light is absorbed, its energy is converted into kinetic energy of these electrons, which fly off to a greater or smaller distance from the atom storing up potential energy. On the return journey of the electron towards the atom, the potential energy is converted partly into light, not necessarily of the same wave-length as that absorbed. This is the explanation of fluorescence. The author's experiments have shown that fluorescence is always accompanied by ionisation of the substance. The effect of diluting the fluorescent substance with other substances is also discussed; the diminution of fluorescence which is always observed is in accordance with the theory, part of the energy of the electrons being absorbed by the diluting molecules. T. E.

Spectro-photometric Investigation of the Opalescence of a Simple Substance in the Neighbourhood of the Critical Condition. W. H. KEESOM (*Ann. Physik*, 1911, [iv], **35**, 591—598).—The diffuse scattering of light rays by ethylene at temperatures slightly above the critical temperature has been investigated in reference to the cause of the opalescence effect. The variation of the intensity of the light, emitted at right angles to the incident beam, with the increase of the temperature above the critical temperature, and the magnitude of the coefficient of scattering are considered to support the explanation put forward by Smoluchowski (*Ann. Physik*, 1908, [iv], **25**, 205). According to this, the opalescence is determined by density differences, the existence of which is rendered evident by a statistical consideration of the molecular movements. H. M. D.

New Type of Abnormal Rotation Dispersion. Contribution to Optical Superposition. LEO TSCHUGAEFF (*Ber.*, 1911, **44**, 2023—2030).—The type of abnormal rotation dispersion described by Biot embraces mixtures of two optically active substances which possess opposite rotatory powers and have different dispersions; it may be termed extramolecular.

l-*Menthyl* d-*β-camphorsulphonate* is an example of a type the two constituents of which rotate in opposite directions, and have different although normal dispersions; in contrast to the type described by Biot, it may be termed intramolecular. The crystalline ester is faintly lævorotatory, and has an abnormal rotatory dispersion, the curve showing a maximum between *E* and *F* both in acetone and toluene.

l-*Menthyl* l-*β-camphorsulphonate*, on the other hand, is strongly lævorotatory, and has a perfectly normal dispersion.

The abnormality in the case of the *d*-camphorsulphonate is due to a partial compensation of the partial rotations in the molecule.

E. F. A.

The Selective Photo-electric Effect for Metals Outside the Alkali Group. ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1911, **13**, 474—481. Compare Abstr., 1910, ii, 379, 472, 922; this vol., ii, 90, 363).—The investigation of the photo-electric properties of barium shows that this exhibits a selective effect similar to that which has been already observed in the case of the alkali metals. For barium the selective maximum corresponds with the wave-length $280\mu\mu$. In reference to the question of the cause of the selective effect, the authors have examined the behaviour of mercury, lead, thallium, tin, cadmium, and bismuth, none of which exhibits selective action for wave-lengths greater than $200\mu\mu$, which is the lowest wave-length attainable with the use of quartz apparatus. As regards the normal photo-electric effect of these metals, it is found that the range of sensibility extends further towards the visible spectrum the more easily oxidisable the metal. H. M. D.

Calculation of the Frequencies of the Electrons Giving Rise to the Selective Photo-electric Effect. F. A. LINDEMANN (*Ber. Deut. physikal. Ges.*, 1911, **13**, 482—488. Compare preceding abstract).—On the assumption that the electrons responsible for the selective effect are caused to rotate in elliptical paths round the positively charged ions by the active ultra-violet light, the author shows that the wave-length of the resonance maximum can be obtained from the formula $\lambda = 65{\cdot}3\sqrt{a/n}$, in which a is the atomic volume and n the valency of the metal. The calculated values for sodium, potassium, rubidium, and barium are in good agreement with the experimental determinations.

In accord with experiment, it is also shown that the wave-lengths of the resonance maxima are less than $200\mu\mu$, except in the case of the alkali and alkaline earth metals. The wave-length range corresponding with the selective effect increases as the frequency of the resonance maximum increases, and when the active metal is alloyed with a second metal its resonance frequency increases more and more as the second metal becomes more electro-negative. H. M. D.

Ionic Mobility in Gases. I. MAX REINGANUM (*Physikal. Zeitsch.*, 1911, **12**, 575—580).—The author takes exception to Wellisch's explanation (this vol., ii, 358) of the large mobility exhibited by heavy ions, like methyl iodide and mercuric iodide, when moving in an electric field through a gas of low density. By means of a detailed analysis of Langevin's formula, it is shown that the heavy gas ions are in all probability represented by entities of molecular weight which corresponds with the chemical formula. H. M. D.

Electric Conductivity of Salt Vapours. GERHARD C. SCHMIDT (*Ann. Physik*, 1911, [iv], **35**, 401—443).—The electric conductivity of the vapours of various salts and organic substances has been investigated. The apparatus consisted of a quartz or hard glass tube, which could be exhausted and heated electrically; the one electrode consisted of a large platinum cylinder, the other of a short platinum wire suspended along the axis of the cylinder. The substance to be examined was placed at the bottom of the tube and volatilised by raising the temperature of the heating jacket.

Preliminary qualitative experiments showed that the vapours of the halogen salts of zinc, cadmium, iron, aluminium, and ammonium are electrical conductors, whilst the vapours of iodine, mercury, arsenic, stannic chloride, mercuric chloride, bromide and iodide and of all the organic substances examined are non-conductors.

The conductivity of the halogen salt vapours varies considerably with the time during which they are heated. In the case of cadmium salts the conductivity decreases from the commencement and tends towards a lower limiting value, but for the other halogen salts the decrease in conductivity is preceded by a rise to a maximum value.

Various experiments are described, the object of which was to ascertain the nature of the conducting ions and the mode of their formation. These experiments show that the ions are not the result of chemical decomposition of the solid substance, but are formed from the vapour itself. The presence of water vapour or oxygen has no influence on the formation of the ions, and the phenomenon cannot be attributed to the presence of traces of a radioactive substance.

The decrease of conductivity with time is found not to be due to fatigue effects, such as are exhibited by photo-electrically active metals. When a current is passed through the salt vapour, the conductivity diminishes more rapidly than in the absence of a current. As time goes on, the mobility of the ions decreases as a result of their combination with neutral molecules, and results are described which indicate that the positive ions are chiefly affected by this process. In addition to the combination of the ions with neutral molecules, the principal changes taking place in the salt vapour are considered to be represented by $CdI_2 \rightleftarrows Cd^{\cdot\cdot} + 2I'$; $Cd^{\cdot\cdot} + 2I' = Cd^{\cdot\prime} + I_2^{\cdot\prime}$. The difference in the rates at which these changes occur is supposed to be responsible for the observed differences between cadmium salts and the halogen salts of the other metals.

The conductivity of the vapours increases rapidly with rise of temperature. At low potentials the current through the vapour is proportional to the applied voltage, but a saturation current is obtained when the voltage is increased sufficiently. At still higher potentials, ions are formed as the result of molecular collision, and this stage is succeeded by luminous discharge.

At low temperatures the nature of the equilibrium in the vapour and the resulting conductivity is influenced by the previous history of the substance under examination. Under these conditions an increase of the surface of the substance undergoing volatilisation leads to an increase in the observed conductivity. H. M. D.

Electrode Potentials in the Electrolytic Manufacture of Chlorine and Alkali. R. SACERDOTI (*Zeitsch. Elektrochem.*, 1911, **17**, 473—478).—In technical processes using diaphragms, hot saturated solutions of sodium chloride are used in order to diminish the voltage required. The author has determined the effect of temperature on the potential difference between anodes of platinum and magnetite and cathodes of iron and platinum and the solutions during the passage of current.

The cathode potential is hardly affected by rise of temperature, but the anode potential is reduced by raising the temperature from 20° to 100° by from 0·4 to 0·8 volt. T. E.

Nature of Electrolytic Dissociation and Solution Pressure. FRIEDRICH KRUGER (*Zeitsch. Elektrochem.*, 1911, **17**, 453—466).—Gases are ionised either by collisions with rapidly moving electrons or ions, or by Röntgen rays or ultra-violet light. The first cause cannot be operative in the case of liquids, consequently analogy leads to the view that they are ionised by some kind of radiation. At the ordinary temperature this must be of long wave-length. The density of radiation in a medium is proportional to the cube of its refractive index or to the 1·5 power of its dielectric constant. Each medium contains molecules the vibrations of which are in equilibrium with the radiation in the medium; they are resonators for the radiation. The larger the number of these the higher is the dielectric constant. The author attempts to show that an electrolyte may be ionised by having the vibrations of these resonators communicated to it, and also that a metal in contact with such a medium will give out ions in a similar way; the analogy to the ionisation of metals by ultra-violet light is pointed out. A quantitative application of these views leads to the conclusion that the dissociation constants of an electrolyte in two different solvents are in the ratio of the cubes of the dielectric constants of the solvents, which is in agreement with Walden s experimental results. It also follows that the solution tensions of metals and the solubility of salts should increase with the dielectric constants of the medium. T. E.

Maximum Tension of Electrolytic Valve Action in Fused Salts. GÜNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1911, **17**, 509—514).—The experiments with aqueous solutions (this vol., ii., 365) have now been extended to fused salts. The majority of the experiments were made with tantalum. The valve action occurs in fused salts in much the same way as in aqueous solutions. The maximum potential is, however, lower in a fused salt than the lowest maximum observed in aqueous solution with the same salt. The rate of development of the action diminishes as the temperature rises, until at high temperatures the action does not take place. For aqueous solutions the author has found that the maximum potential is independent of the temperature (the concentration of the ions being constant) and of the nature of the metal used as electrode. Assuming that the relation between ionic concentration and maximum potential found in aqueous solutions holds for the fused salts, it is possible to draw conclusions about their degree of dissociation from the maximum potentials observed. The results lie between 5% for ammonium nitrate fused at 167° and 56% for silver nitrate at 208°.

Aluminium shows approximately the same maximum potentials as tantalum, but it is very sensitive to traces of moisture in the salts.

T. E.

Behaviour of Carbon Dioxide and of Some Mixtures of Gases in the High Tension Electric Flame. WILHELM MUTHMANN and A. SCHAIDHAUF (*Zeitsch. Elektrochem.*, 1911, **17**, 497—503).—Muthmann and Hofer (Abstr., 1903, ii, 206) measured the temperature of the electric flame by means of the dissociation of carbon dioxide in its path. In the present paper experiments are described with electric flames produced in pure carbon dioxide between electrodes of gold, silver, and platinum. The flame is produced by means of a transformer, the primary circuit of which is supplied with alternating current. When the current in the primary circuit is kept constant (12 amperes) and the length of the arc varied (from 2 mm. up to 2 cm.), the degree of dissociation of the carbon dioxide decreases from 22% to 0·7% with silver and gold electrodes. Platinum electrodes give the same results with arcs longer than 7 mm., but short arcs give very much smaller dissociations (0·4% at 2 mm., for example), obviously owing to the catalytic effect of the platinum on the re-combination of carbon monoxide and oxygen. The authors draw the conclusion that, owing to this re-combination, the degree of dissociation observed is always smaller than that corresponding with the temperature of the flame itself.

Experiments on the formation of nitric oxide from mixtures of nitrogen and carbon dioxide show that the nitrogen only reacts with the oxygen formed by dissociation of the carbon dioxide, and the production of nitric oxide is therefore small.

Mixtures of nitrogen and methane are also investigated. In order to avoid deposition of carbon, the mixtures are diluted with hydrogen so as to contain less than 10% of methane; from 2 to 3 molecules of nitrogen per mol. of methane are employed. In these circumstances the methane is converted quantitatively into hydrogen cyanide, independently of the nature of the electrodes or the size of the flame. T. E.

The Influence of Temperature on the Magnetic Properties of a Graded Series of Carbon Steels. MARGARET B. MOIR (*Proc. Roy. Soc. Edin.*, 1911, **31**, 505—516).—The magnetic quality of steel and cast iron improves with increase of temperature from 15° to 190°, diminishing from 200° onwards, and afterwards again improving. The transformation point at about 200° becomes less marked as the carbon is lessened, and is not observed in soft iron containing 0·06% C. It does not appear in the curves obtained by previous observers, the necessity of submitting the specimen to a series of reversals at the testing temperature (Ross and Gray, this vol., ii, 183) not having been recognised. C. H. D.

Magnetisation Coefficients of Gold. MAURICE HANRIOT and FRANÇOIS RAOULT (*Compt. rend.*, 1911, **153**, 182—185).—The properties of the brown (β) modification of gold, which is obtained by the action of nitric acid on gold-silver alloys, have been investigated by measurements of its coefficient of magnetisation. By repeated treatment with nitric acid, traces of iron are removed, and the magnetisation coefficient increases. The highest values obtained for the brown gold and the yellow form prepared from the former by fusion were $-0·181$ and $-0·234 \times 10^{-6}$ respectively. Conversion of the brown into the yellow modification begins at about 350°, and is completed in about two hours at 400°. Determinations of the magnetisation coefficients of samples of brown gold prepared from alloys containing widely different proportions of silver indicate that the percentage of the β-modification in the product increases with the amount of silver present in the original alloy. H. M. D.

Gaseous Explosions. SIR WILLIAM H. PREECE, DUGALD CLERK, BERTRAM HOPKINSON, WILLIAM A. BONE, BURSTALL, HUGH L. CALLENDAR, ERNEST G. COKER, W. E. DALBY, HAROLD B. DIXON, RICHARD T. GLAZEBROOK, J. E. PETAVEL, ARTHUR SMITHELLS, W. WATSON, JOHN A. HARKER, H. C. L. HOLDEN, H. R. SANKEY, DAVID L. CHAPMAN, and H. E. WIMPERIS (*Brit. Assoc. Reports*, 1910, 199—227).—This report deals with the radiation from gases, practical effects of radiation, amount of radiation from flame, nature and origin of radiation from flames, molecular theory of radiation from gases, and transparency. It contains appendices on the radiation from flames [H. L. Callendar], on radiation in a gaseous explosion [B. Hopkinson], and abstracts from various papers relating to the application of heat radiation from luminous flames to Siemens' regenerating furnaces. T. S. P.

Internal Pressure in Gases; Equations of State and the Law of Molecular Attraction. ANATOLE LEDUC (*Compt. rend.*, 1911, **153**, 179—182. Compare Abstr., 1909, ii, 298, 381, 382, 550, 644).—The internal pressure of a gas diminishes with rise of temperature, but the variation cannot be represented either by the formula of Clausius or that of Sarrau.

From the internal pressure data, communicated previously, it is found that for gases of the same molecular complexity, when compared at low pressures and corresponding temperatures, the attraction between two molecules is proportional to the square of their mass, and inversely proportional to the fourth power of their distance apart. For diatomic gases, the attractive force is only about half as large as that for triatomic gases. H. M. D.

Specific Heat of Gases. KARL DRUCKER (*Zeitsch. Elektrochem.*, 1911, **17**, 466—472).—The total energy, U, of a monatomic, or chemically unalterable, gas and its volume energy, $F=RT$, are related, thus: $F=2/3U$. This relation is usually obtained by means of the kinetic theory, but the author shows that it may be proved without the help of any assumption about the structure of the gas. The volume energy is, therefore, RT per mol., and the total energy is $3/2RT$ for perfect monatomic gases. A polyatomic gas (containing ν atoms per molecule) is imagined to be produced by condensation of ν volumes of monatomic gas. For example, 3 mols. of monatomic gas possess $3RT$ volume and $9/2RT$ total energy; after condensation $2RT$ of volume energy has disappeared, and the total energy is $5/2RT$ at least, but it may be more if some part of the loss of volume energy has appeared as bound energy in the gas. Calling the ratio, increase of bound energy/loss of volume energy $=\epsilon$, the total energy of a polyatomic gas is $U=RT[1+0{\cdot}5\nu+(\nu-1)\epsilon]$. The values of ϵ calculated from the molecular heats of some 30 gases are about 0·5, and diminish slowly with the temperature, the temperature-coefficients being the same in groups of similar substances. Exceptions are explained by dissociation of the gases or molecular association. Putting $\epsilon=0{\cdot}5$, the molecular heats at constant pressure and volume are $Cp=R(\nu+1{\cdot}5)$, $Cv=R(\nu+0{\cdot}5)$, and $Cp/Cv=(\nu+1\ 5)(\nu+0{\cdot}5)$. The values calculated from these formulæ agree very well with the observed values in a large number of cases. T. E.

Critical Solution Temperatures of Liquids. E. Moles (*Anal. Fis. Quim.*, 1911, **9**, 157—172).—Determinations of the critical solution temperatures of the systems water -*iso*butyric acid and water-phenol have been made by means of Smith and Menzies' dynamic isoteniscope (Abstr., 1910, ii, 1038). The values are in close accord with those obtained by other workers. G. D. L.

The Connexion between the Volatility, Fusibility, and Density of Compounds, and the Chemical Forces at Play within their Molecules. Geoffrey Martin (*Chem. News*, 1911, **104**, 29).—It is observed that the relationship between the density of compounds and the degree of chemical attraction between their atoms, pointed out by Richards (*Faraday Lecture*, Trans., 1911, **99**, 1201), is only a particular case of a greater generalisation already noted by the author, namely, that "it is the internal chemical forces which the atoms exert on each other in the molecule which decides the external attractions with which the molecules themselves are attracted together, and consequently properties arising out of this molecular attraction, such as volatility, fusibility, hardness, and density of the compound." The assumption that the atoms are themselves compressed by the forces of chemical attraction is therefore regarded as questionable. J. D. K.

The Viscosity of Certain Organic Liquids in the Condition of Turbulent Flow. Walter Sorkau (*Physikal. Zeitsch.*, 1911, **12**, 582—595. Compare Bose and Rauert, Abstr., 1909, ii, 645; E. and M. Bose, this vol., ii, 257).—Measurements have been made of the rate of flow of water, ethyl alcohol, chloroform, acetone, and amylene through a capillary tube under pressures sufficiently high to give rise to the turbulent condition. Whereas the product of pressure (p) and time of outflow (t) is constant for the state of steady flow, it increases in all cases with the pressure in the turbulent condition. Curves are plotted which show the variation of pt with p for the various liquids at different temperatures. In the case of chloroform, acetone, and amylene, the pt curves show distinct breaks at a particular pressure; this pressure diminishes as the temperature rises. A possible explanation of the transition phenomenon on molecular kinetic grounds is suggested. H. M. D.

Isopiestic Expansibility of Water at High Pressures and Temperatures. W. Watson (*Proc. Roy. Soc. Edin*, 1911, **31**, 456—477).—Pure water attacks quartz glass strongly at high temperatures, and the experiments have therefore been made with water slightly acidified with hydrochloric acid, which does not affect the expansibility. An electrically heated vessel is used, enclosed in a cooled steel cylinder. The dilatometer is of quartz glass.

The rate of change of volume with temperature increases with temperature to a maximum, the value of which decreases with increase of pressure. While liquid, water expands as an ordinary liquid. Above the critical temperature, the coefficient of expansion of water, like that of other gases, is independent of the temperature, and decreases with increase of pressure. C. H. D.

Extension of the Laws of Capillarity to Cases where the Elements of the Capillary System are Mobile with Respect to One Another; Extension Leading to a New View of the Phenomena of Swelling of Dried Wood, of the Dissolution of Gums, Albumins, Etc., and of True Solutions. J. H. RUSSENBERGER (*Compt. rend.*, 1911, **153**, 57—60. Compare Abstr., 1910, ii, 189).—A theoretical discussion. The phenomena mentioned in the title are compared with the increase in height observed when a pile of thin laminæ of mica, lead, etc., is moistened with water. W. O. W.

Solubility. I. J. VARGAS EYRE (*Brit. Assoc. Reports*, 1910, 425—468).—The report classifies, both chronologically and according to subject, the literature on the subject of solubility, and contains a brief statement of the main conclusions arrived at by the various authors. It is divided into the following sections: I. Methods of determination: *A*, solids; *B*, liquids; *C*, gases. II. Influence of nature of solvent: *A*, physical; *B*, chemical. III. Influence of nature of solute: *A*, physical; *B*, chemical. IV. Solubility in relation to: (1) temperature, (2) heat of dissolution, (3) pressure, (4) influence of other substances: (i) non-electrolytes and non-electrolytes, (ii) non-electrolytes and electrolytes, (iii) electrolytes and electrolytes. V. Mutual solubility and distribution coefficients. VI. Theoretical considerations. VII. Chronological bibliography. T. S. P.

Technical Soaps as Colloidal Solutions. J. LEIMDÖRFER (*Koll. Chem. Beihefte,* 1911, **2**, 343—398).—The nature of the various processes incidental to the production of technical soaps is examined from the colloido-chemical point of view. The course of the saponification process, partial and total flocculation, swelling and dehydration, changes in viscosity, and the influence of different electrolytes on the production of soaps from various fats are discussed in detail. Other matters dealt with relate to the part played by the dispersive medium (water, glycerol, and alcohol) and to the adsorption of non-electrólytes and other colloidal substances. H. M. D.

The Equilibrium $CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4$. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1911, **71**, 206—208).—The constant $[Na_2CO_3]/[Na_2SO_4]$ is found to be 0·054, the same value being reached from both sides. Concentrated solutions of sodium carbonate yield irregular values, owing to the formation of gaylussite,

$$Na_2CO_3,CaCO_3,5H_2O.$$

C. H. D.

Cæsium Nitrate and the Law of Mass Action. EDWARD W. WASHBURN and DUNCAN A. MACINNES (*Zeitsch Elektrochem.*, 1911, **17**, 503—509).—Biltz (Abstr., 1902, ii, 310) has stated that cæsium nitrate follows Ostwald's dilution law. This conclusion was drawn from measurements of the freezing points of aqueous solutions of the salt. The authors have redetermined the freezing points of solutions of cæsium nitrate up to 0·45 normal. Calling n the number of gram-molecules dissolved in 1000 grams of water, the depressions of freezing point are given by $\Delta t = 3{\cdot}426n - 1{\cdot}862n^2 + 1{\cdot}373\,n^3$. The dissociation, calculated from these results, follows Ostwald's law for strong solutions (0·2 to 0·5 normal), but does not follow it even approximately for dilute solutions. T. E.

Velocity of Hydrolysis of Glycerolphosphoric Acid. FERNAND MALENGREAU and GEORGES PRIGENT (*Zeitsch. physiol. Chem.*, 1911, **73**, 68—84).—The rate of hydrolysis of glycerolphosphoric acid by water at 100° has been determined by gravimetric estimation of the liberated phosphoric acid. The reaction, in the case of the free acid as well as in that of the acid potassium and sodium salts, is unimolecular, but the salts in question are decomposed about twice as fast as the free acid. On the other hand, when the acid is neutralised by a base, the salt is scarcely attacked by water. The explanation of these results is that $H^{\cdot}$ ions in small concentration (in this case resulting from the ionisation of the acid itself) accelerate the action, but in greater concentration they exercise a retarding effect. Acetic, hydrochloric, and sulphuric acids all retard the action. Salts of strong acids have mostly a slight accelerating effect, but salts of weak acids accelerate the reaction considerably. This is ascribed to a diminution in the $H^{\cdot}$ ion concentration, owing to double decomposition.

The rate of hydrolysis is greatly increased by rise of temperature. G. S.

Catalytic Oxidation of Phenols in Presence of Iron Salts. H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1911, **153**, 76—79).—The addition of sulphuric acid to an artificial peroxydase system produces a diminution in the rate of oxidation of quinol in proportion to the amount added until a minimum is reached, after which the rate increases. The acceleration is probably due to the formation of a persulphuric acid. Weak organic acids show no minimum point. The retarding effect of acetic acid is only noticeable at high concentrations, whilst that of oxalic acid is much more pronounced in dilute solutions. Citric acid has an effect intermediate between these two. The retarding effect of acids is attributed to the formation of complex iron salts. W. O. W.

The Specific Action of Different Compounds of Iron from the Point of View of their Action as Peroxydases. JULES WOLFF and ELOI DE STOECKLIN (*Compt. rend.*, 1911, **153**, 139—141).—The authors maintain their thesis that the specific action of iron compounds in various reactions depends on the particular compound of iron (compare Abstr., 1908, i, 490, 746; ii, 573, 1022; 1909, i, 347, 451) as against the views expressed by Colin and Sénéchal (preceding abstract), and give further experimental evidence in support thereof.

In the presence of an extremely small quantity of colloidal iron ferrocyanide, hydrogen peroxide readily oxidises quinol to quinhydrone, whereas it is necessary to add a large excess of potassium thiocyanate to ferric thiocyanate to produce the same effect. Pyrogallol is similarly readily oxidised to purpurogallin in the presence of the ferrocyanide, whereas the mixture of the thiocyanates produces no effect.

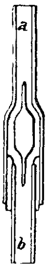
Further experiments on the liberation of iodine from potassium iodide by hydrogen peroxide in acetic acid solution in the presence of various iron salts and potassium thiocyanate gave the following results: (1) If a salt of iron, such as the nitrate, sulphate, chloride, or acetate, acts as a catalyst in the above reaction, its catalytic power is considerably increased by the addition of small quantities of potassium thiocyanate. (2) The catalytic power increases rapidly with increasing quantities of thiocyanate, attaining a maximum when the composition $K_3Fe(CNS)_3$ is reached. Further increase in the quantity of potassium thiocyanate has then very little effect.

It is possible that the accelerating effect of the thiocyanate may be due to the formation of persulphate by the oxidising action of the hydrogen peroxide, but the authors find that the addition of sodium persulphate in quantity exceeding that which would be formed during the reaction has no accelerating effect on the action of iron nitrate.

T. S. P.

A Simple Valve for Water Pumps. ROBERT BEHREND (*Chem. Zeit.*, 1911, 35, 807).—The valve is shown in the diagram. The tube *b* is fitted into *a* by means of india-rubber tubing, which projects past the end of *b* and so forms a seat for the stopper to press against when the valve acts.

T. S. P.



An Improved Funnel. PHILIP BLACKMAN (*Chem. News*, 1911, 104, 30).—A glass funnel of such a form that the lower portion of the paper cone does not touch the funnel itself, with the result that filtration is greatly accelerated.

J. D. K.

A Funnel Support. PHILIP BLACKMAN (*Chem. News*, 1911, 104, 30—31).—A concentrically fluted glass disk, having at the centre an upright tube for holding the funnel steadily. It may be used with beakers, etc., of various sizes, and protects the filtrate from dust.

J. D. K.

Inorganic Chemistry.

Active State of Chlorine Produced by Light. GOTTFRIED KÜMMELL (*Zeitsch. Elektrochem.*, 1911, **17**, 409—412).—An insulated platinum cylinder is placed inside a glass vessel, the walls of which are lined with platinum foil. The cylinder is charged positively to 200 volts, and is in electrical connexion with an electroscope. The platinum foil is earthed. Any loss of the charge of the cylinder by leakage through the gas surrounding it is thus easily observed.

Moist or dry nitrogen, hydrogen, carbon dioxide, or oxygen, all give the same small rate of leakage whether they are in the dark or exposed to the light of an electric arc lamp. Pure, dry chlorine gives the same result, but moist chlorine gives a considerably larger leak in the dark, and this is still further increased by exposure to light. The effect increases with the quantity of water-vapour present. The addition of oxygen to the chlorine diminishes it. Air to which hydrogen chloride has been added in small quantity behaves in the same way as moist chlorine. The conductivity is therefore due to hydrogen chloride formed by the action of chlorine on water vapour.

The positive platinum cylinder was acted on in all cases in which the chlorine was a conductor, but not the earthed (or negative) platinum foil. T. E.

Influence of Current Concentration on the Formation of Chlorates by Electrolysis. ERICH MÜLLER and PAUL KOPPE (*Zeitsch. Elektrochem.*, 1911, **17**, 421—430).—According to Foerster and Müller's theory of the formation of chlorates, two reactions take place, the one being purely chemical, the other electrolytic. The latter converts hypochlorite ions into chlorate and oxygen gas at the anode, and therefore involves a loss of efficiency. The purely chemical action (the oxidation of hypochlorite ions by free hypochlorous acid), on the other hand, involves no loss of oxidising power. Anything that accelerates the purely chemical action without affecting the rate of the electrolytic one will, therefore, increase the efficiency of the process as a whole. Since the chemical action goes on throughout the mass of the solution, whilst the electrolytic action only takes place at the anode, it is fairly obvious that an increase of the volume of solution relatively to the current used will have this effect, and the authors show both on theoretical grounds and by a large number of experiments that this is the case. T. E.

Effect of the Frequency and Form of the Current on the Formation of Ozone. GEDEON LECHNER (*Zeitsch. Elektrochem.*, 1911, **17**, 414—420).—Very pure and dry oxygen was exposed to the silent discharge in a Berthelot ozoniser. The discharge was produced by a Ruhmkorff coil, through the primary circuit of which an interrupted direct current was passed. At first the times during which the current flowed and was interrupted were equal, the number of interruptions per second being varied from 12 to 48. In these circumstances the quantity of ozone produced per hour increased with the number of interruptions, but not in direct proportion to this number. There are two reasons for this: (1) Owing to the self-induction of the circuit the current does not reach its maximum value at once, and therefore the average current is smaller for the shorter periods than for the longer ones. (2) The concentration of ozone in the gas is greater with the larger number of interruptions, and therefore the quantity destroyed by the discharge is greater.

In a final set of experiments, the flow of oxygen through the ozoniser was varied, so that the concentration of ozone was always the same and the interrupter was arranged to give different numbers of current shocks each of the same duration per second.

With this arrangement the quantity of ozone produced per hour was very accurately proportional to the number of interruptions per second.

A comparison of the effects of supplying the primary of the coil with interrupted direct current and with alternating current, the *E.M.F.* curve of which was almost a sine curve, showed that the latter gave about 1/20th the quantity of ozone. This is due to the lower *E.M.F.* of the secondary current produced by the alternating current, a certain minimum *E.M.F.* being required to produce a discharge through the gas at all.

When, however, the apparatus was arranged so as to obtain equal effective currents in the secondary circuit, the alternating current gave larger yields of ozone than the direct current. T. E.

Action of Sulphuryl Chloride on Certain Metals. H. B. NORTH (*Bull. Soc. chim.*, 1911, [iv], 9, 646—649).—Gold and platinum are attacked by sulphuryl chloride after prolonged heating with it in a sealed tube at 150°, anhydrous auric chloride and platinic chloride being formed together with sulphur dioxide. Silver, zinc, and cadmium do not react with sulphuryl chloride even at 300° (compare Abstr., 1910, ii, 296). Iron behaves like platinum and gold, anhydrous ferric chloride being obtained in large crystals.

R. V. S.

Iron as a Catalyst in the Synthesis of Ammonia under Pressure. KARL JELLINEK (*Zeitsch. anorg. Chem.*, 1911, 71, 121—137).—An electric furnace, with nickel resistance wire, is described, which may be heated to 800—1000° under a pressure of 100 atmospheres for several hours. Nitrogen and hydrogen are admitted in theoretical proportions, iron being introduced as a contact material. The ammonia in the issuing gases is estimated by titration. Ammonia is not obtained when a porcelain vessel, not containing iron, is used. At 870°, iron dissolves or adsorbs considerable quantities of ammonia, so that the quantity of ammonia in the issuing gas increases rapidly as the pressure is diminished. Under these conditions the equilibrium concentration of ammonia in the mixture may be exceeded 100 times. C. H. D.

Can Thomsen's Thermochemical Method be Employed to Investigate the Hydration of Metaphosphoric Acid? D. BALAREFF (*Zeitsch. anorg. Chem.*, 1911, 71, 70—72).—Experiments with an ice calorimeter show that when a solution of orthophosphoric acid is added to one of metaphosphoric acid, heat is at first absorbed and afterwards developed. Thomsen's method is therefore not applicable to the hydration of metaphosphoric acid. C. H. D.

The Hydrates of Arsenic Pentoxide. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1911, 71, 73—78).—When a solution of arsenic acid is evaporated in an open vessel at 50°, or under increased pressure at 150°, the crystals which separate always have the composition

$H_5As_3O_{10}$ or $3As_2O_5,5H_2O$. Above 200°, crystals of the oxide, As_2O_5, separate directly. Concentrated solutions, crystallising spontaneously or by freezing, deposit crystals of the hydrate $H_3AsO_4,\frac{1}{2}H_2O$, or mixtures of this with $H_5As_3O_{10}$. The hydrate, $H_3AsO_4,\frac{1}{2}H_2O$, loses water on fusion, passing into $H_5As_3O_{10}$. The formation of any other hydrate was not observed. C. H. D.

Gaseous Combustion. William A. Bone (*Brit. Assoc. Reports*, 1910, 469—505).—The report summarises the results of the principal researches upon the chemical aspects of gaseous combustion during the past thirty years, and is divided into the following sections: I, Ignition temperatures and the initial phases of gaseous explosions; II, the explosion wave; III, the pressures produced in gaseous explosions; IV, the influence of moisture on combustion; V, the combustion of hydrocarbons; VI, the influence of hot surfaces on combustion. T. S. P.

The Formation of Potassium Nitrate by Double Decomposition from the Point of View of the Phase Rule. Ernst Jänecke (*Zeitsch. anorg. Chem.*, 1911, **71**, 1—18).—The author's graphical method of representing the behaviour of reciprocal salt-pairs (Abstr., 1908, ii, 808) has been applied to the systems $NaCl-KNO_3$, $KCl-NaNO_3$ (Uyeda, Abstr., 1910, ii, 836), and $NaNO_3-K_2CO_3$, $KNO_3-Na_2CO_3$ (Kremann and Žitek, Abstr., 1909, ii, 572); the numerical data of these authors are utilised in constructing the diagrams. A method of converting percentages by weight in ternary systems into molecular percentages is also described, and several numerical examples are worked out. C. H. D.

Properties of Potassium Nitrite. Eduard Donath (*Chem. Zeit.*, 1911, **35**, 773—774).—When 96% alcohol is added to an almost saturated solution of potassium nitrite, two liquid layers are formed, the lower aqueous layer containing 71·90% KNO_2, and the upper alcoholic layer, 6·9% KNO_2. When methyl alcohol is used, pure potassium nitrite is precipitated as a fine powder, and since potassium hydroxide is soluble in methyl alcohol, a convenient method is given for the separation of potassium hydroxide and potassium nitrite.

Methyl alcohol precipitates sodium hydroxide from concentrated solutions. Sodium nitrite is neither precipitated from its aqueous solutions by methyl alcohol, nor are two layers formed on the addition of ethyl alcohol. T. S. P.

The Preparation of Pure Hyposulphites and the System Hyposulphite-Water. Karl Jellinek (*Zeitsch. anorg. Chem.*, 1911, **71**, 96).—The salting-out of sodium hyposulphite takes place without difficulty, even when only small quantities of salt are used, if alkali is present, and this method is adopted in the technical preparation of the salt (compare this vol., ii, 278). C. H. D.

Ammonium Carnallite. Wilhelm Biltz and E. Marcus (*Zeitsch. anorg. Chem.*, 1911, **71**, 166—181).—In an investigation of the potash deposits (Abstr., 1909, ii, 571) it was observed that the content of ammonia followed that of carnallite. It is now found that ammonium and potassium carnallites form solid solutions with one another.

The solubility of magnesium chloride in water at 25° is 104·5 mols. in 1000 mols., the value 108 adopted in the usual diagram being too high. The equilibrium of ammonium and magnesium chlorides in water has also been studied. In the preparation of the solutions in contact with two solid phases, a saturated solution of the one salt, containing crystals of that salt, is taken, and ammonium carnallite is added until the composition of the solution is not further changed. The point $NH_4Cl \mid (NH_4)MgCl_3,6H_2O$ is also observed by the appearance of anisotropic crystals together with the isotropic crystals. Ammonium carnallite, like the potassium compound, breaks up on the addition of a small quantity of water.

Potassium and ammonium chlorides form together two series of solid solutions, interrupted by a gap which extends from 20 to 98 mol. % NH_4Cl at 25°. This is confirmed by crystallographic examination.

Potassium and ammonium carnallites form three series of solid solutions, the first of the type of ordinary carnallite, extending to 15 mol. % of the ammonium salt, the second, of the type of ammonium carnallite, containing from 27 to 100 mol. % of that salt, and the third, containing from 15 to 27 mol. %, and crystallising in prisms, probably monoclinic, extinguishing at an angle of 27° to the direction of their length. C. H. D.

Thermal Analysis of Binary Mixtures of the Chlorides of Univalent Metals. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 758—764).—The paper deals with the thermal analysis of the systems NaCl–AgCl, LiCl–AgCl, and LiCl–CuCl. Sodium chloride and silver chloride give mixed crystals of one species only in all proportions (compare Botta, this vol., ii, 293).

Lithium chloride and silver chloride yield mixed crystals of two kinds, and the gap of miscibility extends from 16 mols. % to 50 mols. % of silver chloride, the temperature of the pause being 469°.

Lithium chloride and cuprous chloride also give mixed crystals of two species, and the gap of miscibility extends from 25 mols. % to 55 mols. % of cuprous chloride (temperature 424°). The curve of fusion of the mixed crystals rich in cuprous chloride presents a minimum at about 80 mols. % of cuprous chloride. R. V. S.

The Compounds of Silver and Cadmium. G. J. PETRENKO and A. S. FEDOROFF (*Zeitsch. anorg. Chem.*, 1911, **71**, 215—218).—The authors' results (this vol., ii, 281) indicate the existence of four compounds of silver and cadmium, $AgCd_4$, $AgCd_3$, Ag_2Cd_3, and AgCd, whilst Bruni and Quercigh (Abstr., 1910, ii, 953) find the compound $AgCd_4$. Quenching experiments with the alloy containing 19·5% Ag show that at 480° the solid solution is in equilibrium with the liquid. A polygonal structure is not obtained on annealing. The compound $AgCd_4$ is therefore to be rejected, and whilst the existence of the compound $AgCd_3$ is probable, it is not fully established. C. H. D.

The Periodides and Perbromides of the Alkaline Earth Metals. Walter Herz and Alfred Bulla (*Zeitsch. anorg. Chem.* 1911, 71, 254—256).—Varying quantities of iodine are added to a solution of barium iodide in water, and the solution is then shaken with carbon tetrachloride at 25°. The partition coefficient of the iodine is then determined. A constant is obtained for the value $k=[BaI_2][I_2]/[BaI_4]$ over a considerable range of concentration, indicating the presence of the periodide. At high concentrations of iodine, high values are obtained for k, indicating the formation of higher polyiodides. In a similar manner, the formation of calcium and strontium periodides, and of barium and calcium perbromides, is demonstrated. C. H. D.

Potassium Barium Orthothioarsenate, $KBaAsS_4,6H_2O$; ($K_3AsS_4,Ba_3As_2S_8,18H_2O$). Emanuel Glatzel (*Zeitsch. anorg. Chem.*, 1911, 71, 209—214).—Barium orthothioarsenate (this vol., ii, 282) reacts in a finely-powdered state with a solution of potassium chloride, yielding colourless crystals of *potassium barium orthothioarsenate*, $KBaAsS_4,6H_2O$. The salt is more easily prepared by adding potassium chloride to the solution obtained by saturating barium hydrogen sulphide with arsenic pentasulphide. C. H. D.

Zinc Peroxite (Zinc Moloxide, Zinc Peroxydate), $ZnO_2,\frac{1}{2}H_2O$ and a General Method of Preparing Peroxites. Erich Ebler and R. L. Krause (*Zeitsch. anorg. Chem.*, 1911, 71, 150—165).—It is proposed to use the terms "peroxydate" for additive compounds of hydrogen peroxide, and "peroxite" for the true salts of hydrogen peroxide. The methods of preparing peroxites generally yield products containing added water or hydrogen peroxide. The pure compounds may be obtained by the action of a dry ethereal solution of hydrogen peroxide on the alkyl compounds of metals or on metal-amines.

A solution of hydrogen peroxide is extracted with ether, and the extract is dried with anhydrous sodium sulphate and added gradually to a cooled solution of zinc ethyl in dry ether. Ethane is evolved, and a white, amorphous precipitate is formed, which is washed with ether and dried in a vacuum.

Zinc peroxite, $ZnO_2,\frac{1}{2}H_2O$, is slowly decomposed by acids, yielding hydrogen peroxide, or violently by heat, evolving oxygen. Water hydrolyses it very slowly, an equilibrium being reached. The compound acts on a photographic plate.

For the estimation of zinc, the peroxite is dissolved in dilute sulphuric acid. Oxygen is estimated by titration with permanganate, the oxygen evolved being also measured. Water is estimated by heating in dry air. C. H. D.

The Combining Power of the Chlorides of Copper, Lead, Iron, Zinc, Tin, and Bismuth, and the Combining Power of the Chlorides, Bromides, and Iodides of Copper and Cadmium, and the Sensitiveness of the Solid Solutions to Light. Gottfried Herrmann (*Zeitsch. anorg. Chem.*, 1911, 71, 257—302).—The mixtures of chlorides are examined by Tammann's method of thermal analysis, using Jena glass vessels.

Mixtures of lead chloride and cuprous chloride form a simple eutectiferous series, the eutectic point lying at 281° and 34% Cu_2Cl_2. Cadmium chloride melts at 568°, and the eutectic of lead and cadmium chlorides melts at 385° and contains 30% $CdCl_2$. The eutectic point of lead chloride and ferric chloride is at 178° and 50% $FeCl_3$. Lead chloride and stannous chloride form a continuous series of solid solutions. The eutectic of cuprous chloride and stannous chloride melts at 172° and contains 77·5% $SnCl_2$. Cuprous chloride and zinc chloride form a eutectic melting at 243°, containing 90% $ZnCl_2$, solid solutions being formed to a limited extent at both ends of the series. Cuprous chloride and bismuth chloride have a eutectic point at 190° and 85% $BiCl_3$. Cuprous chloride and ferric chloride form a *compound*,

$$Cu_2Cl_2,2FeCl_3,$$

which melts at 320°. There are two eutectic points, at 306° and 263° and 50% and 88% $FeCl_3$ respectively. This compound, which crystallises in green needles, may also be obtained with $8H_2O$ by crystallisation from an aqueous solution. The eutectic of zinc chloride and stannous chloride melts at 171° and contains 64% $SnCl_2$, and that of bismuth chloride and ferric chloride melts at 171° and contains 23% $FeCl_3$. Ferric chloride and zinc chloride form solid solutions to a limited extent at both ends of the series, the eutectic point being at 214° and 70% $ZnCl_2$. The eutectic of cadmium chloride and stannous chloride melts at 229°, and contains 90% $SnCl_2$, whilst that of cadmium and zinc chlorides practically coincides with pure zinc chloride. Similarly, the eutectic of lead and zinc chlorides is practically pure zinc chloride. Bismuth and zinc chlorides are only partly miscible in the liquid state, but solid solutions are formed to a small extent. The freezing-point curve of mixtures of lead chloride and bismuth chloride has a discontinuity, but it has not been found possible to determine the composition of the compound, which is not formed in aqueous solutions. A similar case is afforded by mixtures of lead and bismuth bromides, the formula of the compound being again unknown. Cuprous chloride and cadmium chloride form a continuous series of solid solutions, the freezing-point curve having a minimum at 410° and 20% $CdCl_2$. A thermal effect is observed at lower temperatures, reaching a maximum at 350° and 30% $CdCl_2$, indicating the formation of a compound $2Cu_2Cl_2,CdCl_2$. This compound is greyish-blue, and is not obtained in the wet way. Its formation from the solid solution is promoted by the action of light. Cuprous bromide and cadmium bromide form solid solutions up to 66% $CdBr_2$, at which composition there is a eutectic point at 420°. Cuprous bromide undergoes a transformation at 394°, and a compound, $Cu_2Br_2,2CdBr_2$, is formed in the solid state.

Cuprous iodide and cadmium iodide melt at 606·5° and 392·4° respectively. They form a single series of solid solutions, with a minimum in the freezing-point curve at 350° and 90% CdI_2. The transformation temperature of cuprous iodide is at 414°, and is lowered by addition of cadmium iodide.

Tammann's first rule, that metals of the same natural group do not form compounds with one another, applies also to the chlorides, but the second rule, that a given element forms compounds either with all the members of a natural group or with none, does not apply.

When a pure chloride shows a tendency to undercooling, this tendency is also observed in its mixtures with other chlorides.

C. H. D.

Thallous Hydroxide. Fritz Bahr (*Zeitsch. anorg. Chem.*, 1911, **71**, 79—95).—Solutions of thallous hydroxide rapidly attack glass and absorb both carbon dioxide and oxygen. The salt is best prepared by shaking fine turnings of thallium with cold water in a special apparatus, through which oxygen is passed. When the saturated solution is further shaken, yellow crystals of thallous hydroxide separate, and further crystals are obtained by evaporation in a vacuum desiccator over potassium hydroxide. The crystals are then collected by means of a special filter in an atmosphere of hydrogen, washed with ice-cold water and alcohol, and dried in hydrogen. The product is free from lead, but must be freshly prepared for each experiment.

Thallous oxide is obtained by heating the hydroxide momentarily to 150—200° in nitrogen. The solubilities of thallous oxide and hydroxide in water between 0° and 100° are identical. Measurements of the dissociation pressure show that the dissociation temperature $2TlOH = Tl_2O + H_2O$ is 139°, the value 78°, calculated from the heat of reaction, being too low.

Thallous hydroxide is darkened by light in a vacuum, but it has not been found possible to determine the nature of the reaction. Thallous lead sulphate is much less soluble than lead sulphate.

C. H. D.

The Extraction of Gas from Copper Heated in a Vacuum. Marcel Guichard (*Compt. rend.*, 1911, **153**, 104—107).—When copper is heated at 600—630° in a vacuum, gas is liberated. The rate of liberation gradually decreases, to remain constant when the heating is considerably prolonged (15—20 hours) and the copper has a relatively large surface. When the surface is relatively small, the evolution of gas soon becomes infinitesimal, but if the copper is allowed to cool for several hours and then re-heated, a renewed evolution of gas takes place, finally decreasing to nil. This sequence of phenomena may be repeated several times, and is due to the slow diffusion of gas from the interior to the exterior layers of the copper, as may be shown by heating copper until the evolution of gas has become very small, removing the outer layer with a file and emery paper, and re-heating; an immediate increased evolution of gas takes place.

For the same weight of copper, the greater the surface the greater is the volume of gas liberated in a given time, whereas with the same surface less gas is liberated from fine wire than from larger rods.

The composition of the gas, expressed in terms of 1 c.c., evolved in different cases is as follows:

	CO_2.	CO.	H + N.	H.
Wire, 0·1 mm. in diameter	0·62	0·00	0·38	—
,, 0·3 ,, ,, ...	0·75	0·12	0·12	—
Electrolytic copper (rods)	0·33	0·09	0·57	—
,, ,, fused at 1200°	0·6	0·1	—	0·26

T. S. P.

Binary System Cuprous Bromide–Potassium Bromide. Pietro de Cesaris (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 749—751).—The author has carried out the thermal analysis of this system with the same experimental arrangements as were employed by him for that of the binary mixtures of cuprous chloride and potassium, sodium, and silver chlorides (this vol., ii, 606). From 730°, the m. p. of potassium bromide, the m. p. of mixtures falls to a minimum at 182°, then rises to 480°, the m. p. of cuprous bromide. At 384° is situated the transition point of two forms of cuprous bromide. At 234° a new solid phase appears, which has the composition $CuBr,2KBr$, similar to that of the corresponding chlorides. R. V. S.

The Action of Alkyl Iodides on Copper Oxide. Henry G. Denham (*Zeitsch. anorg. Chem.*, 1911, **71**, 303—304).—In an attempt to prepare cupric iodide, CuI_4, carbon dioxide and methyl iodide vapour were passed over copper oxide at 310°. Cuprous oxide and gaseous products were obtained, but not free iodine. C. H. D.

The Action of Ammonia on Mercurous Nitrate. Haridas Saha and Kumud Nath Choudhuri (*Zeitsch. anorg. Chem.*, 1911, **71**, 309—312).—Mercurous nitrate and concentrated ammonia react together, and the filtrate from the black precipitate, evaporated in a vacuum over concentrated sulphuric acid, yields a white powder, having the empirical composition $Hg_2N_2H_4O_5$. This compound, mixed with metallic mercury, constitutes the black precipitate.
C. H. D.

Aluminium Sulphide. Wilhelm Biltz and Fritz Caspari (*Zeitsch. anorg. Chem.*, 1911, **71**, 182—197).—Aluminium sulphide may be prepared by mixing aluminium powder and sulphur in a fireclay crucible, heating to fusion, cooling, and igniting by means of Goldschmidt's ignition powder. The reaction is very violent, and the product is crystalline. It may be purified by sublimation in a vacuum at 1100—1250°, and then forms white needles resembling asbestos. Good crystals are obtained by sublimation in nitrogen under atmospheric pressure from a carbon tube at 1500—1600°. A yellow sublimate, containing silicon sulphide, is also obtained, this being more volatile than aluminium sulphide.

The sulphide is readily hydrolysed by moisture, intermediate compounds being probably formed. The product obtained by the prolonged action of moist hydrogen sulphide has a composition corresponding with the formula Al_2O_3,H_2O,Al_2S_3.

Aluminium sulphide forms long, apparently hexagonal needles, D^{13}_{13} 2·02, and melts at $1100 \pm 10°$. Mixtures with aluminium oxide melt at a lower temperature, solid solutions being formed, confirming the partial isomorphism of the oxide and sulphide. Extrapolation of the freezing-point curve gives 1095° as the melting point of aluminium sulphide.

Indications having been observed that aluminium monosulphide, AlS, is also formed in small quantity (compare Regelsberger, *Zeitsch. Elektrochem.*, 1898, **4**, 547), this compound has been prepared by heating the sesquisulphide to 2100°. A non-volatile residue is thus obtained containing carbide and 12% of the monosulphide, which yields hydrogen with acids according to the equation $2AlS + 6HCl = 2AlCl_3 + 2H_2S + H_2$. The hydrogen evolved is estimated in presence of the methane derived from the carbide by Brunck's colloidal palladium method (this vol., ii, 149).

C. H. D.

The Corrosion and Preservation of Iron. J. NEWTON FRIEND (*J. Iron and Steel Inst.*, 1911, Reprint 1—65).—The corrosion of iron by air and liquid water containing traces of an acid is relatively less with large than with small areas of iron, the corrosion being greatest at the periphery. It increases with the quantity of dissolved oxygen and with the illumination, hence the corrosion of columns and plates immersed in water is greatest near to the surface. The presence of previously-formed rust accelerates corrosion.

Experiments with Kahlbaum's iron foil show that rusting is completely inhibited by chromic acid above a limiting concentration ; in the case examined, 0·111 gram per litre when oxygen is bubbled through the corrosion vessel. Concentrated solutions of chromic acid exert a solvent action on iron. Very dilute solutions of alkali hydroxides suffice to prevent rusting, but the presence of alkali hydroxide, together with salts, such as potassium chloride, only inhibits rusting when above a certain concentration. It is therefore possible for rusting to take place in an alkaline solution. Dilute solutions of neutral salts accelerate corrosion, but concentrated solutions retard it, owing to the diminished solubility of oxygen. The action of acids on iron is not comparable with ordinary corrosion, so that acid "accelerated" tests cannot be employed to determine the resistance of iron or steel to rusting.

The solvent action of drying oils on iron is very small. C. H. D.

Chromium Steels. A. PORTEVIN (*Compt. rend.*, 1911, **153**, 64—66. Compare Guillet, Abstr., 1904, ii, 739).—The martensite structure shown by steels containing 0·1% of carbon and 7—22% of chromium can be made to disappear by annealing for a sufficient length of time. The product resembles an ordinary moderately hard steel, and shows grains analogous to ferrite, traversed by filaments of a carbide. The paper is illustrated by two micro-photographs. W. O. W.

Iron Rust. EDUARD DONATH and A. INDRA (*Chem. Zeit.*, 1911, **35**, 773).—The following analyses of different specimens of iron rust are given. *A* is from a steel bomb used for liquid sulphur dioxide, and had thus been exposed for a long time to sulphur dioxide gas. *B* is from a steam boiler, *C* from the base of some machinery, and *D* is wire rust :

	Moisture.	Combined H_2O.	CO_2.	SiO_2.	P_2O_5.	SO_3.	NH_3.	FeO.	Fe_2O_3.	Mn_2O_3.	Graphite.
A.	4·41	12·21	0·83	0·49	0·46	2·72	1·07	2·23	74·52	0·23	?
B.	1·74	7·53	0·25	0·46	0·08	0·06	0·02	2·79	86·45	0·33	?
C.	2·35	6·23	0·65	3·32	0·43	0·18	0·06	6·04	78·56	1·69	0·49
D.	1·60	1·55	0·93	0·84	0·23	0·07	0·02	1·03	92·94	0·41	?

The authors are of the opinion that some sulphuric acid will always be found in ordinary rust, and that carbonic acid plays some part in the process of rusting. T. S. P.

The Dihydrate of Uranic Oxide. William Oechsner de Coninck and A. Raynaud (*Compt. rend.*, 1911, **153**, 63—64. Compare this vol., ii, 403, 496).—Five experiments gave a mean value of 270·46 for the molecular weight of uranous oxide when determined by igniting the hydrate, $UO_3,2H_2O$, in a current of hydrogen. W. O. W.

Thorium Carbonates. Édouard Chauvenet (*Compt. rend.*, 1911, **153**, 66—68).—Thorium oxide absorbs carbon dioxide with formation of orthocarbonates. Under ordinary pressure the hydroxide absorbs the gas until the product has the composition $2Th(OH)_4,CO_2$. Under 30—40 atmospheres, more gas is absorbed until the normal carbonate $ThCO_4,2H_2O$ is obtained. Under the same conditions the anhydrous oxide (ignited at a temperature not exceeding 430°) gives a basic carbonate, $ThCO_4,6ThO_2$. The hydrate $ThCO_4,8H_2O$, prepared by the action of sodium carbonate on a thorium salt in aqueous solution, loses $6H_2O$ when placed in a vacuum. On heating to 120°, it forms the basic salt, $ThCO_4,ThO_2,1{\cdot}5H_2O$. W. O. W.

Bismuth Carbonate. Ludwig Vanino (*Pharm. Zentr.-h.*, 1911, **52**, 761—762).—In most cases, bismuth carbonate has the composition $CO(O{\cdot}BiO)_2$. It is best prepared as follows, by making use of mannitol: a little water is added to 18·2 grams of mannitol and the whole triturated with 48·2 grams of powdered bismuth nitrate, whereby a solution is obtained. To 100 c.c. of this solution at 0° are added 20·7 grams of potassium carbonate dissolved in the minimum quantity of water; when almost all the potassium carbonate has been added, the bismuth carbonate separates as a fine, heavy powder. The precipitate is washed with water, alcohol, and ether, and dried in the air. Ammonium carbonate may be used instead of potassium carbonate.

It is very difficult to wash bismuth carbonate free from alkali, nitrates, or soluble carbonates. Bismuth metahydrate, dissolved in concentrated hydrochloric acid, is not suitable for the preparation of bismuth carbonate. T. S. P.

Some Supposed Iridium Chlorides; Condensed Chlorides. Marcel Delépine (*Compt. rend.*, 1911, **153**, 60—63).—By heating the hydrate $H_2IrCl_6,6H_2O$ at different temperatures, a series of condensed chlorides is obtained. That prepared in ordinary air at 100° has the composition $IrCl_{3{\cdot}84},1{\cdot}66HCl,4{\cdot}5H_2O$, and gives a brown solution in water. When prepared in the same way in dry air the substance forms violet solutions, and has the composition $IrCl_{3{\cdot}54},0{\cdot}66HCl,1{\cdot}5H_2O$; chlorides prepared at higher temperatures are only slowly dissolved by water. The salt $IrCl_3,4H_2O$ described in Wurtz's Dictionary appears to have the composition $IrCl_3,mHCl,nH_2O$, where m is less than unity (compare Claus, *J. pr. Chem.*, 1860, **80**, 282). This also forms condensed chlorides when heated. The author has been unable to prepare the anhydrous trichloride described by Claus. W. O. W.

Mineralogical Chemistry.

A Hitherto Unrecognised Crystallo-chemical Relation. FRANZ LOEWINSON-LESSING (*Centr. Min.*, 1911, 440—442).—It has been already remarked that double salts possess a lower degree of symmetry than either of the component salts, and that hydrated salts have lower symmetry than the corresponding anhydrous salts. It is now pointed out that in complex minerals consisting of a combination of a silicate with some other salt, the degree of symmetry is higher than in the corresponding simple silicate. For example, nephelite is hexagonal, whilst in the sodalite group, where this silicate molecule is combined with sodium chloride, etc., the symmetry is cubic. Again, in the tetragonal marialite there is a combination of the albite molecule (itself triclinic) with sodium chloride. A similar relation is shown to hold with helvine, danalite, melinophane, leucophane, melanocerite, etc. L. J. S.

Eglestonite from San Mateo Co., California. AUSTIN F ROGERS (*Amer. J. Sci.*, 1911, [iv], **32**, 48—50).—The mineral eglestonite, previously known only from Terlingua, Texas (Abstr., 1904, ii, 46; 1907, ii, 788; 1910, ii, 306), has been found as minute crystals, associated with other mercury minerals, in a siliceous matrix in serpentine near Palo Alto in San Mateo County. The crystals are cubic with a cubic, octahedral, or rhombic-dodecahedral habit; sometimes they are acicular, owing to elongation of the rhombic-dodecahedron in the direction of a cubic axis. Their orange-yellow to brownish-yellow colour is changed to black on exposure to light, but the adamantine lustre is retained. An analysis made on 25 mg. gave Hg 88·00, Cl 7·43%, agreeing with the eglestonite formula Hg_4Cl_2O. L. J. S.

Formula of Pearceite and of Polybasite. FRANK R. VAN HORN (*Amer. J. Sci.*, 1911, [iv], **32**, 40—44. Compare this vol., ii, 614).—The formula $9(Ag,Cu)_2S,Sb_2S_3$ given for polybasite by H. Rose in 1829 has always been generally accepted; and Penfield in 1896 described pearceite as a new mineral with the analogous formula

$$9(Ag,Cu)_2S,As_2S_3.$$

Rammelsberg (*Mineralchemie*, 1875) had, however, suggested the formula $8(Ag,Cu)_2S,(Sb,As)_2S_3$. A discussion of the published analyses (seven of pearceite and ten of polybasite) leads the author to the conclusion that the latter formula is the correct one. L. J. S.

Magnesite Deposits of Eichberg on the Semmering Pass: Eichbergite, a New Sulphantimonite. O. GROSSPIETSCH (*Centr. Min.*, 1911, 433—435).—These magnesite deposits closely resemble those of other Alpine occurrences described by Redlich and Cornu (Abstr., 1909, ii, 410). Associated minerals are dolomite, quartz, talc, rumpfite, iron-pyrites, stibnite, galena, fahlerz, and a new species called eichbergite.

Rumpfite occurs as finely granular, dirty-white to greyish-green masses; under the microscope it shows a confused fibrous or sheafy structure; D 2·666. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	H_2O.	Total.
29·55	35·15	2·61	19·37	13·00	99·68
30·71	38·10	1·83	17·83	11·30	99·77

Eichbergite.—A single massive fragment was found embedded in magnesite, and coated with green and yellow alteration products. It is iron-grey, and breaks with an irregular fracture. Hardness over 6; D 5·36. The following analysis agrees with the formula:

$$(Cu,Fe)_2S,3(Bi,Sb)_2S_3.$$

Cu.	Fe.	Bi.	Sb.	S.	Total.
3·62	1·45	51·53	30·00	12·74	99·34

L. J. S.

Schaumopal [Float-stone]. OTTO HAUSER (*Centr. Min.*, 1911, 436—438).—The acid vapours (sulphur dioxide) emitted by the Virunga volcanoes in German East Africa, by their action on the lavas (limburgite, basanite, etc.), have given rise to white cellular masses of opaline silica, intermixed with which is some native sulphur. Analyses I and II are of the pure white material, and III of partly decomposed material (dried at 150°).

	S.	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	SO_3.	Cl.	H_2O.	Total.
I.	5·73	81·34	2·56	1·97	—	0·41	—	—	—	0·03	trace	8·20	100·24
II.	4·52	82·25	2·34	2·03	trace	0·53	trace	—	—	0·21	0·13	7·99	100·00
III.	9·30	73·16	3·59	3·99	7·23	0·55	1·29	0·50	trace	0·24	0·01	—	99·86

L. J. S.

Rare Gases of Thermal Springs and the Information Yielded by Them in Regard to Radioactivity and the Physics of the Earth. CHARLES MOUREU (*Bull. Soc. chim.*, 1911, [iv], 9, i—xxv).—A lecture delivered to the French Chemical Society, in which the author's results and conclusions on this subject are summarised (compare Abstr., 1909, ii, 363; 1910, ii, 136).

R. V. S.

Physiological Chemistry.

The Action of Trypsin on the Different Oxidative Processes in Animal Tissues. FR. BATTELLI and (Mlle.) LINA STERN (*Biochem. Zeitsch.*, 1911, 34, 263—274).—The authors have already shown that there are two classes of oxidative processes in the tissues, namely, those which take place in the presence of the intact cell only (the primary respiration, oxidation of citric and succinic acids, etc.), and those which take place in the presence of extracts of tissue. An investigation on the influence of trypsin, with employment of the same methods and materials used in former investigations, on the two classes of oxidative processes was undertaken. It was found that trypsin has no influence on the oxidative processes of the latter class. On the other hand, it causes a diminution of the oxidative processes of primary respiration, and oxidation by tissues of citric and succinic acids. It has no influence, on the other hand, on the urico- and alcohol-oxydases, at least when the action of the trypsin has exceeded one hour. The authors discuss recent hypotheses on the action of lipoids on oxidative processes. S. B. S.

The Action of Radium Emanations on Some of the Main Constituents of Normal Blood. HELEN CHAMBERS and SIDNEY RUSS (*Proc. Roy. Soc.*, 1911, *B*, **84**, 124—136).—Red corpuscles are hæmolysed by α-rays, and oxyhæmoglobin is converted into methæmoglobin. Leucocytes undergo marked degenerative changes when subjected to α-rays. During clotting, the leucocytes appear to move away from the α-radiated region. This is attributed to changes in the surface-tension of blood serum when radiated. The specific properties of opsonin and hæmolytic complement are lost when serum is exposed to α-rays. The progressive changes caused by these rays indicate that opsonin and complement are not identical. The β- and γ-rays yielded negative results in analogous experiments. W. D. H.

The Interpretation of the Precipitin Reaction. D. A. WELSH and H. G. CHAPMAN (*J. Roy. Soc. New South Wales*, 1910, **44**, 320—333).—Further experimental evidence is given in support of the authors' contention that in the precipitin reaction the main mass of the precipitate is formed by constituents of the anti-serum. W. D. H.

The Action of Minimal Amounts of Acid on the Blood-Vessels. CARL SCHWARZ and FRIEDA LEMBERGER (*Pflüger's Archiv*, 1911, **141**, 149—170).—From perfusion experiments on the sub-maxillary gland of the cat, separated from the central nervous system, and on the intra-cranial vessels of the dog, it is shown that very dilute acids cause temporary vaso-dilatation. Acids weaker than carbonic, aminopropionic and aminoacetic have, however, no action. This occurs whether the animals have been poisoned with nicotine, and, as in the case of adrenaline, the effect is a peripheral one. The conclusion drawn is that the increased production of carbon dioxide and acid products which accompanies activity is a cause of the dilatation of the vessels of the active organs. W. D. H.

Action of Pancreatic Lipase. Contributions to the Biology of Enzymes. SABATO VISCO (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 780—787).—The author has examined the action of pancreatic juice on triolein (sweet almond oil) at 40°, and finds that the amount of fat hydrolysed is increased when a further portion of juice is added to a mixture in which no further hydrolysis is taking place. When, in the same circumstances, more oil is added, the absolute amount of acid present is also increased to some extent, although not always. The addition of bile to a mixture of fresh juice and oil accelerates the hydrolysis, but does not increase its ultimate amount, but when fresh juice is added repeatedly, the addition of bile does not increase even the velocity of hydrolysis, and appears sometimes to diminish it.

R. V. S.

The Relationship of Nitrogen and Sulphur in Metabolism. OSCAR GROSS (*Zeitsch. exp. Path. Ther.*, 1911, **9**, Reprint 19 pp.).—The present research arose from the study of certain features of metabolism in alcaptonuria. In dogs fed on horseflesh, the N : S ratio is practically equal in intake and output. In inanition, the nitrogen and sulphur excretion both fall, but the N : S ratio falls also, with certain rises at intervals. In lecithin feeding, although there is again a general correspondence between the ratio in the food and excreta, there is a tendency to nitrogen retention ; lecithin is, however, not a protein sparer. The administration of alkalis has no effect on the N : S ratio.

W. D. H.

The Action of the Enzymes of the Stomach, Pancreas, and Mucous Membrane of the Small Intestine on Gelatin. D. MINAMI (*Biochem. Zeitsch.*, 1911, **34**, 248—260).—By the action of pepsin, hydrochloric acid, and extract of the mucous membrane of the small intestine on gelatin, only a small amount of hydrolysis takes place (determined by Sörensen's titration method). The pancreas extract has a much stronger action, or largely breaks down the peptide bonds. Peptides, which are not precipitated by tannin solutions, appear to be formed, and also small quantities of *l*-leucine and *l*-proline. No glycine was found, and in this respect the pancreas gelatinase differs from gelatinase *B. prodigiosus*, by the action of which glycine is formed.

S. B. S.

The Resorption of Gelatin in the Small Intestine. D. MINAMI (*Biochem. Zeitsch.*, 1911, **34**, 261—262).—Gelatin, undigested and digested with pepsin and pancreatin, was introduced into isolated loops of the small intestine of dogs, and the amount which had been resorbed determined after intervals of one hour by washing out the contents of the loops and estimating the nitrogen. Very little undigested gelatin is resorbed, but larger quantities of the peptonised protein, and still larger quantities of the pancreatised protein, under the above conditions.

S. B. S.

Fermentation Processes in the Digestive Tract oi Ruminants. I. MARKOFF (*Biochem. Zeitsch.*, 1911, **34**, 211—232).—By means of a modified Haldane gas-analysis apparatus, which is figured, estimations of the hydrogen, methane, and carbon dioxide and nitrogen from the paunch and colon of oxen and goats were made. The gases were withdrawn by means of stomach tubes. In the case of the stomach, the quantity of carbon dioxide was sometimes less than that of the methane, and in the maximum, 1·52 times that of the methane. Where, however, the stomach contents were removed and submitted to fermentation *in vitro*, the quantity of carbon dioxide was three to four times that of the methane. This ratio increased on addition to the contents of soluble sugars. The carbon dioxide is apparently, therefore, resorbed as it is formed in the stomach. In the colon, the ratio of carbon dioxide to methane is smaller than in the stomach, being in two cases 0·35 and 0·18 to 1 respectively. The ratio of the methane to hydrogen was large, varying in a large number of experiments between 9·84 and 789 : 1 in the stomach and 25·8 and 26·8 (in two experiments only) : 1 in the colon. In the fermentation experiments carried out *in vitro* with the contents of the stomach and colon, the amount of hydrogen could be largely increased by the addition of soluble carbohydrates. S. B. S.

The Adaptation Capacity of the Animal Organism to Over-Abundant Nutriment. E. GRAFE and D. GRAHAM (*Zeitsch. physiol. Chem.*, 1911, **73**, 1—67).—In dogs, over-feeding for long periods leads to retention of nitrogen, but the body-weight remains fairly constant. This appears to be due to great activity, increase of oxidation, and loss of water. Full metabolic details are given; the respiratory figures point to the existence of a luxus consumption. W. D. H.

The Behaviour of Glycogen in the Ovary of Rana fusca. MAX BLEIBTREU (*Pflüger's Archiv*, 1911, **141**, 328—342).—The total glycogen in the frog and that of the liver increases from April onwards, reaching its maximum in September and October and diminishing during the winter. The glycogen of the ovary steadily increases from July onwards until the next April, when nearly half the glycogen of the body is contained in the eggs. The results, which on the whole confirm Kato's, point to the importance of glycogen in the nutrition of the eggs. W. D. H.

Chemical Composition of Normal Cerebro-spinal Fluid. True Nature of this Liquid. W. MESTREZAT (*Bull. Soc. chim.*, 1911, [iv], **9**, 683—688).—The paper contains the results of the complete analysis of a mixture of twenty normal fluids preserved by heat, and the means of various estimations carried out with about sixty individual fluids. The following physical constants were determined: d^{15} 1·00759, a − 0·577°. The composition was found to be as follows (in grams per litre): water, 996·69; total solids, 10·90; ash, 8·80. Analysis of the ash gave the following results (in grams per litre of the original liquid):

Na_2O.	K_2O.	CaO.	MgO.	Al_2O_3(?).	Fe_2O_3.	P_2O_5.	SO_3.	N_2O_5.	CO_2.	Cl.	Loss.
4·346	0·251	0·095	0·050	0·0007	0·002	0·029	0·028	traces	0·550	4·448	0·0023

Normal (as distinct from pathological) cerebro-spinal fluid only contains traces of albumin, and no albumoses or peptones. No diastatic action could be observed. The close resemblance between cerebrospinal fluid and blood serum is pointed out, and it is shown that the former, as well as the fluids of the eye and of the internal ear, has the composition which would be expected if it had been produced by dialysis of blood serum. This discredits the view that it is a glandular secretion. R. V. S.

The Functions of the Liver. E. WEHRLE (*Biochem. Zeitsch.*, 1911, **34**, 233—241).—The animals employed were geese, and the action of the liver was partly excluded by exposing the portal vein, and severing it between two ligatures. It was found, from analyses of the urine, that considerable quantities of carbohydrate are assimilated, even when the action of the liver is excluded. The organism under these conditions shows a varied tolerance to different sugars, especially to lævulose, which is not very markedly different from the tolerance under normal conditions. From these results the conclusion is drawn that in certain diseases of the liver, the diminished tolerance to lævulose is not due to injury to the liver parenchyma, so much as to other general disturbed conditions. The exclusion of the liver also causes a marked increase in the ammonia excretion, and, after administration of glycine, the increase of amino-acid excretion is greater when the liver is excluded than in normal animals.

S. B. S.

The Relation of the Spleen to the Fixation of Antigens and the Production of Immune Substances. ARNO B. LUCKHARDT and FRANK C. BECHT (*Amer. J. Physiol.*, 1911, **28**, 257—274. Compare this vol., ii, 217).—When an optimum dose of antigen (goat's or rat's blood) is injected intravenously into a dog, the antigen is partly fixed by the spleen; for if the spleen of the dog is removed, emulsified, and introduced into the peritoneal cavity of a normal dog, the specific immune substances appear in the serum of the latter, whereas the introduction of normal spleen produces no such result. The introduction of "immune" heart muscle, liver, bone-marrow, and lymph glands did not give a positive result. Dogs from which the spleen has been removed do not produce hæmolysins, hæmagglutinins, or hæmopsonins as rapidly, nor in so high a concentration, as normal dogs.

W. D. H.

The Relationship between Muscular Rigor and Protein Coagulation; Chemical Stimulation of Muscle. II. Rigor Produced by Salts. ERNST ROSSI (*Zeitsch. Biol.*, 1911, **56**, 253—273. Compare Abstr., 1910, ii, 730).—If the curarised sartorius of a frog is immersed in thiocyanate solutions it contracts immediately, and after some time becomes quite inactive. The more concentrated the solution, the greater is the initial contraction, which in *N*-solutions becomes partly and in 2*N*-solutions a completely permanent rigor. There are slight differences in the action of the potassium and sodium salts. Salicylates act in a similar way. Potassium and sodium iodides also act similarly, but if the muscle is immersed in 2*N*-sodium bromide, potassium or sodium chloride solutions, the initial contractions pass off. If the 2*N*-sodium and potassium thiocyanate solutions be replaced by the indifferent Göthlin's solution at the commencement of their action, the initial contraction will pass off. If this experiment is repeated several times, the thiocyanates after a time fail to produce contraction. Thiocyanates and salicylates also gradually destroy the irritability of the muscle to chloroform. *N*- and 2*N*-solutions of sodium thiocyanate also produce the rigor contraction when injected into the blood-stream.

S. B. S.

The Action of Veratrine on Striated Muscle. I. G. LAMM (*Zeitsch. Biol.*, 1911, 56, 223—252).—The experiments were carried out on the isolated sartorius muscle of a frog, and the contractions recorded after stimulus and after addition of veratrine to the Ringer's fluid in which the muscle was suspended. The critical toxic amount, that is, the quantity of poison necessary to cause a submaximal tetanus lasting a few seconds after a response to a momentary stimulus, was determined under different conditions of temperature, changes in the concentration of the salts in Ringer's fluid, etc. The tetanus is assumed to be due to the effect of the interaction of the metabolism products and the poison. The most noteworthy effect due to the alteration of the contents of the fluid in which the muscle is suspended is that resulting from the change in the calcium content. Diminution in calcium content increases the sensitiveness of the muscle to the poison, whereas an increase diminishes the sensitiveness.

S. B. S.

Biochemistry of Protozoa. THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1911, 73, 109—127).—Masses of *Goussia Gadi* removed from the swim-bladders of various sea-fish contained 14% solids, 12·9% organic matter, and 1·25% nitrogen. Considerable quantities of cholesterol were separated out, but no chitin or other carbohydrate-like substance. Among the proteins a phosphorus-free glucoprotein and a gelatin-yielding material were identified, with traces of a substance resembling elastin, and from the sporozoites, proteoses.

W. D. H.

Acapnia and Glycosuria. YANDELL HENDERSON and FRANK P. UNDERHILL (*Amer. J. Physiol.*, 1911, 28, 275—289).—Acapnia (diminution of carbon dioxide in the body) is a frequent concomitant of hyperglycæmia and of glycosuria. In some experimental forms of diabetes, prevention of acapnia obviates disturbances of the sugar-regulating functions. Traumatic and emotional glycosuria, and that produced by etherisation are believed usually to be due to acapnia. Injection of "peptone" is well known to cause acapnia (Lahousse, 1889); it is now found that it also leads to hyperglycæmia. In diabetic coma, an acute and true acapnia occurs as a result of hyperpnœa, and not merely due to the expulsion of carbon dioxide from the blood by acids; for in acidosis the acidity (H ion concentration) is probably below the normal, and the hyperpnœa is induced by the ethereal (not the acid) acidosis substances, for instance, acetone. The only certain criterion of acapnia or hypercapnia is analysis of the alveolar and blood gases. W. D. H.

The Composition of Human Milk in Nephritis. ST. ENGEL and HANS MURSCHHAUSER (*Zeitsch. physiol. Chem.*, 1911, 73, 101—108).—In nephritis, the residual nitrogen of both blood and milk is increased, but on the whole the secretion and composition of the milk are but little altered. The mammary gland can act as an excretory organ for urinary constituents, but neither mother nor child suffers.

W. D. H.

Anæsthetics. AUGUSTUS D. WALLER, FREDERICK W. HEWITT, BLUMFELD, JOHN A. GARDNER, and GEORGE A. BUCKMASTER (*Brit. Assoc. Report*, 1910, 268—281).—This report deals with the principles of anæsthesia by ether vapour [Waller], the rate of assumption of chloroform by the blood and the percentages of chloroform found in the blood of cats at the asphyxial point, using different strengths of chloroform-air mixture [Buckmaster and Gardner], and the influence of oxygen on the anæsthetic effect of chloroform [Hewitt and Waller]. T. S. P.

Glycogenic Property of Glucosamine. F. ROGOZIUSKI (*Compt. rend.*, 1911, **153**, 211—213).—Glucosamine is an important constituent of many proteins. Several investigators have experimented with rabbits to ascertain whether the introduction of glucosamine, as such or as a derivative, increases the amount of glycogen; the results, however, have all been negative. The author has experimented on a young chicken, four days old, but here again, after the introduction of glucosamine hydrochloride through the stomach, the amounts of glycogen in the liver and in the muscles are not greater than the customary amounts in chicken of this age.

Comparative experiments have been made on the behaviour of an emulsion of yeast (freed from glycogen) on distilled water, 1% aqueous sucrose, 1% aqueous glucosamine acetate, and 1% aqueous *iso*glucosamine acetate. Fermentation commenced at once in the sugar solution, and after four hours the presence of glycogen was detected by the coloration with iodine. The solutions of glucosamine and *iso*glucosamine, however, did not ferment, and glycogen could not be detected, the microscopic aspects of the two cultures being exactly like that in the distilled water. C. S.

Phloridzin- and Phloretin-glycuronic Acids. I. JOS. SCHÜLLER (*Zeitsch. Biol.*, 1911, **56**, 274—308).—Investigations were carried out with the object of determining the fate of phloridzin injected into the organism, and for this purpose experiments were undertaken with the object of quantitatively isolating phloridzin or a derivative from the urine. It was found incidentally that when this substance is treated with bromine, it undergoes hydrolysis in addition to bromination, and yields quantitatively the theoretical amount of dextrose, together with tetrabromophloretin. If the bromination is carried out in methyl alcohol instead of water, the methyl glucoside is obtained instead of dextrose. Other glucosides, such as arbutin, undergo a similar hydrolysis on treatment with bromine, whereas others, such as aesculin, quercitrin, etc., yield no free sugar on similar treatment. In the urine of animals treated with phloridzin, more reducing substance is set free than can be accounted for by phloridzin in itself, and the author has shown that this is due to the fact that the glucoside is excreted in the form of its glycuronic acid, $C_{27}H_{32}O_{16}$, which has $[\alpha]_D -102\cdot2^\circ$. The substance is easily soluble in hot water, alcohol, or acetone, but sparingly so in ether or ethyl acetate. On hydrolysis with dilute sulphuric acid under certain conditions, there is scission of the glucose, and not the glycuronic group from this substance of diglucosidal nature. As a result of this action, phloretinglycuronic acid, which begins to decompose between 110° and 120°, is obtained; this decomposes on treatment with bromine, yielding tetrabromophloretin and glycuronic acid. The author discusses the older theories as to the formation of glycuronates in view of these results, and draws the conclusion that it is possible that dextrose is first oxidised to glycuronic acid before pairing with the infected substance takes place. He shows, furthermore, that phloridzinglycuronic acid is practically non-toxic, causing no glycosuria in rabbits, and only relatively little glycosuria in dogs as compared with the effect of the free phloridzin. S. B. S.

The Influence of Urea on the Blood and Milk of Suckling Women. St. Engel and Hans Murschhauser (*Zeitsch. physiol. Chem.*, 1911, **73**, 131—137).—The administration of urea leads to an increase of the residual nitrogen both in the blood and milk of suckling women. W. D. H.

Oil of Phosphorus and its Combinations in the Organism Investigated by means of the Electroscopic Detection of Phosphorus. H. Schmidt (*Biochem. Zeitsch.*, 1911, **34**, 280—305).—The experiments were carried out by means of a modification of Elster and Geitel's electroscope. It was found that phosphorus, even in solution in oil, made the air a conductor of electricity, the effect being proportional to the amount of phosphorus. The temperature optimum was 60°. The ionisation diminishes as the oxidation of the phosphorus proceeds; as in oily solutions, a protective layer of insoluble oxides is formed. Inactive gases, such as hydrogen, carbon dioxide, etc., can become saturated with phosphorus vapour, and can then cause the air, as soon as oxidation commences, to become ionised. Pure oxygen can also be saturated with phosphorus vapour, and oxidises only on dilution, when ionisation commences. Phosphorus, in oily solutions, enters into combination with both arterial and venous blood, but not with serum. Elementary phosphorus can be detected in the expired air from animals poisoned by this substance. The air expired from animals, after large intra-arterial doses of phosphorus, is ionised. In such cases, elementary phosphorus passes from the blood to the alveolar wall, where it is oxidised. S. B. S.

Experimental Poisoning by Oxalic Acid. Localisation of the Poison in the Various Organs. Sarvonat and Roubier (*Ann. Chim. anal.*, 1911, **16**, 256—258).—To a dog weighing 18 kilos. were administered increasing doses of sodium oxalate, until after fourteen days 50·4 grams had been given; the last few days the animal suffered from diarrhœa with hæmorrhage, and seemed disgusted with its food, so that it did not take the full dose given. The dog was then killed by severing the femoral vein, and the organism washed out by injection with physiological salt solution. The various organs were, including the blood, then examined for oxalic acid.

The blood showed 0·0017%, a portion of the liver 0·0098%, two lungs 0·0106%, two kidneys 0·0225%, a portion of the sinews 0·0250%, and the brain 0·0270% of oxalic acid. L. de K.

Forensic Detection of Veronal. Alfr. Heiduschka (*Arch Pharm.*, 1911, **249**, 322).—The examination, almost immediately after death, of the body of a woman killed by veronal, showed the presence of only extremely small quantities of the poison in the urine, spleen, heart, liver, bile, œsophagus, stomach, and intestines. The author points out that this is a case where the greater part of the poison must have been eliminated from the system before death occurred. C. S.

Influence of Oxidation on the Toxicity of Urohypotensine. J. E. Abelous and E. Bardier (*Compt. rend.*, 1911, **153**, 122—123).—Urohypotensine has been oxidised at 40° for two hours by sodium permanganate, persulphate, and chlorate respectively. On rabbits, 0·03 gram of urohypotensine per kilo. of body-weight is never a lethal dose, but the injection of the oxidised toxin into the blood stream causes death almost instantly. Sodium chlorate is the best oxidising agent, in that its effects are constant and regular.

At present little can be said regarding the nature of the oxidised urohypotensine. Possibly very toxic nitriles are produced, because agents, such as sodium thiosulphate, which are antitoxic to certain nitriles show a similar behaviour towards oxidised urohypotensine. C. S.

Chemistry of Vegetable Physiology and Agriculture.

The Mechanism of Alcoholic Fermentation. Alexandre Lebedeff (*Compt. rend.*, 1911, 152, 136—139. Compare Abstr., 1910, i, 706).—From the analysis of the *p*-bromophenylhydrazone of hexosephosphoric acid which he has now succeeded in recrystallising, the author concludes that hexosephosphoric acid has the composition previously ascribed to it by Young (Abstr., 1910, i, 12). Extract of dried yeast is stated to ferment a 5% solution of dihydroxyacetone as readily as saccharose. When the fermentation takes place in presence of phosphate, an organic compound is obtained which is identical with the hexosephosphate produced from a hexose under similar conditions. A theory of the alcoholic fermentation of sugar is given, according to which in the presence of the enzyme the hexose is first converted into two molecules of a triose; these then condense with the phosphate to form trioso-phosphate, and this polymerises to form a hexosephosphate, which then reacts with water with production of carbon dioxide, alcohol, and free phosphate. W. J. Y.

The Reduction of Furfuraldehyde by Yeasts During Alcoholic Fermentation. Carl J. Lintner and H. J. von Liebig (*Zeitsch. physiol. Chem.*, 1911, 72, 449—454).—The disappearance of furfuraldehyde in yeast cultures is due to its reduction to furfuryl alcohol, and not to its oxidation to pyromucic acid. This change is also induced by yeast suspended in water, but the rate of change is not so great as in the case of fermenting yeast.

Under favourable conditions about 70% of the furfuraldehyde supplied is converted into a mixture of two parts of furfuryl alcohol and one part of a crystalline substance which has not been identified. This substance appears to be related to furfuryl alcohol, and is probably produced by secondary action. An experiment, in which 20 grams of furfuraldehyde were added to 4 litres of 10% sucrose solution and 200 grams of carefully washed bottom yeast, after incubation at 18—20° for four days, gave 4 grams of furfuryl alcohol, b. p. 166—170° (uncorr.)/720—730 mm. For identification, furfuryl diphenylcarbamate was prepared according to Erdmann's method (Abstr., 1902, i, 553). H. B. H.

The Behaviour of Yeast Enzymes when Free and United to Protoplasm. HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, **73**, 85—100).—Details are given of the action of various antiseptics, anæsthetics, and drying on the activity of the maltase, invertase, and zymase of yeast. The enzymes are believed to be original constituents of the plasma, and are separated in the living cell from the plasma, and again regenerated there; they are then easily extracted, and are present in relatively large quantities; or the separation may be produced partly by drying the cells or by mechanical means, which lead to the death of the plasma. Towards antiseptics they are comparatively insusceptible when freed from the living plasma. W. D. H.

Electromotive Phenomena in Plants. AUGUSTUS D. WALLER, (Mrs.) A. M. WALLER, F. GOTCH, J. B. FARMER, VICTOR H. VELEY, and F. O'B. ELLISON (*Brit. Assoc. Reports,* 1910, 281--290).—This report deals with the rate of intoxication and temperature, the evolution of hydrocyanic acid by laurel leaves, protoplasm and water, and a new method for the quantitative estimation of hydrocyanic acid (compare Waller, Abstr., 1910, ii, 759). There is an appendix on the blaze currents of laurel leaves in relation to their evolution of hydrocyanic acid [(Mrs.) A. M. Waller]. T. S. P.

Mechanism of Carbon Assimilation. III. FRANCIS L. USHER and J. H. PRIESTLEY (*Proc. Roy. Soc.*, 1911, *B*, **84**, 101—112).—The catalase enzyme is not exclusively localised in the chloroplasts, as previously stated; subsequent experiments merely indicated that it is more concentrated in the green residue obtained when the juice of crushed leaves is filtered than in the filtrate.

Evidence is given that the primary products of the photolysis of aqueous carbon dioxide are formaldehyde and hydrogen peroxide, and that the evolution of oxygen is due to the decomposition of the hydrogen peroxide by catalase. Up to this point the process is, therefore, non-vital. N. H. J. M.

Composition of the Plasma Membrane. W. W. LEPESCHKIN (*Ber. Deut. bot. Ges.,* 1911, **29**, 247—261).—The colloidal solution of plasma membrane (*ibid.*, 1910, **28**) contains oily substances in addition to water and proteins. It is uncertain whether it contains a mixture of lecithin and cholesterol, as assumed by Overton.

N. H. J. M.

Increased Rate of Diffusion of Dextrose. S. RYWOSCH (*Ber. Deut. bot. Ges.*, 1911, **29**, 204—210).—Dextrose in 2% solutions containing 2% of sucrose was found to diffuse more quickly than in absence of sucrose. The conclusion is drawn that the migration of substances in plants is mainly due to diffusion and that diffusion is assisted by the presence of two or more kinds of sugars.

N. H. J. M.

The Behaviour of Green Plants towards Gaseous Formaldehyde. VICTOR GRAFE (*Ber. Deut. bot. Ges.*, 1911, **29**, 19—26. Compare Abstr., 1909, ii, 922; 1910, ii, 335).—Experiments with *Phaseolus vulgaris*, in which the above-ground portions were supplied with formaldehyde in the form of vapour, showed that the production of starch is hindered by formaldehyde, and that the plants contained more than twice as much reducing sugar as similar plants grown under normal conditions.

Acetaldehyde (10 c.c. of a 0·5% solution) and benzaldehyde (20 c.c.) checked the growth of the plants more or less completely. Acetic acid is more active than acetaldehyde, whilst benzoic acid had no appreciable effect. N. H. J. M.

Direct Guaiacum Reaction Given by Plant Extracts. (Miss) M. WHELDALE (*Proc. Roy. Soc.*, 1911, *B*, **84**, 121—124).—Catechol can be detected with ferric chloride in extracts of plants which give the direct action and a brown pigment when exposed to chloroform vapour. It was not found in any appreciable quantity in plants giving the indirect action only.

A slightly alkaline solution of catechol which has developed a brown colour by exposure to air produces a blue coloration when added to a peroxydase solution and guaiacum tincture. Similar experiments with phenol, resorcinol, quinol, pyrogallol, phloroglucinol, with benzoic, salicylic, *m*-hydroxybenzoic, *p*-hydroxybenzoic, protocatechuic, gallic, and tannic acids, and quercitin gave negative results.

The conclusion is drawn that the direct action given by extracts of the plants examined is due to the presence of catechol.

N. H. J. M.

The Localisation of Betaine in Plants. VLADIMIR STANĚK (*Zeitsch. physiol. Chem.*, 1911, **72**, 402—409. Compare Abstr., 1910, ii, 336).—The method of isolating betaine from plants is described. Analyses of the different parts of *Beta vulg. sacchar.*, *Triticum vulgare*, *Lycium barbarum*, *Atriplex canescens*, and *Amaranthus retroflexus*, indicate an irregular localisation of the compound. The highest percentages are found in the leaf, with a gradual decrease from the early stages of growth to dead ripeness. Young shoots are also rich in betaine, whilst the bark and wood (*Lycium* and *Atriplex*) contain very little. The root and leaves of *Amaranthus* contain 0·48% and 2·16%

respectively, and those of the sugar beet 0·95—1·20% and 2·62% betaine. The seeds of all the plants tested were strikingly poor in this compound. The whole of the analyses appear to indicate a localisation of betaine at points of energetic physiological activity. The high percentages found in young leaves, shoots, and the root of a biennial plant such as sugar-beet lead to the conclusion that betaine plays an important part in the nitrogen metabolism of plants, but does not serve as reserve food-stuff. H. B. H.

Relation of the Odorous Constituents of Certain Plants to Plant Metabolism. Frank Rabak (*J. Amer. Chem. Soc.*, 1911, **33**, 1242—1247).—From experiments on the Canada fleabane (*Erigeron canadensis*), bergamot mint (*Mentha citrata*), peppermint (*Mentha piperita*), and wormwood (*Artemisia absinthium*), the following general statements are made. In every case the plant is distilled with steam, and the essential oil obtained is analysed for its content of esters and alcohols. The esters (which are regarded as the odorous constituents of the plant) do not seem to be affected during the fructification of the plant. The amount of the esters increases very largely during the growth of the plant, the amount after flowering being sometimes two or three times as great as that before flowering; the percentage of alcohols, however, bears a very slight relation to the life processes of the plant. The odorous constituents apparently are simply products of excretion, and are of no further use to the plant. The effects of drying, budding, blossoming, and fruiting on the life processes of the plants have been examined; in every case there is a change in the aromatic constituents, but in no instance has a decided consumption of the ester or alcoholic constituents been observed. C. S.

Rôle of Nucleo-proteins in Plants. W. Zaleski (*Ber. Deut. bot. Ges.*, 1911, **29**, 146—155).—The production of nucleo-proteins takes place in all growing cells; a considerable increase was observed in the growing portions of seedlings of *Zea mays* and in *Vicia faba*. From the results of experiments with different plants, the conclusion is drawn that the nucleo-proteins are formative substances which have a share in the production of protoplast. N. H. J. M.

Composition of Various Oleaginous Seeds from French West Africa. Alexandre Hébert (*Bull. Soc. chim.*, 1911, [iv], **9**, 662—672).—The paper gives in detail the yield and composition of the fats extracted from the fruits of a number of tropical plants, and the composition and agricultural value of the residual cakes.

Dumoria Heckeli.—The adult tree yields per year about 30 kilos. of fat ("Doumori butter") containing 33% of unsaturated acids (chiefly oleic acid) and 67% of solid acids (apparently stearic, palmitic, carnaubic, and cerotic acids).

Chrysophyllum africanum yields but little fatty matter (2% of the fruit). *Chrysophyllum d'Adzopé* and *Omphalocarpum anocentrum* also give only small quantities of oil.

The seeds of *Carapa microcarpa* yield 35% of fat, which consists of olein, stearin, palmitin, and myristin, together with volatile esters.

The oil from *Balanites tieghemi* contains much oleic acid, but the yield does not exceed 2% of the seeds.

Ricinodendron africanum yields only 8·7% of an oil containing 70% of unsaturated acids (probably oleic and linoleic acids) and 30% of solid acids (probably palmitic and some myristic acid).

Saccoglottis Gabonensis gives in very small quantity an oil resembling olive oil, and 5% of a resin can also be obtained from the fruits.

Pentadesma butyracea yields a fat known as "Tama butter," which contains 10% of liquid acids (oleic acid) and 90% of solid acids (stearic and palmitic acids). R. V S.

Chemical Examination of Woody Aster. L. CHARLES RAIFORD (*J. Amer. Chem. Soc.*, 1911, **33**, 1189—1195).—The woody aster (genus *Xylorrhiza*), which apparently has been the cause of extensive sheep poisoning in Wyoming for several years past, is being thoroughly examined. The present paper describes the collection of the plant at the flowering season and the preparation of the roots and tops (that is, everything above the surface of the ground) for analysis, the action of various extractives, the proximate analysis of the roots and tops for moisture, ash, fibre, pentosans, proteins, dextrin, and starch, and the analysis of the ash of the tops and of the roots. Alkaloids are not present in the leaf. C. S.

Chemical Nature of Organic Nitrogen in the Soil. S. L. JODIDI (*J. Amer. Chem. Soc.*, 1911, **33**, 1226—1241).—Practically all of the nitrogen in soils is of an organic nature. Various plots on the Experimental Station on the Wisconsin Drift have been treated with manure, hay, straw, and other materials representing the principal sources for humus formation. After three years, samples of the soils have been examined. After having found that boiling water extracts at most about 8% of the total nitrogen from the soil, the author uses boiling concentrated hydrochloric acid for ten to fifteen hours, or 20% hydrochloric acid for twenty to thirty hours, whereby about 76% of the total nitrogen is extracted. The hydrochloric acid extract is evaporated to dryness, and the residue is distilled with cream of magnesia; the distillate contains, in the form of ammonia, all the nitrogen present as amides in the soil, the amount of nitrogen being from 25·5% to 33% of the nitrogen extracted. The residue from the distillation with the magnesium oxide is extracted with water, and the solution, after being acidified with sulphuric acid, is treated with phosphotungstic acid, whereby the diamino-acids are precipitated, whilst the amino-acids remain in the filtrate. The nitrogen from the diamino-acids and the amino-acids respectively represents 12—13% and 22—56% of the nitrogen extracted. The rest of the nitrogen is present in compounds other than amides or amino-acids. Such nitrogen is present to the extent of 47—60% in soils which have not been recently manured. C. S.

Disinfection of Plants. L. DANESI and M. TOPI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 772—778).—The authors record the results of experiments on the value of the following insecticides in destroying phylloxera in its various stages: (1) water at 55° for five minutes; (2)

a solution of copper sulphate (1%) at 55° for five minutes; (3) a solution of potassium thiocarbonate (3%) and black soap (1%) for twelve hours; (4) pyridine vapour (0·05%). The eggs when ready to open are killed by (1), (3), and (4), the duration of exposure in the case of the last named being two hours. The same modes of treatment destroy the root-form of the insect. The action of pyridine vapour on the leaf galls was also examined, and it was found to have no ill effect on the plant itself, even after acting on it for six to eight hours. It destroys the larvæ in the galls after three or four hours, but its action on the eggs in that situation is incomplete.

R. V. S.

"Sugar Sand" from Maple Sap. Source of Malic Acid WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1911, **33**, 1205—1211).—"Sugar sand" or "nitre" is the sandy, insoluble substance deposited during the evaporation of the sap of the sugar-maple tree (*Acer saccharum*). When practically free from sugar, it is a light grey, microcrystalline powder, tasteless, but slightly odorous. Its composition varies slightly in different samples, but on the average it contains SiO_2 7·74, P_2O_5 0·05, Fe_2O_3 0·39, Ca 17·16, Mg 0·03, moisture 2·60, malic acid 51·48, invert sugar 2·31, sucrose 3·46, matter soluble in ether 0·37, CO_2 0·66, extraneous organic matter 2·35, and undetermined substances 11·40% (by difference). To prepare malic acid from the "sand," the best method is first to prepare calcium hydrogen malate, and from this to obtain the malic acid by means of aqueous oxalic acid.

C. S.

Action of Manganese Sulphate on Vegetation. GIULIO MASONI (*Staz. sper. agrar. ital.*, 1911, **44**, 85—112).—Pot experiments in which magnesium and iron sulphates, both separately and together, and sodium sulphate were applied to maize and lupins.

As regards maize, the addition of small amounts of manganese sulphate reduced the amount of dry produce considerably. With the largest amount of manganese sulphate (Mn = 0·005%) and iron sulphate in addition, there was a slightly increased production of dry matter, and with iron sulphate alone there was also an increase in dry matter. Sodium sulphate gave nearly the same amount of dry matter as when nothing was added, but greatly increased the amounts of manganese and iron taken up from the soil.

Manganese sulphate alone (Mn = 0·001%) increased the dry produce in the case of lupines, and also the percentage of manganese in the dry matter. Manganese sulphate (Mn = 0·005%) in conjunction with iron sulphate produces the highest amounts of dry matter (lupines), whilst sodium sulphate also gave an increase in dry matter and an increase of manganese, but not of iron, taken up from the soil.

Manganese sulphate would seem to be injurious rather than beneficial, and any beneficial action is probably due to the acid portion of the salt. Its physiological action is diminished by the presence of iron.

N. H. J. M.

Analytical Chemistry.

Estimation of Ozone by an Alkaline Solution of Potassium Iodide. GEDEON LECHNER (*Zeitsch. Elektrochem.*, 1911, **17**, 412—414).—The quantity of ozone produced is first found by accurate measurement of the diminution of pressure in the ozoniser. A neutral or an alkaline solution of potassium iodide is then run into the ozoniser; after complete absorption of the ozone, sulphuric acid is added and the iodine titrated; in other experiments the ozone is swept out of the ozoniser by oxygen and bubbled through the potassium iodide solution. In all cases the quantities of ozone found agree very closely with those calculated from the diminution of pressure. The use of an alkaline solution has the advantage that no iodine is set free, and therefore there is no risk of its being carried away with the current of gas. T. E.

Rapid Estimation of Sulphuric Acid with the Porous Clay Crucible. FREDERICK KLEIN (*Amer. J. Pharm.*, 1911, 83, 342—346).—The process suited more particularly for the checking of normal sulphuric acid consists in diluting exactly 10 c.c. of the acid with 3 or 4 times its volume of water and heating to boiling. A few c.c. of hydrochloric or nitric acid are added, and then, without interrupting the boiling, 15 c.c. of 10% solution of barium chloride or nitrate. The beaker is then kept hot in a water-bath, and as soon as the barium sulphate has settled completely, it is collected on a specially constructed porous clay crucible of known weight by means of a pump with the so-called carbon filter with rubber stopper, well washed with acidified water until free from chloride or nitrate, dried, heated, and weighed.

A table is annexed facilitating the adjustment of the acid from the result obtained. L. DE K.

The Action of Hydrazine Sulphate on Nitrites and a New Method of Estimating Nitrogen in Nitrites. BIMAN BEHARY DEY and HEMENDRA KUMAR SEN (*Zeitsch. anorg. Chem.*, 1911, 71, 236—242. Compare Girard and de Saporta, Abstr., 1904, ii, 678).—Solutions of metallic nitrites and hydrazine sulphate react vigorously, even at 0°, the gases evolved containing 2 vols. of nitrous oxide to 1 vol. of nitrogen. The decomposition of hydrazine nitrite,

$$N_2H_4,2HNO_2,$$

would yield equal volumes of nitrous oxide and nitrogen, whilst the mononitrite would yield only nitrous oxide and ammonia. The presence of ammonia was confirmed. Amyl nitrite does not react with hydrazine sulphate.

The method may be used to estimate nitrites, the volume of nitrogen, after the removal of nitrous oxide by washing with water, being always two-thirds of that contained in the nitrite. C. H. D.

Colorimetric Estimation of Phosphoric Acid. Isidore Pouget and D. Chouchak (*Bull. Soc. chim.*, 1911, [iv], **9**, 649—650. Compare Abstr., 1909, ii, 266).—Further details are given as to the exact mode of working, and the preparation of the necessary reagents.

R. V. S.

Detection of Perboric Acid and Some Similar Compounds. Wilhelm Lenz and E. Richter (*Zeitsch. anal. Chem.*, 1911, **50**, 537—544).—Sodium perborate may be readily distinguished from borax by adding to its solution a little potassium dichromate and shaking with ether, which turns blue owing to formation of perchromic acid; the reaction is really due to liberation of hydrogen peroxide from the perborate.

The reaction with potassium iodide is particularly interesting. If to a 1% solution of a per-salt are added 2 drops of 10% solution of potassium iodide, iodine is liberated by ammonium persulphate only. On acidifying with dilute sulphuric acid, iodine is also liberated by ammonium perborate and potassium percarbonate, but not by perchlorate. If potassium bromide is substituted for potassium iodide, no bromine is liberated.

L. de K.

Elementary Analysis. Albin Kurtenacker (*Zeitsch. anal. Chem.*, 1911, **50**, 548—565).—The author has substituted several metallic oxides for the almost universally used copper oxide in elementary analysis. All combustions were made in a current of mixed air and oxygen or pure oxygen in the usual manner. Instead of the oxidised copper spirals, a boat containing the respective oxides was employed. Special experiments were also made in the case of nitrogenous substances by substituting other metals for metallic copper, in order to reduce nitric oxides formed.

Ferric oxide, obtained by igniting the hydroxide, gives satisfactory results when operating in a current of pure oxygen, but on the whole it is less suitable than copper oxide. Manganese oxide, when obtained by ignition of the nitrate, gives approximate results only; this is chiefly due to the fact that it persistently retains nitrate, which is given off gradually on heating, and renders it unsuitable in the case of nitrogenous compounds. Cobalt oxide obtained from the nitrate, however, is a very suitable oxidiser, and the combustion takes place rapidly, even at a dull red heat. Nickel oxide obtained from the nitrate also gives good results, but it is less suitable than cobalt oxide. Tungstic acid does not cause a complete oxidation, and although with great care fairly satisfactory results are obtained with molybdenum trioxide, its use offers no advantage.

When burning nitrogenous substances, the usual copper spirals may be replaced by a boat filled with porous nickel, prepared by reducing the oxide in a current of hydrogen; nickel spirals proved very unsatisfactory. As, however, metallic nickel slightly reduces carbon dioxide to carbon monoxide, and also slightly liberates hydrogen from water-vapour, the gases must be reoxidised by passing them over red-hot cobalt oxide.

Cobalt cannot be substituted for nickel, as it affects the carbon and hydrogen results.

L. de K.

Electro-analysis. FREDERIC S. KIPPING, F. MOLLWO PERKIN, GEORGE T. BEILBY, THOMAS M. LOWRY, WILLIAM J. POPE, and HENRY J. S. Sand (*Brit. Assoc. Report*, 1910, 79—80).—This report deals with the "electro-deposition of metals" (Perkin and Hughes, Abstr., 1910, ii, 898), with "apparatus for the rapid electro-analytical separation of metals" (Sand, Abstr., 1910, ii, 66) and the "electro-determination of lead as peroxide" (Sand, Abstr., 1910, ii, 456). Reference is also made to the separation of the four metals, copper, antimony, tin, and lead (Sand, Proc., 1909, **25**, 228). T S. P.

Volumetric Estimation of Mercury. CARL E. SMITH (*Amer. J. Pharm.*, 1911, **83**, 311—315).—The methods given in the German Pharmacopœia for the volumetric estimation of mercury in mercuric chloride tablets, ointment of ammoniated mercury, mercuric salicylate, mercury plaster, mercury ointment, and ointment of red mercuric oxide are recommended.

The first three are tested by the iodine titration method, the others by the thiocyanate process. L. DE K.

Analysis of Artificial Pearls and Rubies. RAFAEL CERERO and ENRIQUE BAYO (*Anal. Fis. Quim.*, 1911, **9**, 178—181).—The chemical compositions of the artificial agree with those of the natural gems, excepting that no calcium phosphate is found in artificial pearls. Distinctions between the two kinds are to be made by means of microscopical examination of the structural differences. G. D. L.

The Manganese Content of Honeys. ARTHUR GOTTFRIED (*Pharm. Zentr.-h.*, 1911, **52**, 787—788).—The author estimates the manganese in honey as follows: The ash obtained from 25 grams of the sample is dissolved in hot dilute nitric acid and transferred to a 100 c.c. cylinder. After adding some silver nitrate and ammonium persulphate, the solution is warmed and the pink colour developed is matched with a standard permanganate solution.

The amount of manganese seems to bear some kind of relation to the matters precipitable by tannic acid. The average quantity in virgin honeys was found to be 0·04 mg. %; that in commercial samples, 0·065 mg. % of manganese. L. DE K.

The Simultaneous Volumetric Estimation of Iron and Vanadium. ERICH MÜLLER and OTTO DIEFENTHÄLER (*Zeitsch. anorg. Chem.*, 1911, **71**, 243—249).—The reduction of vanadium salts by repeated evaporation with hydrochloric acid, conversion into sulphate, and titration with permanganate (Campagne, Abstr., 1903, ii, 761) yields low results with ferro-vanadium. The use of alcohol together with hydrochloric acid reduces the error, without removing it, the results in presence of much iron being too high, owing to the organic compound being retained on evaporation by the large mass of salts. The error is avoided if the evaporation with sulphuric acid is omitted.

One gram of ferro-vanadium is dissolved in concentrated nitric acid, evaporated with hydrochloric acid, and then boiled with hydrochloric acid and alcohol, evaporated to about 5 c.c., and diluted to a known volume. An aliquot part is titrated with permanganate, giving the vanadium. Another portion is used for the iodometric estimation of the iron. The amount of iron found by this method is 0·5% more than that actually present. The iron is more accurately estimated after the titration with permanganate by reducing with sulphur dioxide and titrating the iron and vanadium together with permanganate.

C. H. D.

Analytical Application of Certain Xanthates. JAIME FERRER and ANGEL DEL CAMPO (*Anal. Fis. Quim.*, 1911, **9**, 173—174).—Potassium propyl xanthate gives a yellow precipitate with salts of nickel, and a green precipitate with those of cobalt. When a dilute solution of the reagent is used, the nickel is precipitated before the cobalt.

Potassium methyl xanthate is also a delicate reagent for these metals, the nickel salt being soluble and the cobalt salt insoluble in ammonia.

G. D. L.

Reaction of the Stannous Ion. JULIO DE GUZMÁN CANANCIO (*Anal. Fis. Quim.*, 1911, **9**, 177—178).—Stannous chloride yields a carmine-red coloration with ammonium thiocyanate (preferable to the potassium salt) and ammonium molybdate in hydrochloric acid solution in the cold. Excess of hydrochloric acid is to be avoided. The test recognises 0·0001 gram of stannous chloride in 1 c.c., but is given by other reducing agents.

G. D. L.

The Detection and Estimation of Thorium by means of Iodic Acid. RICHARD J. MEYER (*Zeitsch. anorg. Chem.*, 1911, **71**, 65—69. Compare Meyer and Speter, Abstr., 1910, ii, 459).—Even very small quantities of thorium in mixtures of the rare earths may be readily detected and estimated by means of iodic acid. Two solutions are used: solution I, containing 15 grams of potassium iodate, 50 c.c. of concentrated nitric acid, and 100 c.c. of water; and solution II, 4 grams of potassium iodate, 100 c.c. of dilute nitric acid, D 1·2, and 400 c.c. of water. In making the test, 2 c.c. of the solution to be tested, which must be free from hydrochloric acid, are mixed with 5 c.c. of solution I. Thorium iodate is precipitated together with some iodates of other earths. These are re-dissolved by adding 10 c.c. of solution II and boiling, when the thorium precipitate remains insoluble. About 0·1 gram ThO_2 per litre may be detected in this way, and the sensitiveness is almost unchanged in the presence even of a large excess of other rare earths. Zirconium is precipitated under the same conditions, but zirconium iodate may be dissolved out by means of oxalic acid. Ceric salts are also precipitated, but may be removed by previous boiling with a little sulphurous acid. The cerous salt is very slowly oxidised by nitric and iodic acids, but this is without influence under the conditions of the experiment.

The separation of thorium and scandium (compare Meyer and Winter, Abstr., 1910, ii, 853) is best accomplished by this method after a double precipitation with ammonium thiosulphate from hydrochloric acid solution, the thorium iodate being decomposed with ammonia and ignited to oxide. Specimens of orthite from Impilak, Finland, examined by this method, gave 0·80% Sc_2O_3 and 1·32% ThO_2 in the fresh mineral, and 1·00% Sc_2O_3 and 1·10% ThO_2 in the weathered mineral. This concentration of scandium in a cerium mineral is purely local, and does not occur in other specimens of orthite.

C. H. D.

Estimation of Active Hydrogen in Organic Molecules.

BERNARDO ODDO (*Ber.*, 1911, **44**, 2048—2052 *).—The method is based on the interaction of the organic substance and magnesium ethyl iodide in a special weighed apparatus, the loss of weight corresponding with the ethane formed. The apparatus consists of a small flask, *A*, containing the substance dissolved in pyridine, *iso*amyl ether, toluene, or heavy petroleum. This is connected with a similar flask, *B*, containing magnesium ethyl iodide dissolved in *iso*amyl ether, into which the delivery tube of the first flask dips. The magnesium ethyl iodide is prepared fresh for each experiment, and contains slightly less than the theoretical quantity of alkyl iodide required by the magnesium taken. A suitable absorption vessel of sulphuric acid is attached to the second flask, and the three are weighed together; the free end is then protected by a calcium chloride tube and a flask of pyrogallic acid.

By suction, air is drawn from *A*, and on release the organo-metallic compound passes over from *B*. Ethane is liberated and escapes from the apparatus, being freed from solvent and moisture in passing out of the apparatus. In pyridine, action takes place at once, and cooling is sometimes necessary; in the other substances it is advisable to warm *A* at 50—60° to complete the reaction. After cooling, the apparatus is re-weighed and the loss determined.

Experiments are quoted for a number of substances showing the number of hydroxyl and active hydrogen groups present.

E. F. A.

A Reaction for Aromatic Inner Anhydrides Based on the Modification of the Crystalline Form of Iodoform.

BRUNO BARDACH (*Zeitsch. anal. Chem.*, 1911, **50**, 545—548).—To the not too strong aqueous solution of the supposed aromatic anhydride (for example, euxanthone or its derivatives), which should be practically neutral and prepared with spring water, is added drop by drop a 2% alcoholic solution of iodoform. If the iodoform separates in delicate needles, inner aromatic anhydrides are present. Albumin, if present, should first be removed.

If, however, the normal hexagonal iodoform crystals are obtained, 3 c.c. of the original solution are mixed with a few drops of Lugol's iodine solution (4 iodine, 6 potassium iodide, 100 of water), and 1 to 2 c.c. of ammonia are added. If the solution clears completely, a little more iodine should be added. After waiting for an hour and filtering, alcoholic solution of iodoform is added, and a needle-shaped precipitate now points to the presence of aromatic inner anhydrides (such as coumarin) or aromatic hydroxy-acids with a long side-chain or to polyhydroxy-ketones.

L. DE K.

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* and *Gazzetta*, 1911 **41**, i, 709—716.

Estimation of Volatile Fatty Acids [in Fæces]. F. Edelstein and Ernst Welde (*Zeitsch. physiol. Chem.*, 1911, **73**, 152—156. Compare Welde, Abstr., 1910, ii, 1118).—A reply to McCaughey (this vol., ii, 666). It is shown that when fæces are suspended in water and distilled with phosphoric acid (D 1·12) under reduced pressure, the greater portion of the volatile acids is removed within two hours. J. J. S.

The Titration of Potassium Cyanide in Presence of Potassium Ferrocyanide. W. D. Treadwell (*Zeitsch. anorg. Chem.*, 1911, **71**, 219—225).—Liebig's method of titrating cyanides in presence of chlorides and thiocyanates fails in presence of ferrocyanides, owing to the solvent action of these salts on silver cyanide, causing the quantity of silver used to be too high. The addition of potassium iodide has been recommended, and is now shown to be satisfactory. The silver solution must be added slowly at the end, as otherwise the precipitate is coarse, and does not redissolve readily. About 0·1 gram of potassium iodide is used in each titration. The results are then quite unchanged by the presence of ferrocyanide.

Electrolytic measurements have also been made, using a concentration cell, the two solutions of which are *N*/10-silver nitrate, and the solution undergoing titration. With pure potassium cyanide, the electrolytic end point coincides with the first appearance of a precipitate. At this point the *E.M.F.* of the cell is 0·500—0·520 volt. Ammonia raises the *E.M.F.* Thiosulphate has a greater disturbing influence than ammonia, but its effect may be greatly lessened by the addition of a larger quantity of potassium iodide as an indicator. Potassium ferrocyanide raises the *E.M.F.*, but not to such an extent that potassium iodide fails to produce a precipitate. C. H. D.

Separation and Estimation of Ammonia and of Pyridine. Marcel Delépine and René Sornet (*Bull. Soc. chim.*, 1911, [iv], **9**, 706—710.)—The authors employ Gerresheim's method (compare Abstr., 1879, 438; see also Buisson, Abstr., 1907, ii, 306) for precipitating the ammonia from solution in hydrochloric acid by means of mercuric chloride in the presence of sodium carbonate and sodium hydroxide. The pyridine is set free in the filtrate, distilled off, and weighed either as the aurichloride or platinichloride. The ammonia is subsequently liberated from its precipitate by sodium thiosulphate, distilled off, collected in dilute hydrochloric acid, and finally weighed as ammonium chloride. W. G.

Estimation of Nicotine. Gabriel Bertrand and Maurice Javillier (*Ann. Chim. anal.*, 1911, **16**, 251—256).—Twelve grams of the powdered sample of tobacco are boiled in a reflux apparatus with 300 c.c. of 0·3% hydrochloric acid for thirty minutes; when cold, 250 c.c. of the clear liquid or filtrate are taken for analysis. When dealing with *bona fide* tobacco extracts, 5 grams of the sample are diluted to 100 c.c., and 1 c.c. of 10% hydrochloric acid is added.

The solution is now precipitated by adding an excess of 10—20% solution of silicotungstic acid, and after twenty-four hours the precipitate is collected and washed with water acidified with hydrochloric acid; this operation may be accelerated by centrifugal action. The precipitate, which contains all the nicotine present, is then distilled with excess of magnesium oxide; the volatilisation of the alkaloid is much assisted by passing a current of steam, care being taken not to let the contents of the flask get diluted by condensing steam. The distillate is then titrated with standard sulphuric acid with alizarinsulphonic acid as indicator.

Should the tobacco extracts contain pyridine bases, the results will be vitiated. In this case the titrated liquid is mixed with 1—2% of ammonium chloride, and, after acidifying with hydrochloric acid, reprecipitated with silicotungstic acid. The precipitate after being washed is decomposed by dilute sodium hydroxide, and the nicotine, etc., is removed from the solution by shaking thrice in succession with chloroform; the final volume of the chloroform should be 5 or 10 c.c. This solution is then examined polarimetrically in a 10 or 20 cm. tube. The specific rotatory power of nicotine in a 1 to 2% chloroform solution at 20° is 161·35°. Pyridine bases are optically quite inactive.

If, instead of using sodium hydroxide, the precipitate is treated with ammonia, then, by way of a check, the resulting liquid may, after extraction with chloroform, be evaporated to dryness, and the ignited residue weighed; the weight × 0·1139 = nicotine. When dealing with unadulterated juices, the volumetric, polarimetric, and ignition results should be practically the same. L. DE K.

The Technique of the Phosphotungstic Acid Precipitation.

ELKAN WECHSLER (*Zeitsch. physiol. Chem.*, 1911, **73**, 138—143).—The solubilities of the phosphotungstates derived from the following bases have been determined. The numbers give the % of substance dissolved by a mixture of four volumes of acetone and three of water: Deuteroalbumose, 2·94; heteroalbumose, 2·24; silk-peptone, readily soluble; *d*-arginine, 120—130; *dl*-arginine, 120—130, *l*-histidine, 160; *d*-lysine, 140; guanidine, 22·8; creatinine, 13·34; guanine, 7·21; adenine, 10·50. Determinations were not possible with methylguanidine or phenylalanine. In most cases the mixtures were shaken for an hour before the solubility was determined. The solubility of protalbumose is 0·67 when the precipitation takes place from aqueous solution in the absence of acid, but 6·76 when precipitated in the presence of acid.

Histidine phosphotungstate has the composition

$$3C_6H_9O_2N_3,2H_3PO_4,24WO_3.$$

J. J. S. 2

General and Physical Chemistry.

Anomalous Molecular Refraction in the Series of Substituted Glyoximes. LEO TSCHUGAEFF and P. KOCH (*Compt. rend.*, 1911, **153**, 259—261).—The molecular refraction of substituted β- and γ-glyoximes is normal, but is abnormally high in the case of those compounds in which the oximino-groups are in the α-position relatively to one another. The molecular exaltation is practically constant in the aliphatic series, about 1·3 for the *D*-line, but considerably higher in the aromatic compounds, pyridine solutions of the two benzildioximes showing an exaltation of 3·45. The results of measurements for eight oximes are recorded. W. O. W.

Rotatory Dichroism of a Definite Organic Compound (*l*-Bornyl Diphenyldithiourethane). G. BRUHAT (*Compt. rend.*, 1911, **153**, 248—250. Compare Tschugaeff, Abstr., 1910, ii, 812).—The substance occurs in red crystals showing dichroism and anomalous dispersion in toluene solution. When in the superfused condition, it forms a green liquid showing anomalous rotatory dispersion and measurable circular dichroism. The results of polarimetric measurements are given, and it is shown that the dispersion and dichroism curves are similar, those for the toluene solution being slightly nearer the violet than those for the superfused substance. In both cases Natanson's rule is followed, the rotation being to the left on the red side of the absorption band and to the right on the side towards the violet. W. O. W.

The Ultra-violet Spark Spectrum of Air. FRANZ L. WAGNER (*Zeitsch. wiss. Photochem.*, 1911, **10**, 69—89).—Accurate wave-length measurements have been made of the lines in the spark spectrum of air by means of a Rowland concave grating of 6·5 metres radius of curvature and 16,000 lines to the inch. The method used consisted in photographing the spark spectra obtained in air between copper, silver, and aluminium electrodes. The lines common to the three spectra were then sorted out as representing the air lines. In carrying out this process, precautions were taken to ensure that the common lines were not due to the presence of traces of a common impurity in the three metals. In some cases, lines found on only two or even one of the photographic records have for special reasons been adopted as air lines.

The measurements, which extend from $\lambda = 4146$ to $\lambda = 2370$, are given in tabular form and compared with those of previous observers. In the case of each line, the table shows the relative intensity, the particular spark spectra in which it has been observed, and whether the line is due to nitrogen, oxygen, or argon.

As an appendix, the measured lines due to the metals in the three spark spectra are tabulated. These tables have been compared with the spectra of iron, antimony, arsenic, lead, carbon, calcium, magnesium, manganese, and silicon for the purpose of eliminating lines due to traces of possible impurities. H. M. D.

Secondary Spectrum of Hydrogen. C. PORLEZZA and G. NORZI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 819—828).—The authors find that the intensities of the lines in the secondary spectrum of hydrogen are as stated by Hasselberg (compare Dufour, Abstr., 1907, ii, 1). They record in tables the wave-lengths of lines not seen by Watson (Abstr., 1909, ii, 453), and of some lines not mentioned by previous observers, and they have confirmed the existence of certain lines seen only by Watson (*loc. cit.*). R. V. S.

The Ultra-red Absorption Spectrum of Carbon Dioxide in its Dependence on Pressure and Partial Pressure. G. HERTZ (*Ber. deut. physikal. Ges.*, 1911, **13**, 617—644. Compare von Bahr, Abstr., 1909, ii, 630; 1910, ii, 914).—In reference to Arrhenius's theory that the earth's climate is essentially determined by the absorption of the earth's heat rays by the carbon dioxide and water vapour in the surrounding atmosphere, the author has investigated the absorption of ultra-red rays of wave-length $\lambda = 14{\cdot}7\mu$ by carbon dioxide under different conditions.

As found by von Bahr for rays of shorter wave-length, the absorption is not solely determined by the product of the partial pressure and the thickness of the absorbing layer, but is influenced to a large extent by the magnitude of the total pressure. The absorption also differs appreciably according to whether a given value of the total pressure is reached by compressing the pure gas or by mixing it with another gas, such as air or hydrogen. The observations lead to the conclusion that the temperature changes on the earth's surface cannot be attributed to heat ray absorption by the carbon dioxide in the atmosphere.

Absorption measurements were also made with rays in the neighbourhood of $4{\cdot}3\mu$ and $2{\cdot}7\mu$. The relationships exhibited in the absorption of these shorter waves appear to be very similar to those found for $\lambda = 14{\cdot}7\mu$. The absorption band at $\lambda = 2{\cdot}7\mu$ possesses two maxima, of wave-length $2{\cdot}67\mu$ and $2{\cdot}75\mu$ respectively.
H. M. D.

Anode and Cathode Spectra of Various Gases and Vapours. G. STEAD (*Proc. Roy. Soc.*, 1911, *A*, **85**, 393—401).—A comparison of the two kinds of spectra was effected by means of a discharge tube divided into two halves by an aluminium plate, one side of which formed an anode and the other a cathode. Observations were made with hydrogen, hydrogen chloride, chloroform, carbon tetrachloride, silicon tetrachloride, stannic chloride, benzene, chlorobenzene, carbon disulphide, hydrogen sulphide, sulphur dioxide, hydrogen bromide, hydrogen iodide, ethyl bromide, methyl iodide, cyanogen, and hydrogen cyanide. The general conclusion drawn by the author is that the spectra of electronegative elements tend to appear at the anode, whilst those of electropositive elements show a preference for the cathode. The difference in the potential gradient and the temperature is supposed to be in some measure responsible for the distribution of the spectra.

In the case of an elementary gas these are probably the chief determining factors, and in the case of hydrogen, which shows the secondary spectrum at the anode and the "four line" spectrum at the cathode, it would appear that a low potential gradient is favourable to the appearance of the secondary spectrum. H. M. D.

Measurements in the Silver Spectrum. FRANZ JOSEPH KASPER (*Zeitsch. wiss. Photochem.*, 1911, **10**, 53—62).—Wave-length measurements of the lines in the arc and spark spectra of silver have been made. The arc spectrum measurements are compared with the data of Kayser and Runge and of Exner and Haschek. It has been found that an arc spectrum can be obtained by the employment of silver rods as arc electrodes if the potential and current are suitably adjusted and arrangements are made for the adequate supply of oxygen to the neighbourhood of the electrodes. With an efficient air draught the arc can be maintained continuously for periods of twenty to twenty-five minutes. H. M. D.

Photographic-photometric Absorption Measurements oı Silver Iodide in the Ultra-violet Spectrum. CURT SCHELL (*Ann. Physik*, 1911, [iv], **35**, 695—726).—A photographic method of measuring the intensity of ultra-violet light is described, and this is applied to the determination of the absorption of ultra-violet light by silver iodide. According to this method, the blackening produced by the light of unknown intensity during a given time is compared photometrically with the effects produced by two beams of known intensity, the blackening produced by one of which is greater and by the other less than that produced by the ultra-violet light of unknown intensity. By this means, measurements of the absorption-coefficient of silver iodide have been made for wave-lengths extending from $\lambda = 215\mu\mu$ to $\lambda = 450\mu\mu$. Chemically prepared silver films, after conversion into the iodide, exhibit the same absorption capacity as those obtained by cathodic pulverisation.

Certain irregularities which are exhibited by the developed photographic plates have been traced to differences in concentration of the developing solution, and it has been found that these can be avoided by previous washing of the plates in water and the employment of slow acting developers. H. M. D.

The Band Spectrum of Lead. HERMANN LAMPRECHT (*Zeitsch. wiss. Photochem.*, 1911, **10**, 16—29, 33—52).—Detailed wave-length measurements of the band spectrum of lead have been made, the source of illumination employed being a coal-gas and oxygen blow-pipe flame into which lead chloride was introduced according to Hartley's method. The same spectrum is obtained when the oxide, sulphate, and carbonate are introduced into the flame, but much longer exposures are required than when the chloride is used. The wave-length measurements, expressed in terms of the normal iron lines, are compared with those of Hartley and of Hagenbach and Konen.

By the use of an optical system of greater dispersive power, the constitution of some of the strongest bands has been investigated. The line measurements in four series are in good agreement with the requirements of Deslandres' law, but in other series considerable deviations are found. H. M. D.

The Spectrum of Glucinum and its Bands in Different Luminous Sources.

P. É. LECOQ DE BOISBAUDRAN and ANTOINE DE GRAMONT (*Compt. rend*, 1911, **153**, 318—321).—Employing the apparatus previously described (*Ann. Chim. phys.*, 1909, [viii], **17**) a new faint band in the indigo has been observed in addition to the two already known in the blue and green. This shows a maximum intensity at λ 4709. The wave-lengths and relative intensities of the components of the three bands are recorded. The intensities are considerably increased by employing a spark with self induction up to 0·122 Henry units, when the ultra-violet lines also become perceptible. Strong self induction does not diminish the very sensitive doublet λ 3131·2, 3130·5; this also appears in the arc spectrum.

In general there is a striking resemblance between the band spectra of aluminium and glucinum. W. O. W.

Influence of Temperature and Magnetisation on Selective Absorption and Fluorescence Spectra. II.

HENRI E. J. G. DU BOIS and G. J. ELIAS (*Ann. Physik,* 1911, [iv], **35**, 617—678. Compare Abstr., 1908, ii, 337, 547).—In continuation of previous measurements, further data relating to the influence of temperature and a magnetic field on the absorption bands of certain substances are recorded. In the case of erbium nitrate and to a less extent ruby, the influence of these factors has been examined in great detail.

H. M. D.

Fluorescence of the Vapours of the Alkali Metals.

LOUIS DUNOYER (*Compt. rend.*, 1911, **153**, 333—336).—The fluorescence of cæsium vapour, which from analogy to that of the other alkali metals should be very intense, is found to be too faint at 350° to admit of spectroscopic examination. The green fluorescence of sodium vapour observed by Wood (Abstr., 1908, ii, 150, 546) is due to impurities, for if the metal is pure, the fluorescence is bright yellow and appears at a lower temperature, namely, at about 210°. The purer the metal the more the resonance spectrum is favoured at the expense of that of fluorescence. Potassium vapour commences to be fluorescent at about 215° and is brilliant at 320°.

The fluorescence of rubidium produced by white light is purple-red, and is visible at 180°, but becomes orange at 400°. It appears to be due to two bands, one corresponding with an absorption band and the other appearing at the higher temperature having no obvious relation to absorption.

The polarisation of fluorescence has been studied at different temperatures. The curves connecting partial polarisation and temperature are similar whether the incident light is polarised or not. Rubidium vapour shows maximum fluorescence at 370°, potassium and sodium at lower temperatures. The cause of depolarisation appears to depend on a mutual action between fluorescing molecules, since polarisation is strongest when the vapour is not saturated, that is, not in contact with an excess of fused metal. W. O. W.

Fluorescence Absorption and Lambert's Absorption Law in the Case of Fluorescein. F. KAEMPF (*Physikal. Zeitsch.*, 1911, **12**, 761—763).—Experiments have been made to determine whether the fluorescence of fluorescein solutions is accompanied by a special absorption effect. The results obtained with two different forms of apparatus indicate that within the limits of experimental error (5%) there is no special fluorescence absorption, and that the absorption, for different intensities of the incident light, takes place in accordance with Lambert's law. H. M. D.

Systems of Series in the Spectra of Zinc, Cadmium, and Mercury. II. FRIEDRICH PASCHEN (*Ann. Physik*, 1911, [iv], **35**, 860—880. Compare Abstr., 1910, ii, 3).—Quartz lamps worked with a large current were used in the production of the spectra of the metals, and the influence of a magnetic field on the various lines was investigated in order to throw light on the constitution of the spectra. For zinc and cadmium the data indicate definitely the existence of three systems of series—simple lines, doublets, and triplets. In the case of both metals the triplets appear to be largely combined with the simple lines, but the extent of the combination is much greater for cadmium than for zinc. Mercury also appears to exhibit the same three systems of series, and in this case the combination of triplets with simple lines is extremely large. H. M. D.

Ultra-violet Radiation from Quartz-mercury Lamps. VICTOR HENRI (*Compt. rend.*, 1911, **153**, 265—267).—The variation in the intensity of the ultra-violet radiation from a quartz-mercury lamp with the strength of the current has been measured by chemical methods. The reactions employed for the purpose include decomposition of dry hydrogen chloride by the rays, decomposition of hydrogen peroxide or of potassium iodide in solution, the appearance of hydrogen ions in a solution of sucrose, the blackening of silver citrate paper, and the sterilising action of the rays on *B. coli.* In the last two cases the radiation increased very rapidly with the current, but the intensity of the rays affecting potassium iodide increased more slowly. A spectrophotometric comparison showed that the extreme ultra-violet radiation increased more rapidly than the total visible radiation from the lamp. W. O. W.

Influence of Different Physical Conditions on the Ultra-violet Radiations from Quartz-mercury Lamps. VICTOR HENRI (*Compt. rend.*, 1911, **153**, 426—429. Compare preceding abstract).—Employing the silver citrate method mentioned in a previous paper, the intensity of the ultra-violet radiation from a quartz-mercury lamp was measured under different conditions. The radiation is more intense as the temperature of the lamp tube is higher. When burning in air, the radiation is about fourteen times as intense as when cooled in water. The length of service has but little effect in diminishing the activity of the radiation from a well evacuated lamp.

W. O. W.

The Grouping of Photochemical Reactions. FRITZ WEIGERT (*Zeitsch. wiss. Photochem.*, 1911, 10, 1—15).—The characteristics of photochemical reactions are discussed from the point of view of the energy changes which are involved, and a scheme is proposed for the systematic grouping of the different types of change. H. M. D.

Photochemical Studies. II. The Classification of Light Reactions. JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1911, 77, 472—481. Compare this vol., ii, 452).—A classification of chemical changes influenced by light is represented in tabular form and discussed in detail. The reactions in question are divided into irreversible and reversible changes. There are three main types of irreversible change: (1) May be subdivided into (1*a*) simple photocatalytic actions, changes which only take place in light and show no after-effect, and (1*b*) which differs from (1*a*) inasmuch as the change proceeds in the absence of light. (2) Photochemical catalysis, where the reaction does not proceed either in the presence or absence of light, but when a catalyst is added in small concentration, the change takes place in presence of light, but ceases when the light is withdrawn. (3) Photochemical after-effect differing from (2) inasmuch as the reaction, once started by a catalyst in light, proceeds with the same velocity in the dark. There are two main types of reversible change: (1) in the light a new equilibrium is established; (2) light displaces the equilibrium established in the dark. For details and examples of the different types of change the original paper must be consulted. G. S.

The Transformation of Energy in Photochemical Reactions in Gases. EMIL WARBURG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 746—754).—The proportion of absorbed radiant energy which is converted into chemical energy in the decomposition of ammonia under the influence of ultra-violet light has been determined. If a is the thermal and β the chemical absorption coefficient, the photochemical yield s is given by the ratio $s=\beta/a+\beta$. As the final result of a large number of experiments, it is found that the photochemical yield for the action of rays of wave-length $\lambda=0{\cdot}203\mu$ to $0{\cdot}214\mu$ on ammonia at a pressure of 80—90 cms. of mercury is about 2%. There is some evidence of a slight decrease in the yield as the wave-length of the absorbed light diminishes. Since, however, the total absorption coefficient increases considerably with diminishing wave-length, it follows that the chemical absorption coefficient β must also increase with diminishing wave-length within the range of rays investigated.

It is pointed out that the observed small photochemical yield does not really measure the amount of chemical work performed by the absorbed rays, for the primary photochemical change, $NH_3=N+3H$, is followed by the strongly exothermic reaction, $2N+6H=N_2+3H_2$.

The secondary reaction is quite independent of the light action, but its occurrence obviously results in a diminution of the measured photochemical yield. H. M. D.

Measurements of Photochemical Action in Ultra-violet Light by means of Sensitive Films. Carl Schall (*Zeitsch. wiss. Photochem.*, 1911, **10**, 89—116. Compare Abstr., 1908, ii, 139; 1909, ii, 359; 1910, ii, 249).—The nature of the photochemical change which gives rise to the coloration of papers impregnated with solutions of diamines under the influence of ultra-violet light is discussed. Measurements have been made which show that the colour change of *p*-phenylenediamine nitrate and of tetrabromoethane, when subjected for a given period to the action of ultra-violet rays, is proportional to the light intensity. A spectroscopic comparison of the active rays in the use of these and other photo-sensitive substances has also been carried out. H. M. D.

Photolysis of Alcohols, Acid Anhydrides, Ethers, and Esters by Ultra-violet Light. Daniel Berthelot and Henry Gaudechon (*Compt. rend.*, 1911, **153**, 383—386. Compare Abstr., 1910, ii, 814; this vol., ii, 86).—A continuation of the previous communication, giving the relative volumes of the gaseous products from a number of substances, principally esters, exposed to light from a quartz-mercury lamp. The gases from alcohol contain 70% of hydrogen by volume; acetaldehyde was detected amongst the products, and formaldehyde recognised in methyl alcohol exposed to the light. Ether gives 14·5 volumes of carbon monoxide and 85·5 volumes of a mixture of hydrogen, methane, and ethane, the latter predominating. Acetic anhydride gives the same gases and also carbon dioxide. Carbon monoxide is the chief product from aliphatic esters. Benzyl formate gives carbon monoxide and dioxide, but ethyl benzoate and salicylate remain unaltered after eight hours' exposure under diminished pressure. W. O. W.

Oxidising Action of Dilute Nitric Acid in Sunlight. Alfred Benrath (*J. pr. Chem.*, 1911, [ii], **84**, 324—328).—Solutions of acetic, aminoacetic, propionic, butyric, *iso*butyric, malonic, succinic, and pyrotartaric acids in 2*N*-nitric acid, containing ferric nitrate, acquire a cherry-red colour on exposure to light and continuously evolve a gas, consisting mainly of nitrous oxide together with some carbon dioxide, All the acids yield formaldehyde, which is accompanied, in the case of propionic acid and probably also succinic acid, by acetaldehyde, the latter being produced by the loss of carbon dioxide from the intermediately formed pyruvic acid. *iso*Butyric acid yields acetone, which is furthur oxidised to formaldehyde and acetic acid. With butyric and pyrotartaric acids, the formaldehyde is accompanied by other aldehydes, which, however, could not be isolated. All the acids investigated, with the exception of acetic acid, yield hydrogen cyanide in large quantities.

According to Hantzsch, the formation of hydrogen cyanide by the action of nitric acid on organic substances is due to the intermediate formation and decomposition of formaldoxime, according to the following scheme:

$$\mathrm{R{\cdot}COMe + HNO_2 \longrightarrow R{\cdot}CO_2H + CH_2{:}N{\cdot}OH \longrightarrow H_2O + HCN.}$$

But since the oxime may also undergo decomposition by hydrolysis into hydroxylamine and formaldehyde, the latter substance may be expected as a product of all photochemical oxidations, resulting in the formation of hydrogen cyanide. This view is supported, not only by the experiments described above, but also by the simultaneous formation of hydrogen cyanide and formaldehyde by the action of nitric acid on ketones and ketonic acids containing the group R·COMe. Acetone, methyl alkyl ketones, lævulic and pyruvic acids, together with all substances (such as *iso*propyl alcohol, citric acid, and lactic acid) which may be oxidised to acetone, lævulic acid, or pyruvic acid, yield both hydrogen cyanide and formaldehyde when oxidised by nitric acid.

The red colour observed during oxidations in the presence of ferric nitrate is considered by the author to be due to the formation of hydroxamic acids (compare Baudisch, this vol., ii, 523).

These results confirm the conclusion of Baudisch that the assimilation of nitrogen in plants is a photochemical process. F. B.

Effect of Light on Insulation by Sulphur. F. W. Bates (*Le Radium*, 1911, 8, 312—313).—The mean leak of a leaf insulated by sulphur was found to be greater during the day than during the night. Strong sunlight much increased the leak, and this increase was reduced by interposing blue or red glass screens. In total darkness the leak during the day was reduced to practically the same value as at night. The increase is not due to increased ionisation of the air, nor to a photo-electric effect on the sulphur similar to that of ultraviolet light on zinc. The leak is the same whether the charge is positive or negative. By surrounding the sulphur, exposed to light, with a guard-ring, the leaf when charged oppositely to the guard-ring lost its charge and took an opposite charge. When the charges were similar in sign, they tended to become the same in magnitude in the light. In the dark the leaf lost its charge by ionisation of the air only, independently of the sign and amount of the charge on the guard-ring. The conductivity of the sulphur is thus increased by light. Ebonite shows a slight effect of the same kind, but amber is not influenced by light. F. S.

The Number of Electrons Concerned in Metallic Conduction. J. W. Nicholson (*Phil. Mag.*, 1911, [vi], 21, 245—266).—The view that the velocities of the effective electrons are distributed in accordance with Maxwell's law is shown to be in satisfactory agreement with Drude's experimental determinations of the optical constants of the metals. This assumption leads to values for the number of effective electrons in the atom, which are all very close to integers or half-integers, except in the case of cadmium. For nickel, cobalt, silver, copper, gold, magnesium, platinum, lead, tin, zinc, and aluminium the differences are all within the experimental limit of accuracy. The integers vary from two (nickel) to six (aluminium).

H. M. D.

Ionic Mobility in Gases. II. Max Reinganum (*Physikal. Zeitsch.*, 1911, **12**, 666—671. Compare this vol., ii, 788).—Further arguments are advanced in support of the author's view that the observed high velocity, with which heavy ions move through gases of low density under the influence of an electric field, is in accordance with the requirements of theory. The calculated velocities of heavy ions are approximately equal to the velocity of the ions of the surrounding gas. H. M. D.

Certain Ionisation Effects Observed in Gases in Presence of Non-radioactive Substances. Activity and Luminescence of Quinine Sulphate. Maurice de Broglie and L. Brizard (*Le Radium*, 1911, **8**, 273—279. Compare this vol., ii, 174).—Experiments have been made to determine whether the scintillation exhibited by quinine and cinchonine sulphates when exposed to the air after being heated at 120° is connected with the ionisation of the surrounding gas.

It is found that those factors which increase the intensity or prolong the period of luminescence have a similar influence on the ionisation of the surrounding gas. The suggestion is made that both phenomena are connected with the triboluminescence of the crystals, and experiments are described in support of this view. In particular, the triboluminescent effect which is observed when crystals of either salt are rapidly cooled in liquid air is found to be accompanied by ionisation.

From observations of the action of luminescent quinine sulphate on photographic plates under different conditions, the authors draw the conclusion that the ionisation cannot be due to the emission of ultra-violet rays of the type which have been shown to have ionising properties. The photographic effects appear to be produced equally well through thin plates of glass and fluorite as through a thin layer of air. On the other hand, fluorite appears to prevent the ionisation of air on the further side of the plate. In explanation of the various facts, it is suggested that the conductivity of the gaseous medium in the vicinity of the luminescent crystals is due to minute electrical discharges which accompany the rupture of the crystals during the process of hydration (or dehydration). Those factors which would be expected to favour this discharge phenomenon are found by experiment to result in increased luminescence and increased ionisation.

H. M. D.

The Ionisation of Liquid Hydrocarbons. Tcheslas Bialobjeski (*Le Radium*, 1911, **8**, 293—299. Compare Jaffé, Abstr., 1909, ii, 208; 1910, ii, 481).—The conducting properties of various fractions of American petroleum, when subjected to the influence of the β- and γ-rays of radium, have been investigated. The boiling points of the separate fractions, which were subjected to careful purification, were 47—52°, 52—58°, 58—70°, 75—82°, 82—90°, 90—105°, 150—200°, and 200—250°. The apparatus employed consisted of a condenser, the distance between the plates of which could be varied and accurately adjusted. Penetrating rays from a radium preparation entered the liquid in which the plates were immersed through the upper plate, which was in connexion with a Moulin electrometer, whilst the lower plate was connected with a battery, the potential of which could be varied from 4 to 864 volts.

Data are recorded which show the variation of the current with the applied potential difference for each hydrocarbon fraction with the condenser plates at a distance of 2 and 8 mm. For three fractions, experiments of the same kind were also made with a less active radium preparation. In a third series of measurements the three fractions 52—58°, 82—90°, and 200—250°, as well as vaselin, were investigated with the condenser plates at a distance of 0·5, 1, 2, and 4 mm.

From these data it appears that for small potential differences, the current diminishes rapidly as the boiling point of the hydrocarbon fraction rises, but that the current differences are relatively very much smaller when a strong electrical field is applied. At the highest potential differences the current approximates to a condition of saturation when the plates are close together, whereas at lower potentials the observed currents are not very different from those required by Ohm's law. With a less active radium preparation, evidence of saturation is obtained at smaller potential differences.

From the data of the last-mentioned series the author calculates the sum of the mobilities of the ions in cms. per second for a potential difference of one volt per cm.; these are respectively: fraction 52—58°, $11·7 \times 10^{-4}$; 82—90°, $3·7 \times 10^{-4}$; 200—250°, $1·5 \times 10^{-4}$; vaselin, $0·94 \times 10^{-7}$. From these numbers it is evident that the mobility decreases very quickly as the boiling point rises, the decrease being more rapid than the increase in the viscosity.

As observed by Jaffé in the case of hexane, the current through the various hydrocarbon fractions exhibits a certain amount of unipolarity, and this is attributed to the presence of a certain proportion of ions of much smaller mobility than those which are mainly responsible for the conduction of the current. H. M. D.

A New Radiant Emission from the Spark. Walter Steubing (*Physikal. Zeitsch.*, 1911, **12**, 626—630).—The rays emitted by a condenser spark passing between aluminium electrodes, which have been been described by Wood (Abstr., 1910, ii, 915) as a new form of radiant emission, have been examined by the author, whose apparatus was closely similar to that employed by Wood. The experiments described indicate that the so-called new emission consists of rays from the spark discharge which have been scattered by the particles of metal in the vapour given off from the electrodes. These rays are independent of the nature of the gas in which the spark discharge takes place, and the emission is no longer observed if the spreading of the metal vapour is prevented by a rapid current of gas. If under these conditions a hermetically-sealed tube containing vapour of the metal is brought into the neighbourhood of the discharge, the emission effect is again observed. Resolution of the emission shows the absence of any bands, and the spectrum appears to be the same as that obtained directly from the spark discharge. H. M. D.

Transformation of the Energy of Homogeneous Röntgen Radiation into Energy of Corpuscular Radiation. CHARLES A. SADLER (*Phil. Mag.*, 1911, [vi], **21**, 447—458).—The results obtained in a previous investigation (Abstr., 1910, ii, 251) have been further analysed. The author now arrives at the conclusion, that not only is there a very close connexion between the emission of corpuscular radiation and the production of homogeneous Röntgen radiation, but that there is strong evidence that, whenever the characteristic secondary radiation is excited, there is always produced a strictly proportional amount of corpuscular radiation. H. M. D.

The Spectra of the Fluorescent Röntgen Radiations. CHARLES G. BARKLA (*Phil. Mag.*, 1911, [vi], **21**, 396—412. Compare Abstr., 1909, ii, 457; 1910, ii, 8).—A summary is given of the results which have been obtained in previous papers relative to the properties of the characteristic secondary or fluorescent rays which are emitted by metals under the influence of a primary *X*-ray beam. The fluorescent radiations which have been examined up to now fall into two distinct series, and it is probable that these include all fluorescent radiations which are actually emitted. Each element has its own characteristic fluorescent ray spectrum, which may be conveniently represented like an ordinary light spectrum, except that it is necessary to define the radiations by their absorption in some standard substance. The lines corresponding with the two series of rays move towards the penetrating end of the spectrum as the atomic weight of the emitting element increases. H. M. D.

Dissymmetry of Positive and Negative Ions Relatively to the Condensation of Water Vapour. E. BESSON (*Compt. rend.*, 1911, **153**, 250—253).—Langevin's modification of C. T. R. Wilson's cloud chamber has been adapted to enable instantaneous microphotographs of the clouds produced to be obtained. An image of the positive crater of a powerful arc is formed in the chamber, and the cloud is viewed with a low-power microscope, the axis of which makes an angle of 40° with the pencil of illumination. Exposures of 0·02 second are employed, which are not sufficiently short to depict the droplets quite motionless.

The formation of the cloud has been observed in all its details. Alternate photographs, using *X*-ray ionisation, with the positive and negative ions respectively predominating, showed always a much larger cloud when the negative ions were in excess. F. S.

The Mass of Gaseous Ions. WILLIAM DUANE (*Compt. rend.*, 1911, **153**, 336—339).—To obtain evidence on the question of the existence of positive electrons, the ratios of the mass m to the charge e of the ions formed in air by the α-rays of radium have been determined. The emanation from 0·3 gram of radium chloride was enclosed in a glass bulb of volume less than 0·5 mm.^{3}, with walls thin enough to allow the α-rays to escape. This was placed outside the mica window of an apparatus, which could be exhausted to a very low vacuum, containing two metallic plates 2 cm. apart, one connected to the electroscope and the other to the battery. This was placed in a magnetic field, so that ions formed between the plates, under the combined action of the electric and magnetic fields, would pursue cycloidal paths, and not reach the plates when these paths were sufficiently restricted. From the values of the electric and magnetic fields necessary to prevent the ions reaching the plates, the value of e/m could be calculated. The results were in accordance with the view that at low pressures the negative ions are entirely composed of electrons, and the positive ions of atoms or molecules of the gas.

No negative ions of molecular magnitude exist at low pressure, hence none are formed by loss of a positive electron from the molecule. The positive ions in air are all much larger than those in hydrogen, indicating that in air no positive ions of the order of magnitude of the hydrogen positive ion or less are formed. The conclusions are opposed to the hypothesis of the existence of positive electrons.

F. S.

The β-Rays of the Radium Family. J. Danysz (*Compt. rend.*, 1911, **153**, 339—341).—The emanation, from 0·12 gram of radium chloride condensed in thin-walled Thuringian glass tubes, 5 mm. long, 0·3 mm. diameter, and 0·04 mm. thickness of wall, was used as the source. Becquerel's disposition was employed, whereby the trajectories of the several bundles of rays, coiled into circles by a magnetic field, were registered on a photographic plate. The results are ascribed to the small amount of matter in the neighbourhood of the source, and to the suppression of secondary rays which fog the plate uniformly. A magnetic spectrum of seven separate beams of rays, sharply separated from one another, was obtained. The approximate values of the velocities in terms of that of light, deduced by the Lorentz equation from the radii of curvature, are as follows:

Beam	I.	II.	III.	IV.	V.	VI.	VII.
Velocity	0·98	0·95	0·86	0·81	0·75	0·69	0·63

Exact determinations, and experiments to determine how the beams are distributed among the various members of the family are in progress.

F. S.

Secondary β-Rays. W. A. Schaposchnikoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, *Phys. Part*, 187—195. Compare McClelland, Abstr., 1908, ii, 650; Bragg and Madsen, *ibid.*, 921; Allen, *Phys. Rev.*, 1909, **29**, 177; 1910, **30**, 276).—The author's experiments show that, under the conditions employed, the penetrating power of the secondary rays does not depend on the magnitude of the angle of incidence, provided that the sum of the angles of incidence (α) and reflexion (β) remains constant.

The mean values of the ratio J'/J for different angles of incidence, and under the condition $\alpha+\beta$ = constant, are approximately equal to that corresponding with equality of α and β, that is, with the condition of maximal secondary radiation.

With increase of the angle of incidence, $\alpha+\beta$ remaining constant, the penetrating power of the secondary rays increases, that is, they become harder.

The composition of the secondary radiation, while the sum of α and β is constant, does not change appreciably with change in the angle of incidence, and for the condition of maximum radiation, $\alpha=\beta$, it is the same as for non-equality of these two angles. T. H. P.

Some Chemical Effects of the Rays of Radium. S. C. LIND (*Le Radium*, 1911, 8, 289—292).—The action of the rays of the emanation of radium and of the β- and γ-rays of radium on mixtures of hydrogen and bromine, and on hydrogen bromide gas, is too slow to be studied quantitatively. No measurable decomposition was observed in a tube filled to two-thirds of an atmosphere with hydrogen bromide after thirty-seven days' exposure to the penetrating rays of 0·2 gram of radium chloride. Neither is any combination of hydrogen and bromine detectable under the same conditions. The emanation of radium in equilibrium with 1 mg. of radium produced slight combination of the mixture (2·6% after fourteen days), but no decomposition of the compound. The rate of combination of the mixture in the dark at 303° was not appreciably increased by the presence of radium emanation. Anhydrous liquid hydrogen bromide is decomposed to a slight extent in the dark in presence of the emanation, about 3·5% of the energy of radiation being utilised in the decomposition in one experiment. Aqueous solutions of hydrogen bromide and potassium iodide are decomposed by the emanation in absence of light and of oxygen. F. S.

The Influence of Acids and Salts on the Amount of Radium Emanation Liberated from a Solution of Radium. A. S. EVE and DOUGLAS MCINTOSH (*Trans. Roy. Soc. Canada*, 1910, [iii], 4, III, 67—68).—Various barium salts were found to contain from 2·84 to 0·11 ($\times 10^{-12}$) gram of radium per gram, which must be taken account of in the measurement of minute amounts of radium. Sulphuric acid, barium chloride and sulphuric acid, and barium sulphate, respectively added to a standard solution of radium, reduced the emanation liberated on boiling 5, 87 and 73%. The amount of radium used was $7{\cdot}8 \times 10^{-10}$ gram. F. S.

δ-Rays. NORMAN CAMPBELL (*Phil. Mag.*, 1911, [vi], 22, 276—302). —The velocity of the δ-rays produced in plates and films of metals by the impact of α-rays from polonium has been deduced from their behaviour in an electric field. The apparatus consisted of a metal plate connected with the electrometer placed opposite a slightly smaller hole in a metal box, the hole being covered with a thin metal foil capable of allowing α-rays to pass through. Behind the foil inside the box was a plate coated with polonium. The value of the ionisation current was measured when the box was charged to different potentials, the plate connected to the electrometer being maintained at earth potential by a compensating current, by means of a potentiometer and high resistance. Certain negative conclusions have been drawn. There appears to be no difference between the speeds of the incident and emergent δ-radiations. The speed of the δ-rays appears to be independent of the speed of the α-rays exciting them, and probably of the material from which they are emitted, although the possibility of reflexion makes the interpretation of the results difficult. This, if correct, is of the utmost importance for the theory of ionisation, for the act of ionisation in gas is presumably similar to the expulsion of δ-rays by solids. There is no evidence that the number of δ-rays depends on the nature of the material, about ten being emitted for each α-particle in the cases of the metals, copper, silver, gold, and aluminium, which were employed. Other conclusions are withdrawn in a subsequently-added note. In an appendix particulars are given of the high resistances employed. These are constructed of thermometer tube 13 cm. long, held in an earthed metal clamp, the electrodes being sealed into bulbs at the end, and are filled with a mixture of 1 part of alcohol to from 3 to 8 parts of xylene, dried by lime. They ranged from 4×10^{11} to 7×10^{9} ohms, and did not show any undesirable polarisation effects. F. S.

Concentration of the Radioactive Emanation of the Gases of Boracic Suffioni by means of Carbon at a Low Temperature. C. Porlezza and G. Norzi (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 932—934).—The authors find that the radioactive emanation in the gas from the suffioni of Larderello can be concentrated by passing the gas over charcoal cooled to $-77°$ with solid carbon dioxide and ether. Under these conditions, all the emanation is absorbed, but only a portion of the other gases present, so that on heating the charcoal the gas evolved is thirty-four times more radioactive than was the gas treated. The gas employed for this concentration was previously freed from the carbon dioxide and hydrogen sulphide which it contains in large amount (94%).

R. V. S.

The Solubility of the Emanation of Radium in Organic Liquids. Eva Ramstedt (*Le Radium*, 1911, **8**, 253—256).—The apparatus used consisted of a closed tube divided into two equal parts by a wide tap. One part was filled with the liquid under examination, and the other part with the emanation, usually two days' accumulation of 0·01 gram of radium chloride. Equilibrium was established

		α.		
Liquids.	18°.	0°.	−18°.	$d\alpha/\alpha.dt$.
Glycerol	0·21	—	—	—
Water	0·285	0·52	[0·39 at 9°]	0·031
Aniline	3·80	4·43	—	0·0130
Alcohol (abs.)	6·17	8·28	11·4	0·0163
Acetone	6·30	7·99	10·8	0·0153
Ethyl acetate	7·35	9·41	13·6	0·0174
Paraffin oil	9·2	12·6	—	—
Benzene	12·82	[16·34 at 3°]	—	—
Xylene	12·75	—	—	—
Toluene	13·24	18·4	27·0	0·0193
Chloroform	15·08	20·5	28·5	0·0182
Ether	15·08	20·9	29·1	0·0184
Hexane (66—70°)	16·56	23·4	35·2	0·0203
*cyclo*Hexane (80°)	18·04	—	—	—
Carbon disulphide	23·14	33·4	50·3	0·0210

by allowing the liquid to flow from one part of the tube to the other several times. The tap was closed and the tube left five hours, and the γ-radiation of the two parts successively measured in a suitable condenser. The table on p. 842 gives the result. a denotes the coefficient of solubility at the temperatures given, and $da/a.dt$ the proportionate increase of the coefficient by 1° lowering of temperature from zero. The results fully bear out those of other investigators, all organic liquids examined, except glycerol, absorbing more than water, carbon disulphide absorbing six times more than aniline and eighty times more than water. The volatile and very mobile liquids appear to absorb more than the non-volatile and viscous, but there are exceptions. F. S.

Action of the Radium Emanation on Thorium Salts.

HEINRICH HERSCHFINKEL (*Compt. rend.*, 1911, **153**, 255—257).—The experiments of Ramsay and Usher (Trans., 1909, 624; Abstr., 1909, ii, 850) have been repeated to see if the formation of carbon dioxide from thorium salts under the action of radium emanation was not due to organic impurities in the salt. The thorium nitrate employed was specially purified by Merck to avoid as far as possible these impurities. The emanation in equilibrium with 0·1 gram of radium acting on 125 grams of the thorium nitrate for twelve days produced 1 c.c. of carbon dioxide. The solution left without emanation for the same time, or the emanation acting on distilled water, gave only traces of carbon dioxide. Small quantities of potassium permanganate gave more carbon dioxide than the emanation. The impurity present is probably a trace of oxalic acid. The formation of carbon dioxide by the action of the emanation does not prove the transformation of the thorium atom into carbon. F. S.

Action of Niton (Radium Emanation) on Thorium Salts.

SIR WILLIAM RAMSAY (*Compt. rend.*, 1911, **153**, 373—374).—Herschfinkel's experiment (preceding abstract) only proves that his specimen of thorium contains compounds capable of yielding carbon dioxide by the action of permanganate. In the author's first experiments the thorium nitrate was not exposed to radium emanation, but yielded quantities of carbon dioxide proportional to the time of accumulation. To settle the question whether the carbon was derived from the transformation of the thorium, a specimen of thorium nitrate was prepared by heating to redness, and solution of the product in nitric acid. The solution was crystallised many times with precautions to exclude dust, and some c.c. of solution from well formed crystals of the salt were exposed to the radium emanation from 0·6 gram of radium bromide, purified by long contact with moist potassium hydroxide, which had not come into contact with grease or rubber. Carbon dioxide was always found in the gas. Nitrates of bismuth, mercury, and silver gave no trace of carbon dioxide.

F. S.

Molecular Weight of the Thorium Emanation.

MAY SYBIL LESLIE (*Compt. rend.*, 1911, **153**, 328—330).—Using Debierne's apparatus (Abstr., 1910, ii, 675) with some modifications, the molecular weight of the thorium emanation has been determined by the method of effusion through a small hole in a plate. A preparation of radiothorium is the source of emanation which diffuses into a vessel containing a cylinder, the activity imparted to which furnishes a measure of the emanation present. The activity is measured with the vessel closed and open through fine holes in a platinum plate to a large, exhausted receptacle, the time of exposure varying from one to four days. The experiments are done at a pressure of a few hundredths of a millimetre of mercury. If q and q' are the activities with the vessel open and closed, μ and λ the coefficients respectively of effusion and decay of the emanation, $q/q' = \lambda + \mu/\lambda$. The coefficient of effusion of oxygen is determined in the same apparatus, and the molecular weight of the emanation obtained from the inverse ratio of the squares of the coefficients of effusion. According as 54 and 53·3 seconds are accepted for the half-period of the thorium emanation, the molecular weight in the one day's experiments is 210 or 203, and in the two days' experiments either 201 or 194. An error of 1% in the activity measurements makes a 5% error in the calculated molecular weight, but the experiments show clearly that the molecular weight is in the neighbourhood of 200. F. S.

The Disintegration Products of Uranium. GEORGE N. ANTONOFF (*Phil. Mag.*, 1911, [vi], 22, 419—432).—Uranium nitrate, specially purified from other radio-elements by adding lanthanum or thorium and precipitating these with oxalic acid, and in other ways, was employed. The uranium-*X* was separated in two ways, the first by precipitating barium sulphate in the solution, and the second by adding an iron salt and precipitating it by boiling. The first product showed a normal decay curve, both when measured bare and when covered with sufficient aluminium foil to absorb the soft β-rays. The second product showed a normal decay curve under the latter conditions, but a larger proportion of soft β-rays were initially present which decayed with a half-period of 1·5 days. This is attributed to a new product, termed uranium-*Y*, which could only be separated in very small amount from the uranium, and which gave a very feeble α-radiation as well as the soft β-radiation. The latter has a coefficient of absorption, $\mu(\text{cm.})^{-1}$, about 300, and causes about 25% of the total ionisation. The latter was only about 1/60,000th of that given by the uranium from which it was separated. It cannot be the second α-ray product of uranium on account of the large proportion of β-radiation. Thin layers of uranium oxide do not shown any β-radiation other than that of uranium-*X*. The β-ray recovery curve of uranium shows no evidence of the regeneration of uranium-*Y*. In absence of any definite evidence as to the connexion of uranium-*Y* with uranium, it is suggested that it may be a branch product of uranium. In chemical nature the product resembles uranium-*X*, and has not been separated from it. F. S.

Attempts to Prepare Metallic Radium. HEINRICH HERSCHFINKEL (*Le Radium*, 1911, 8, 299—301).—The attempt to prepare metallic radium by decomposing the azoimide by heating in a vacuum (Ebler, Abstr., 1910, ii, 1024) is not in agreement with the facts found by Mme. Curie and Debierne that radium is not volatile at 100° in a vacuum, and very readily forms nitride in presence of nitrogen. Repetitions of the experiment gave no metallic sublimate, but a dark product and nitrogen. The product probably contains a very little alkaline-earth metal, very impure, and contains nitride. Pure barium azoimide, on rapid heating to explosion in a vacuum, gives only 86% of its nitrogen as gas. On rapid heating to 600° in a vacuum, it melts and gives yellow drops, which have an odour of acetylene, and become white in the air. Curtius's method of preparing the alkaline-earth metals thus gives very impure products. F. S.

The Properties of Technically Prepared Mesothorium and its Evaluation. Otto Hahn (*Chem. Zeit.*, 1911, **35**, 845—846).—An account is given of the well-known chemical and radio-active properties of mesothorium (compare this vol., ii, 8; Trans., 1911, **99**, 72). The monazite sand from which mesothorium is technically prepared contains 0·3% U and 4—5% ThO_2, and the activity is due, 75% to mesothorium and 25% to radium. In this mesothorium the maximum activity is reached in 3·2 years, whilst after ten years the activity is still somewhat greater than when prepared, and after twenty years is about half as great. When purified from inactive material the activity is four times greater than that of pure radium compounds, the weight of mesothorium present being estimated at 1%, the remainder being radium. The strength of the activity is compared with that of pure radium compounds by means of an air-tight electroscope of brass, of wall thickness 1—2 mm., lead plates being interposed if necessary, of thickness not greater than 0·5 cm. Under these conditions the γ-rays are compared, the somewhat greater absorbability of the γ-rays of mesothorium not affecting the measurements more than a few per cent. F. S.

The Ratio between Uranium and Radium in the Active Minerals. Mlle. Ellen Gleditsch (*Le Radium*, 1911, **8**, 256—273. Compare Abstr., 1909, ii, 533, 714).—A full description is given of the methods employed in determining radium and uranium, and the subject is discussed from the point of view of all the publications made since the first results of the author were published. Results are given for twenty-one specimens of minerals, including chalcolite, carnotite, gummite, autunite, pitchblende, samarskite, broeggerite, uranothorite, fergusonite, and thorianite. The proportion of radium to uranium varies from 1·82 to $3·74 \times 10^{-7}$. The minerals with highest ratio come from Cornwall (one chalcolite and one pitchblende), next comes a Ceylon thorianite (the only one included), next six minerals from Norway. The variations in the ratio are considered to be established, and are ascribed possibly to the existence of intermediate substances between uranium and radium with period comparable with that of uranium itself, or to the influence of the external conditions or of the presence of other active elements on the rate of transformation. F. S.

The Radioactive Tufa of Fiuggi. Occluded Gases Content of Radium and Uranium. C. PORLEZZA and G. NORZI (*Atti R. Accad. Lincei*, 1911, [v], 20, i, 935—939. Compare Nasini and Levi, Abstr., 1908, ii, 401).—The tufa of Fiuggi contains occluded helium only in very small quantities. The quantity of radium present in a gram of the rock is high, amounting to 5×10^{-12} gram. The quantity of uranium is $0·76 \times 10^{-5}$ gram per gram of rock.

R. V. S.

Radioactivity of the Gas Obtained from the Thermal Springs of S. Saturnino (Benetutti-Sardegna). ARCIERO BERNINI (*Nuovo Cim.*, 1911, [vi], 1, i, 455—461).—The conductivity of the gaseous mixture increased for about three hours, attaining a maximum value nearly twice the initial activity. The same phenomenon has previously been observed by Rutherford and Soddy for radium emanation. The rate of decay of the induced radioactivity and other data prove that the activity of the mixture in this case is due to radium emanation. The slight radioactivity of the water which has also been measured is due to the presence of a little of the radioactive gas in solution. G. S.

The Amount of Radium and Radium Emanation Present in the Water and Gases of the Caledonia Springs, near Ottawa. A. S. EVE (*Trans. Roy. Soc. Canada*, 1910, [iii], 4, III, 53—54).—The amount of radium in the spring water varies from 10 to 18×10^{-12} gram of radium per litre, whilst the amount of radium emanation corresponds with between 620 and 210×10^{-12} gram of radium per litre of gas, which is from 4000 to 6000 times the amount present in the atmosphere. The water from Quelle am Schweizergang, Joachimsthal, the most radioactive known, is about 7000 times as active as that of the Caledonia Springs. F. S.

The Radium Contents of Specimens from a Deep Boring at Beachville, Ontario. A. S. EVE and DOUGLAS MCINTOSH (*Trans. Roy. Soc. Canada*, 1910, [iii], 4, III, 69—70).—A determination of the amount of radium in samples varying from a depth of 30 feet to 2580 feet showed a fairly uniform distribution of radium, between 0·5 and $1·42 \times 10^{-12}$ gram of radium per gram, the mean being 1·02, which is in agreement with the values found for other materials of the earth's crust. The solution obtained by leaching with water the material, after fusion with alkali carbonate, contained on the average one-fourth of the total radium. There was no relation between the depth and the amount of radium. F. S.

The Probable Influence of the Soil on Local Atmospheric Radio-activity. JAMES COX SANDERSON (*Amer. J. Sci.*, 1911, [iv], 32, 169—184).—A current of air from a tube buried about 120 cm. beneath the floor of the Physical Laboratory, New Haven, U.S.A., was drawn through the ionisation chamber of an electroscope. The natural leak of the instrument immediately increased eighteen times, and continued to increase at first rapidly, then more slowly for three hours, and then very gradually for three days, when it attained a maximum. This is what is to be expected if both radium and thorium emanations are present in underground air. By variations of the experiment the proportion of the effect due to the thorium and radium emanations separately was found. The effect due to the thorium was standardised in terms of a known weight of thorium by passing air into the electroscope through sand to which a known quantity of thorite in solution had been added. The amounts of thorium in various soils and other materials were estimated by comparison with the standard. Since the emanating power of the standard is probably a maximum and greater than that of the materials tested, the quantities of thorium so found are necessarily a minimum; thus solid monazite and thorianite crystals possessed respectively 420 and 6100 times less emanating power per unit of thorium than the standard. The results were that 1 c.c. of underground air contained radium emanation in equilibrium with $2\cdot4\times10^{-13}$ gram of radium, and that 1 c.c. of the earth emits thorium emanation equivalent to that produced by $1\cdot35\times10^{-6}$ gram of thorium. The radium value is 4000 times that found by Eve for the atmosphere at Montreal, and the thorium value is one-tenth of that found by Joly for the average of many common rocks. F. S.

Electrical Conductivity of Salts and Mixtures of Salts.

ALFRED BENRATH and J. WAINOFF (*Zeitsch. physikal. Chem.*, 1911, **77**, 257—268).—The measurements were carried out as described in a previous paper (compare Abstr., 1909, ii, 12). The electrical conductivities of the binary systems AgCl–KCl, KCl–NaCl, and $KCl–K_2CrO_4$, and of the components were determined at a series of temperatures up to the melting points of the individual salts.

The conductivities of the single salts are represented fairly satisfactorily by the formula $\log K = a + bt$, where K is the specific conductivity at the temperature t, and a and b are constants. As regards the binary systems, silver and potassium chlorides are not miscible in the solid state, and the conductivity of the system is the sum of the conductivities of the components. The chlorides of potassium and sodium are miscible in the solid state in all proportions, and the conductivity of the mixtures is greater than that of the components, the isothermals rising fairly rapidly from the points representing the conductivities of the salts. Potassium chloride and potassium chromate are not miscible in the solid state, except for mixtures containing 0—4% of the former salt. The curve obtained by plotting the conductivities as ordinates against the composition of the mixture as abscissæ shows a distinct maximum with no definite breaks. The form of conductivity curve to be anticipated for such systems is discussed.

At the melting points and other transition points there are sudden, and sometimes very great, alterations in the resistance. At the transition point the conductivity of the red modification of potassium chromate is six times that of the yellow form. G. S.

Mercurous Sulphate as Depolariser in Normal Elements. GEORGE A. HULETT (*Zeitsch. physikal. Chem.*, 1911, **77**, 411—419. Compare Abstr., 1904, ii, 695; *Phys. Rev.*, **30**, 648; van Ginneken, this vol., ii, 179).—A theoretical paper in which van Ginneken's views on this subject are adversely criticised. The assumption that the mercury ion concentration diminishes steadily with the progress of hydrolysis appears to be opposed to the experimental data. The author upholds his earlier views on the subject. G. S.

Rapid Formation of Lead Accumulators with Solutions of Sulphuric Acid and Chlorate or Perchlorate. G. SCHLEICHER (*Zeitsch. Elektrochem.*, 1911, **17**, 554—569).—The rapid production of lead plates carrying an adherent coating of lead peroxide suitable for use in an accumulator by alternate electrolytic oxidation and reduction of the lead in solutions of sulphuric acid containing varying quantities of a chlorate or perchlorate is studied. The results are almost identical with those obtained by Just, Askenasy, and Mitrofanoff (Abstr., 1910, ii, 96), using an addition of nitric acid in place of the chlorate or perchlorate. The perchlorate is preferable to the other substances, because it is not reduced at the cathode. T. E.

The Electromotive Behaviour of Ternary Alloys. The Ternary System Zinc–Silver–Lead. ROBERT KREMANN and F. HOFMEIER (*Monatsh.*, 1911, **32**, 597—608).—Measurements of the *E.M.F.* of the cell Zn | $N/1$-$ZnSO_4$ | Ag–Zn alloy give results in good agreement with those of Herschkowitsch (Abstr., 1898, ii, 583). Similar measurements with ternary alloys of zinc, lead, and silver show that when the ratio Ag : Zn is from 0 : 100 to 30 : 70, the potential is entirely unaffected by the presence of lead. The alloy in which the ratio is 30 : 70 has the same potential as lead, and alloys richer in silver generally give the potential of lead, except in accidental cases, when the particles of lead do not come into contact with the solution. The potential when obtained is that of the corresponding silver–zinc alloy. The results show that lead does not form solid solutions with zinc and silver. C. H. D.

Equilibria and Potentials at Membranes in the Presence of Non-dialysing Electrolytes. FREDERICK G. DONNAN (*Zeitsch Elektrochem.*, 1911, **17**, 572—581).—Two solutions, 1 and 2, separated by a membrane are considered. Solution 1 contains a salt, NaR, the anion of which cannot pass through the membrane; solution 2 contains a salt, for example, sodium chloride, both the anion and cation of which can pass through it. When equilibrium is reached the cations and anions will be divided between the two solutions in such a way that the reversible, isothermal transference of one mol. of $Na^{\cdot}$ and one mol. of Cl' from one solution to the other can be effected without expenditure of work. From this it follows that $[Na^{\cdot}]_2[Cl']_2 = [Na^{\cdot}]_1 \cdot [Cl']_1$, where the bracketed symbols represent equilibrium concentrations. Assuming complete dissociation of both electrolytes and equal volumes of the two solutions, it follows that $x = c_2^2/(c_1 + 2c_2)$, where c_1 and c_2 are the initial concentrations of NaR and NaCl in solutions 1 and 2 respectively, and x is the diminution of concentration of the sodium chloride by diffusion from 2 to 1. From this it is easily seen that the presence of the salt NaR in sufficient relative concentration on one side of the diaphragm has the effect of making the diaphragm almost impermeable for sodium chloride in the direction 2 to 1, whilst it remains freely permeable in the reverse direction.

The case of two electrolytes with no common ion (NaR and KCl, for example) is then treated in exactly the same way. Calling x the diminution of concentration of the $\mathrm{K}^{\cdot}$ ions, and y that of the Cl' ions in solution 2, $x = (c_1 + c_2)c_2/(c_1 + 2c_2)$ and $y = c_2^2/(c_1 + 2c_2)$. The effect of a relatively large concentration of the salt NaR is that the greater part of the potassium ions in solution 2 diffuses through the membrane into solution 1, whilst the chlorine ions remain behind in solution 2.

When a solution of non-dialysing electrolyte NaR is separated by the diaphragm from pure water or a very dilute solution of an alkali, it is shown that sodium ions will pass from 1 to 2, which is only possible if they are accompanied by an equal number of hydroxyl ions formed by dissociation of the water. The solution remaining in 1 is therefore acid and the salt NaR partly decomposed If the acid HR is weak, this membrane hydrolysis may become very large.

Owing to the differences in the concentrations of the ions in the two solutions separated by the membrane, there is a difference of electrical potential between them. By means of a reversible, isothermal cycle of operations, it is shown that the difference of potential $\pi_1 - \pi_2 = RT/F.\log\lambda$, where $\lambda = [\mathrm{Na}^{\cdot}]_2/[\mathrm{Na}^{\cdot}]_1 = [\mathrm{Cl}']_1/[\mathrm{Cl}']_2 = [\mathrm{OH}']_1/[\mathrm{OH}']_2$.

The many important applications which the theory may have in physiology are pointed out. T. E.

Electrolysis of Solutions of Salts of Fatty Acids in the Corresponding Anhydrous Acids. KARL HOPFGARTNER (*Monatsh*, 1911, **32**, 523—561).—The electrolytic decomposition of alkali acetate dissolved in glacial acetic acid, of alkali propionate in anhydrous propionic acid, and of sodium formate in formic acid has been investigated, and the influence established of concentration, temperature, and current density on the gases liberated.

Qualitatively the products of electrolysis in the anhydrous acid solutions are the same as those given by acidified aqueous solutions of the same salts, but quantitatively the proportions are very different. An exception is afforded by the formation of carbon monoxide from formate, and possibly of butylene from propionate.

The effect of an increase of temperature, of concentration, or of current intensity is also in the same sense as in aqueous solutions, but quantitatively it is much less in the case of the anhydrous acid solutions.

Accordingly in both cases the main reactions must be the same, and any formulation of the changes which take place must exclude all reactions in which water plays a part. E. F. A.

Formation of Hydrogen Cyanide in the Electric High Tension Arc. A. V. LIPINSKI (*Zeitsch. Elektrochem.*, 1911, **17**, 761—764).—Mixtures of methane, nitrogen, and hydrogen, the composition of which varies between the limits CH_4 8%, N_2 75%, H_2 16%, and CH_4 34%, N_2 53%, H_2 12% are used. An alternating current arc at 2000 volts and 0·05 to 0·12 ampere is passed through 3·8 litres of the mixture for one to three hours between platinum terminals. The hydrogen cyanide formed is then estimated. Carbon is deposited from mixtures containing more than 20% of methane. With this mixture the whole of the methane can be converted into hydrogen cyanide (compare this vol., ii, 790). T. E.

Use of the Magnetic Field in Determining Constitution. X.

PAUL PASCAL (*Bull. Soc. chim.*, 1911, [iv], **9**, 809—812. Compare this vol., ii, 464).—Although the rules already enumerated in previous papers of this series for the calculation of molecular magnetic susceptibilities give results in close agreement with those determined experimentally, there are a certain number of apparent exceptions in the case of tautomeric compounds, some of which have been dealt with already (Abstr., 1909, ii, 859). *cyclo*Hexanone has a mol. susceptibility -661×10^{-7}; the *keto*-form should have the value -631×10^{-7}, and the *enol*-form the value -669×10^{-7}, whence it appears that the equilibrium mixture at atmospheric temperature contains 78% of the latter form (compare Harding, Haworth, and Perkin, Trans., 1908, **93**, 1943). In the methyl*cyclo*hexanones the equilibrium moves towards the *keto*-form as the methyl group approaches the carbonyl group; thus the meta-isomeride contains 52% *enol* form, and the ortho-isomeride only 35%.

Resorcinol and phloroglucinol, examined in a solid state, behave as pure phenols in the magnetic field, and quinone as a diketone, whilst nitrosophenol and dinitrosoresorcinol behave as quinoneoximes. The molecular susceptibilities of a number of compounds of these types are given, with the percentages of enol-form in the equilibrium mixture at the ordinary temperature. T. A. H.

Solutions of Salts Heterogeneously Magnetic in a Heterogeneous Magnetic Field.

C. STATESCU (*Compt. rend.*, 1911, **153**, 547—549).—A solution of a paramagnetic substance in a glass cell was rendered heterogeneous by adding water, so that the solution and water were separated by a zone of varying concentration. The cell being illuminated and placed between the poles of an electromagnet, was viewed through a slit placed at the focus of a double convex lens. On establishing the magnetic field, layers of different concentrations were seen to arrange themselves in a series of concentric equipotential surfaces, the most concentrated round the poles. The phenomenon is shown very indistinctly by diamagnetic salts, owing to the small magnetic permeability of these substances. W. O. W.

The Conception of the Pressure of Expansion.

L. GAY (*Compt. rend.*, 1911, **153**, 262—264. Compare Abstr., 1910, ii, 935, 1043).—A mathematical paper relating to the pressure exerted by one constituent of a binary mixture if it remained in the ideal state of a perfect gas and in equilibrium with the fluid solvent. Dolezalek's results (Abstr., 1910, ii, 184) for solutions of carbon dioxide are explained. W. O. W.

Relationships between Atomic Heat, Coefficient of Expansion, and Compressibility of Solid Elements. EDUARD GRÜNEISEN (*Ber. deut. physikal. Ges.*, 1911, **13**, 491—503. Compare Abstr., 1910, ii, 824).—In connexion with the theory of solid monatomic elements, it is shown that the thermal expansion and the change of compressibility with temperature at low temperatures can be expressed in terms of the characteristic atomic frequency and its variation with volume or pressure. Data for copper, platinum, and iron are utilised in showing the relationships which are involved. H. M. D.

Modulus of Elasticity and Thermal Expansion of Metals. H. SIEGLERSCHMIDT (*Ann. Physik*, 1911, [iv], **35**, 775—782).—It is shown that the relationship between the elastic and thermal properties of a large number of metals can be expressed by means of the equation $E/s = C(1/A\beta)^n$, in which E is the elastic modulus, s the density, A the atomic weight, β the coefficient of thermal expansion, and C and n are constants. H. M. D.

Thermo-calorimetric Measurements. R. MELLECŒUR (*Ann. Chim. Phys.*, 1911, [viii], **23**, 556—566).—A form of calorimeter, indicated by Regnault (*Compt. rend.*, 1870, **70**, 664), has been tried in the measurement of the specific heat of liquids. The liquid is contained in a cylindrical reservoir, surrounded by an annular space containing mercury, which serves as thermometric substance. This piece of apparatus is suspended centrally in a chamber with blackened walls, the chamber being immersed in a bath of constant temperature. The temperatures of the liquid under examination and of the outside bath having been suitably adjusted, observations of the rate of cooling of the liquid are taken.

From experiments with water, benzene, acetone, acetic acid, and carbon disulphide, it is found that results accurate to about 1% can be obtained with this apparatus when certain precautions are taken. Exhaustion of the chamber in which the cooling liquid is suspended makes the rate of cooling too small for the purpose of ordinary laboratory measurements. H. M. D.

Calculation of Specific Heats of Simple Solutions. N. P. PASCHKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, *Phys. Part*, 166—184).—The author first discusses the various formulæ which have been given for the calculation of specific heats of solutions, and then deduces formulæ in the following manner.

If δ and s represent respectively the specific heat and density of a solution containing X grams of solvent and Υ grams of solute per c.c., and Φ and θ are the specific heats of the solvent and solute respectively, the law of mixtures would give :

$$\delta s = X\Phi + \Upsilon\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1) ;$$

allowing for possible variations of Φ and θ with concentration, this equation takes the form (2) $\delta s = X(\Phi - \Delta_1) + \Upsilon(\theta + \Delta_2)$.

A necessary condition for the validity of this expression is

$$X\Delta_1 - \Upsilon\Delta_2 = 0 \text{ or } \Delta_1/\Delta_2 = \Upsilon/X.$$

In order to allow for possible divergence from this normal case, the ratio Δ_1/Δ_2 may be equated to aY/bX (3), where a and b are constants and a may be greater than, equal to [as in equation (2)], or less than, b. Equation (3) may be satisfied in two ways:

$$[A]\ \Delta_1 = aY\Delta_0 \text{ and } \Delta_2 = bX\Delta_0,$$

where Δ_0 is a constant, or

$$[B]\ \Delta_1 = a\Delta_0'/X \text{ and } \Delta_2 = b\Delta_0'/Y.$$

Of these, [B] leads to no new expression, but application of [A] to equation (2) gives:

$$\delta s = X\Phi + Y\theta + (b - a)XY\Delta_0 \quad . \quad . \quad . \quad . \quad . \quad (4),$$

which is the general form for the calculation of specific heats of solutions of non-electrolytes.

Similarly, for electrolytes, $\Delta_1/\Delta_2 = aiY/bX$, where $i = [1 + (n - 1)\alpha]$, n being the number of active particles which can be formed by a molecule of the electrolyte and α the degree of dissociation. Substitution of $\Delta_1 = aiY\Delta_0$ and $\Delta_2 = bX\Delta_0$ in equation (2) gives:

$$\delta s = X\Phi + Y\theta - a(n - 1)\alpha XY\Delta_0 + (b - a)XY\Delta_0,$$

which is the general form for the calculation of the specific heats of electrolytic and all other simple solutions. For solutions of normal electrolytes alone, this expression becomes:

$$\delta s = X\Phi + Y\theta - a(n - 1)\alpha XY\Delta_0.$$

Application of these expressions to solutions of a number of salts and organic compounds indicates their validity. In general, it is found that the specific heat of a substance changes when it is dissolved.

The method employed for the experimental determination of specific heats of solutions is described. T. H. P.

Latent Heat of Fusion and Specific Heat of Fatty Acids. GUSTAVE MASSOL and A. FAUCON (*Compt. rend.*, 1911, **153**, 268—270. Compare Abstr., 1909, ii, 791).—Formic and acetic acids have given results analogous to those already described for propionic acid. Lauric acid was found to have a latent heat of fusion 46·68 Cal., whilst the latent heat of solidification was 37·42 Cal. The difference was greater for slightly impure acids, and is attributed to the presence of two modifications, a crystalline form having discontinuous physical properties at the melting point, and an amorphous form showing continuous variation in properties in the interval between complete solidification and liquefaction. W. O. W.

Comparison of Platinum Thermometers with the Nitrogen-, Hydrogen-, and Helium-Thermometer, and the Determination of Certain Fixed Points between 200° and 450°. LUDWIG HOLBORN and F. HENNING (*Ann. Physik*, 1911, [iv], **35**, 761—774).—From a comparison of the records of platinum-resistance thermometers with those of various gas thermometers, three of which contained nitrogen, hydrogen, and helium respectively in bulbs of Jena glass 59^{III}, and the fourth, nitrogen in a quartz bulb, the authors find that the temperatures recorded by the resistance thermometers between 200° and 450° are probably correct within 0·1°. For this interval, Callendar's formula holds quite satisfactorily.

In connexion with this thermometric comparison, the following fixed points were determined: freezing points—tin, 231·83°; cadmium, 320·92°; zinc, 419·40°; boiling points—naphthalene, 217·96°; benzophenone, 305·89°; sulphur, 444·51°. The boiling-point values in particular are in good agreement with those recorded by Callendar and Griffiths and by Waidner and Burgess. H. M. D.

Experiments with Liquid Helium-*E*. A Helium Cryostat. H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 204—210. Compare this vol., ii, 368, 487, 575, 687).—A modified form of helium cryostat is described, in which the cryostat chamber is separated from the helium liquefier by a valve, and in which the liquid helium is syphoned over from the liquefier through a well-cooled syphon tube. H. M. D.

Thermoelectric Method of Cryoscopy. HENRY H. DIXON (*Proc. Roy. Dubl. Soc.*, 1911, **13**, 49—62).—A differential method of determining small differences in the freezing points of solutions is described in detail. Two test-tubes, one containing water, the other the solution the freezing point of which is to be determined, are placed side by side in a larger test-tube acting as air chamber; the large tube is immersed in a freezing mixture. As thermoelement, copper-eureka junctions proved suitable; they were connected with a galvanometer in the usual way, as few contacts as possible being used. Corrections were applied for the difference between the temperature of the freezing mixture and that of the solution at its freezing point. The chief source of error in the experiments is the occurrence of thermo-*E.M.F.*'s, owing to differences of temperature at the metallic junctions, and to eliminate these as far as possible the galvanometer had to be placed in a thermostat. When the water and the solution have been cooled just below their freezing points, separation of ice is started by adding a minute amount of ice, and the solutions are stirred continuously while readings are being taken. G. S.

Cryoscopy of Certain Mineral Acids and Phenols. EUGÈNE CORNEC (*Compt. rend.*, 1911, **153**, 341—343. Compare Abstr., 1909, ii, 972; 1910, ii, 121).—The author continues his studies of the curves representing the variations of the lowering of freezing point of acids undergoing progressive neutralisation by alkali hydroxides.

The graphs for chloric acid, perchloric acid, and phenol correspond with that of a monobasic acid. That of iodic acid shows a minimum corresponding with the normal salt, but is remarkably rectilinear up to this point, giving no indication of the existence of an acid having the double formula. Selenious, dithionic, and carbonic acids and resorcinol behave as dibasic acids; pyrophosphoric acid as tetrabasic. This method may be applied to acids too weak to influence the ordinary indicators, but not to such feeble acids as hydrogen sulphide.

Boric acid on neutralisation with potassium hydroxide behaves as if some molecules of the acid united with molecules of the monopotassium salt, forming condensed salts. It appears to be monobasic, and to contain only one boron atom in the molecule. Arsenious acid behaves in the same way.

A new type of curve has been found in the case of chromic acid and periodic acid, due to phenomena other than those of simple neutralisation. W. O. W.

Solidification Point of Some Organic Liquids.

JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1911, **25**, 300—326).—In the first part of the paper the author discusses the various kinds of thermometers for use in low temperature work. He makes use of a platinum resistance thermometer for standardising his thermometers filled with different liquids (compare Abstr., 1909, ii, 121). Toluene and amylene are recommended as the best liquids with which to fill thermometers for such work, provided that they are not subjected to too rapid variations in temperature.

In the second part of the paper the results are given, to 0·1°, of the determinations of the solidification points of some sixty pure organic liquids. From his results with ether the author draws the conclusion that solid ether is dimorphous, the stable form solidifying at −116·2°, and the unstable form at −123·3°, the latter only being obtainable by slow cooling. W. G.

Isotherms of Monatomic Substances and of their Binary Mixtures. XI. The Critical Temperature of Neon and the Melting Point of Oxygen.

H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 163—165. Compare this vol., ii, 203, 467).—A vacuum jacketed cryostat, containing liquid oxygen and surrounded by a similar larger vacuum tube containing liquid air, was connected with a vacuum pump of large capacity and the pressure on the oxygen reduced. At a pressure of 1 mm., solid oxygen began to separate out, and the freezing point thus obtained was −218·4°. This differs considerably from the values given by Rankine (−210·4° and −212·0°), and by Estreicher (−227°).

When a piezometer tube containing neon was introduced into the liquid oxygen cryostat at −218·4°, the raising of the pressure to sixty atmospheres did not produce any trace of liquid neon. This indicates that the critical temperature of neon is below −218°. H. M. D.

Densities of Co-existing Phases (Orthobaric Densities) and the Diameter for Sulphur Dioxide in the Neighbourhood of the Critical Point.

ETTORE CARDOSO (*Compt. rend.*, 1911, **153**, 257—259).—Determinations of the rectilinear diameter were made, using Natterer tubes in pairs. The influence of stirring and of temperature was studied, and the results will be published later. When the liquid phase only was stirred, the diameter was found to be perfectly rectilinear to within 4° of the critical point, when a distinct inflexion appeared. Extrapolation of the rectilinear diameter gave 0·520 as the critical density. W. O. W.

General Relationship between Heat of Vaporisation, Vapour Pressure, and Temperature.

IVAR W. CEDERBERG (*Zeitsch. physikal. Chem.*, 1911, **77**, 498—509).—By combination of the Clausius-Clapeyron equation, the vapour pressure formula of van der Waals, and an equation given by Nernst, the equation

$$\lambda = [R\theta_0 \log(\pi_0/p) \times (1 - p/\pi_0)]/M(\theta_0/T - 1),$$

has been deduced, where λ is the molecular heat of vaporisation, θ_0 and π_0 represent the absolute temperature and pressure respectively, and the other symbols have the usual significations. It is shown that this formula is applicable in the neighbourhood of the ordinary boiling point, and the molecular heat of vaporisation can be obtained more accurately by it than by any other formula previously put forward. As it contains no constants which have to be determined empirically, it affords full information as to the deviations from Trouton's rule. G. S.

Retrogressive Melting-point Lines. II. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 170—177. Compare Abstr., 1909, ii, 971).—Theoretical. Reference is made to the relationships exhibited by the system sodium sulphate–water. H. M. D.

Retrogressive Melting-point Lines. III. ANDREAS SMITS and J. P. TREUB (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 189—192). —The influence of pressure on the form of the melting-point lines is discussed in reference to the experimental data for the binary system ethyl ether–anthraquinone. H. M. D.

Retrogressive Vapour Lines. I. ANDREAS SMITS (*Proc. K. Akad., Wetensch. Amsterdam*, 1911, **14**, 177—182).—A theoretical paper in which the equations for certain equilibrium curves are deduced, and the forms of the curves examined in detail. H. M. D.

Three Forms of the Equation of Condition and the Internal Heat of Vaporisation. THORKELL THORKELSSON (*Physikal. Zeitsch.*, 1911, **12**, 633—637).—Three modified forms of the van der Waals' equation are analysed and discussed with reference to the calculation of the internal heat of vaporisation of liquids and of the critical data. H. M. D.

Latent Heat of Vaporisation of Liquids. WILLIAM C. McC. LEWIS (*Phil. Mag.*, 1911, [vi], **21**, 268—276).—The author deduces the relationship $L = -Ta/\rho\beta$, in which L is the latent heat of vaporisation of a liquid at temperature T, ρ its density, a its coefficient of expansion with temperature, and β its compressibility coefficient at constant temperature. For normal liquids, the latent heat values obtained from the formula are in approximate agreement with the observed values, but large discrepancies are found in the case of liquids which are presumably associated. H. M. D.

Heats of Reaction in Non-aqueous Solutions. J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1911, **33**, 1291—1309).—The heat of neutralisation of 1 mol. of pyridine by 1 mol. of acetic acid has been measured in a number of different solvents and also in the absence of solvent, the method of measurement being that employed by Richards and Burgess (Abstr., 1910, ii, 391, 930) and Richards and Jesse (Abstr., 1910, ii, 269). In the first set of experiments the pyridine was dissolved in the solvent, and the pure acid (not in solution) was run into this solution. The weight of the solvent was kept constant (=96·4 grams) for all the different solvents. The observed heat effects, expressed in calories, for the different solvents were as follows: acetone, 2100·6; water, 1758·0; benzene, 2168·3; carbon tetrachloride, 2177·5; nitrobenzene, 2305·4; carbon disulphide, 2055·6; ethyl acetate, 2263·6; methyl alcohol, 1155·4; ethyl alcohol, 1253·4; *iso*amyl alcohol, 1639·6; when no solvent was used the heat effect was 2286·1 cals. Only in one case, namely, nitrobenzene, is the heat evolved greater than when no solvent is present. The value obtained with water as solvent is considerably less than the values for the other solvents, excepting the alcohols, which are not comparable because of esterification. In the case of solvents such as carbon disulphide, benzene, etc., where no side reactions are to be expected, the values obtained are more nearly of the same order as that obtained when no solvent is used.

In the second series of experiments both the acid and base were dissolved in the solvent before neutralisation took place, the concentration of both the acid and base being the same, namely, 1 mol. in 100 grams of solvent. The following heat effects, in calories, were observed: water, 2715·2; acetone, 1794·8; chloroform, 2358·4; carbon tetrachloride, 2210·4; benzene, 2274·6; ethyl acetate, 2140·2. When these figures are corrected for the heat absorbed or evolved in the process of solution of the pyridine acetate formed in the reaction, they become 786·8, 2125·6, 1152·5, 2317·2, 2481·7, and 2376·4 respectively.

It is obvious that the heat liberated varies greatly from solvent to solvent. These considerable differences cannot be explained as being due to any electrolytic dissociation of the acetate, neither are they due to differences in the heats of solution of the acetate in the different solvents. The chemical nature of the solvents does not seem to give any clue as to the magnitude of the heat of neutralisation, or of the magnitude or sign of the heat of solution of the resulting acetate.

T. S. P.

Chemical Affinity. V. The Formation of Potassium Lead Sulphate. J. N. Brönsted (*Zeitsch. physikal. Chem.*, 1911, **77**, 315—330).—The energy relations associated with the formation of the double salt containing lead and potassium sulphates, $PbSO_4,K_2SO_4$, already described by previous observers (compare Barre, Abstr., 1909, ii, 733; Fox, Trans., 1909, **95**, 878) have been measured. At 0°, the compound is in equilibrium with a 0·0112 molar solution, at 22° with a 0·0227 molar solution of potassium sulphate.

The affinity, determined by measurements of *E.M.F.* in the usual way, amounts to $4240 - 2·9\ (t - 22)$ calories, where t is the temperature, in good agreement with the same magnitude calculated from the results of cryoscopic measurements, which gave the value 4330 cals. at 0°. From these results the heat of formation of the compound, calculated by means of the Helmholtz formula, amounts to 5090 cals.

per mol., whilst direct calorimetric determination of the same magnitude gave the value 5310 cals. In the last case, the heat of formation of the double salt from solid lead sulphate and dissolved potassium sulphate, and also the heat of precipitation of potassium sulphate, were measured in a calorimeter; the difference represents the heat of formation of the compound from the solid components.

It has been suggested that Thomsen's thermochemical data for compounds of lead are in some respects inaccurate, but the author contends that no good grounds have been shown for this assumption.

G. S.

Heat of Combustion of Compounds of Physiological Importance. ALBERT G. EMERY and FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1911, **28**, 301—307).—The experiments were made with an idiabatic calorimeter. The heat of combustion was determined for dextrose, lævulose, lactose, maltose, glycogen, alanine, allantoin, asparagine, aspartic acid, creatine, creatinine, cystine, glutamic acid, glycine, hippuric acid, tyrosine, urea, uric acid, acetone, alcohol, β-hydroxybutyric acid, lactic acid, glycerol, palmitic, stearic and oleic acids. The results are given in a table. Special attention is called to urinary constituents, in determining the energy value of pathological urine, as for instance in diabetes, where it is now shown that every gram of β-hydroxybutyric acid excreted means a loss of 4693 calories.

W. D. H.

The Weight of a Falling Drop and the Laws of Tate. IX. The Drop Weights of the Associated Liquids, Water, Ethyl Alcohol, Methyl Alcohol, and Acetic Acid, and the Surface Tensions and Capillary Constants calculated from Them. J. LIVINGSTON R. MORGAN and A. McD. McAFEE (*J. Amer. Chem. Soc.*, 1911, **33**, 1275—1290).—From measurements of the drop weights of water, ethyl alcohol, methyl alcohol, and acetic acid at various temperatures, the following formulæ showing the relation between the surface tension (γ) in dynes per cm. and the temperature (t) have been found: water, $\gamma_t = 75{\cdot}872 - 0{\cdot}1547t - 0{\cdot}000222t^2$. Methyl alcohol, $\gamma_t = 23{\cdot}740 - 0{\cdot}0834t$. Ethyl alcohol, $\gamma_t = 23{\cdot}295 - 0{\cdot}0795t$. Acetic acid, $\gamma_t = 28{\cdot}749 - 0{\cdot}0933t$. Similar equations are also given for the capillary constants.

In each case the new definition of normal molecular weight as a liquid (this vol., ii, 698, 699) does not hold, since the value of t_c (= critical temperature) calculated from the normal benzene constant does not remain constant, but increases with an increase in the temperature of observation. These liquids therefore, according to that definition, are not normal, but associated.

Comparison of the results with those obtained by other methods shows that for finding either the surface tension or the capillary constant of a liquid, the drop weight method is more consistent than any other, leading not only to a smaller variable error, but probably also to a truer absolute value.

T. S. P.

Variation with Temperature of the Viscosity of Gases of the Argon Group. MAX REINGANUM (*Physikal. Zeitsch.*, 1911, **12**, 779—780).—The relationship between Sutherland's constants which measure the attraction between the molecules and the absolute critical temperatures referred to by Rankine (Abstr., 1910, ii, 829) has already been pointed out by the author (*Diss.*, Göttingen, 1899).

H. M. D.

Viscosity of Liquid-crystalline Mixtures of *p*-Azoxyanisole and *p*-Azoxyphenetole. HANS PICK (*Zeitsch. physikal. Chem.*, 1911, **77**, 577—586).—It has been suggested by previous observers that the hardness or elasticity of a metal (compare Faust and Tammann, Abstr., 1910, ii, 1039) is comparable with the viscosity of a liquid. In order to find whether mixtures of crystalline liquids behave like mixed crystals of solids, the author has measured the density and viscosity of mixtures of *p*-azoxyanisole and *p*-azoxyphenetole at 136°, and finds that, whereas the densities follow the mixture rule, the viscosity of the mixtures is smaller than that calculated according to the mixture rule, the viscosity curve showing a minimum. In this case therefore the expected agreement is not observed, since the curve obtained by plotting the hardness against the composition of a binary system where the components form mixed crystals usually shows a maximum.

G. S.

The Viscosity and Fluidity of Emulsions, Crystalline Liquids, and Colloidal Solutions. XI. EUGENE C. BINGHAM and GEORGE F. WHITE (*J. Amer. Chem. Soc.*, 1911, **33**, 1257—1275).—From the analogy between viscosity and fluidity, and electrical resistance and conductivity respectively (compare Abstr., 1906, ii, 218), the authors deduce that when liquids are thoroughly mixed, their fluidities will be additive; but if the liquids form an emulsion, a crystalline liquid, or a colloidal solution, or if the mixture is for any other reason incomplete, the fluidity of the mixture will be less than would be the case in a homogeneous solution.

The above conclusions have been verified experimentally by a study of the viscosities of mixtures of phenol and water at various temperatures, especially at those in the neighbourhood of the critical solution temperature. In all the mixtures the fluidity increases with the temperature very rapidly in the neighbourhood of the critical solution temperature, and the various explanations which have been offered to explain this are fully discussed. T. S. P

Adsorption Experiments. S. J. LEVITES (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 1—5).—The adsorption of potassium dichromate and carbamide by bone charcoal, of potassium dichromate and potassium chromium alum by hide powder, and of potassium dichromate by egg-albumin has been investigated. The data show that the dependence of the adsorption on the concentration of the aqueous solution can be satisfactorily represented by the exponential equation $x/m = K.C^{1/n}$ if n is made equal to 2. In very dilute solutions, however, the agreement between the observed and calculated values is not satisfactory.

The data obtained for the adsorption of potassium dichromate and sodium sulphate by gelatin show that the adsorbed quantity is nearly proportional to the concentration of the aqueous solution, so that in these cases $n = 1$.

The reduction of potassium dichromate in gelatin under the influence of light has also been examined, and numbers are recorded which show the variation of the extent of the reduction during a given period of illumination with the concentration of the adsorbed salt.

H. M. D.

Determination of the Surface Tension at the Contact of Two Liquids. (Mlle.) L. VAN DER NOOT (*Bull. Acad. roy. Belg.*, 1911, 493—502).—The method described in a previous paper (this vol., ii, 701) has been applied to the measurement of the tension at the contact surface between two layers of liquid. The apparatus employed consists of a series of U-tubes with limbs of unequal diameter; the lower portion of the tube is occupied by the heavier liquid, and communication between the two portions of the lighter liquid in the two limbs is established by means of a small syphon tube. The differences in level of the contact surfaces in the two limbs are measured, and are then reduced to absolute values by a method of approximation which is described. From these values and the known diameters of the tubes, the capillary constant (a^2) for the liquid-liquid contact surface can be calculated. The following values were obtained: water-benzene, 0·389; water-ethyl ether, 0·0840; water-carbon disulphide, 0·287; water-nitrobenzene, 0·220. In every case the pairs of liquids were mutually saturated before being brought into contact. From the capillary constants and the densities of the liquid layers, the liquid-liquid surface tension values are calculated to be: water-benzene, 21·0; water-ethyl ether, 10·0; water-carbon disulphide, 38·4; water-nitrobenzene, 23·0 H. M. D.

The Vapour Pressure of Hydrates, Determined from their Equilibria with Aqueous Alcohol. HARRY W. FOOTE and SAMUEL R. SCHOLES (*J. Amer. Chem. Soc.*, 1911, 33, 1309—1326).—Several grams of the finely powdered salt were weighed in to a small bottle with a ground-glass stopper. Alcohol was then added from a calibrated pipette, the stopper tightly inserted, and the bottle shaken in a thermostat at 25° for at least two days. When equilibrium had been attained, the compositions of the liquid and solid phases were determined. Only those salts were chosen which were practically insoluble in alcohol.

To find the pressure of aqueous vapour in equilibrium with a given dilution of alcohol (the liquid phase as above determined) the relative proportion of alcohol and water molecules in the vapour was determined by combustion. The vapours from the alcohol at 25° were carried into a combustion furnace by means of a stream of pure, dry air, and the products of combustion collected and weighed. Having thus determined the composition of the vapour, its average molecular weight could be calculated and then used in finding the total pressure From the total pressure of the mixture, using as a factor the molecular %. of water in its vapour, the partial pressure of aqueous vapour for the mixture could be calculated.

The following vapour pressures, in mm. of mercury, for various systems at 25° were obtained: $CuSO_4$,3—5H_2O, 7·0; $CuSO_4$,1—3H_2O, 4·7; $CuSO_4$,0—1H_2O, 0·8; Na_2SO_4,0—10H_2O, 18·2; K_2CO_3,0—1·5H_2O, 1·1; CaO,0—1H_2O, 0·8; $ZnSO_4$,6—7H_2O, 13·6; $ZnSO_4$,1—6H_2O, 12·8; $ZnSO_4$,0—1H_2O, 1·0; $MgSO_4$,6—7H_2O, 11·5; $MgSO_4$,5—6H_2O, 9·8; $MgSO_4$,4—5H_2O, 8·8; $MgSO_4$,1—4H_2O, 4·9; $MgSO_4$,0—1H_2O, 1·0; $BaCl_2$,1—2H_2O, 4·8; $BaCl_2$,0—1H_2O, 2·5; Na_2HPO_4,7—12H_2O, 18·0; Na_2HPO_4,2—7H_2O, 12·4; Na_2HPO_4,0—2H_2O, 8·9.

The above results are discussed in connexion with the choice of salts as drying agents for organic liquids. T. S. P.

Formation of Solid Metallic Solutions by Diffusion in the Solid State. GIUSEPPE BRUNI and D. MENEGHINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 927—931. Compare this vol., ii, 703).—When a wire consisting of a gold core on which a layer of copper has been electrolytically deposited is heated at 800° a solid solution of the two metals is completely formed after about one hundred hours. The alloy produced contained 52·5% of gold. Gold and silver similarly treated behave in the same way, the temperature employed being 900° and the resulting alloy containing 62·8% of silver. The extent of the surface of contact of the two metals influences the velocity of diffusion very greatly. A wire was prepared which consisted of sixty thin layers alternately of copper and nickel, and it was found that complete solution had occurred after two hours at 1000°. In this case the change could be detected, not only electrically, but also by means of the microscope. R. V. S.

Diffusion Phenomena in [Solutions] of Electrolytes. B. LINO VANZETTI (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 54—58).—Experiments are described in which simple diffusion leads to the partial separation of the acid and basic constituents of salts. Fresh distilled water, to which neutral litmus or phenolphthalein (faintly reddened) is added in small quantity, is placed in a vertical tube (15—40 cm. long), and a concentrated solution of some salt is then carefully introduced through a capillary tube, reaching to the bottom of the diffusion tube. After some time the colour changes which are observed indicate the separation of acid and base by diffusion. Positive results were obtained with ferric chloride, copper sulphate silver sulphate, potassium chloride, sodium chloride, ammonium chloride, aluminium sulphate, and zinc chloride. In each case the changes observed are described in detail. Although the presence of an indicator seems to modify the results which are obtained in certain cases, blank experiments without indicator show that this influence is of secondary importance. H. M. D.

Preponderating Rôle of Two Electrostatic Factors in the Osmosis of Solutions of Electrolytes. Normal Osmotic Movements. PIERRE GIRARD (*Compt. rend.*, 1911, **153**, 401—404).—Certain abnormal results in biological experiments on osmosis are explained by supposing that the direction of osmosis depends, not on relative osmotic pressures, but almost exclusively on two electrostatic factors, the sign of the walls of the capillaries composing the septum and the orientation of the active field by which is understood the sum of the difference in potential of the liquid couple, and that corresponding with the polarisation of the septum (Abstr., 1908, ii, 456). Loeb's experiments on the change in volume of the muscles of frogs when immersed in salt solutions are explicable on this theory. Similar anomalies have been realised *in vitro*. Two isotonic solutions, one containing an electrolyte, separated by a membrane, remained in equilibrium until the difference in potential was established, when osmosis occurred in a direction depending on the sign of the charge on the septum, and the orientation of the field; when these were reversed osmosis proceeded in the opposite direction. W. O. W.

Proof of the Applicability of Boyle's and Gay-Lussac's Laws to Emulsions. B. Ilyin (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, *Phys. Part*, 134—142).—The author has applied the theoretical considerations and experimental methods of von Smoluchowski (*Ann. Physik*, 1908, [iv], **25**, 205) and Svedberg (Abstr., 1910, ii, 773) to the examination of emulsions of gamboge in water of definite concentrations.

The results show that, within the limits of experimental error, variations of concentration in emulsions follow the theoretical laws, and that, for the concentrations employed, the ratio β/β_0 (compare Svedberg, *loc. cit.*) approximates to unity, or, in other words, the motion of any one particle is independent of the motions of the remaining particles. T. H. P.

Certain Objections Recently Raised by A. Colson Against the Ionic Theory. Georges Urbain (*Bull. Soc. chim.*, 1911, [iv], **9**, 753—758).—The author criticises the objections to the ionic theory which have been made from time to time by Colson on the basis of the properties of solutions of the green chromium sulphates (compare Abstr., 1908, ii, 45). H. M. D.

Properties of Salt Solutions in Relation to the Ionic Theory. II. Electrical Transference Numbers. Arthur A. Noyes and K. G. Falk (*J. Amer. Chem. Soc.*, 1911, **33**, 1436—1460. Compare Abstr., 1910, ii, 929).—In the theoretical part of this paper, the theory of transference numbers is fully discussed, taking into account the solvation of the solute and transport of the solvent from one electrode to the other (compare Lewis, Abstr., 1910, ii, 683). A review is then given of previous investigations on transference numbers, and the results of these investigations are collated. The transference numbers obtained by three different methods, namely, the gravimetric, moving-boundary, and conductivity methods, are then carefully compared. At 18° the values obtained by the first two methods are concordant within about 1% for hydrochloric, nitric and sulphuric acids, potassium chloride and sulphate, and ammonium chloride, but for other substances the gravimetric method gives much higher values (2·5—3%) than the moving-boundary method. The conductivity method also gives values higher by 1—3% than those of the moving-boundary method for uni-univalent salts. The authors are of the opinion that the moving-boundary method requires further investigation before trust can be placed in the values obtained by it.

In the case of almost all uni-univalent substances the values obtained by the conductivity method at zero concentration agree within about 1% with those obtained by the gravimetric method at 0·005 to 0·02-*N*. The agreement between these two methods falls outside the experimental error in the case of uni-bivalent salts.

In the last section of the paper the change of the transference number with the concentration and temperature is discussed. With respect to the latter factor, the general statement may be made that the transference number invariably decreases with rising temperature if it is larger than 500×10^{-3}, and increases if smaller than this quantity. T. S. P.

The Laws of "Concentrated" Solutions. II. The Estimation of the Degree of Ionisation of Electrolytes in Moderately Concentrated Solutions. Edward W. Washburn (*J. Amer. Chem. Soc.*, 1911, **33**, 1461—1478. Compare Abstr., 1910, ii, 1044).—It is pointed out that in calculating the degree of ionisation of an electrolyte by the conductivity method, the neglect of the viscosity effect may produce errors as high as 7 and 8%, even at such low concentrations as 0·1*N*, and for such simple electrolytes as uni-univalent salts.

From a consideration of the experiments of Johnston (Abstr., 1909, ii, 854) and Green (Trans., 1908, **93**, 2049), the author proposes the relation $\Lambda = kf^m$ as a basis for applying the viscosity correction in calculating the degree of ionisation of univalent salts, up to a concentration of one equivalent per litre, at least. Λ is the equivalent conductivity of an ion, f is the fluidity of the solution, m is a constant not far from unity and dependent chiefly on the nature of the ion, and k is a constant. This relation gives very good results when applied to Green's figures, m being given the value 0·94.

From the above relation it may be deduced that the degree of ionisation is given by the expression $\gamma = \Lambda/\Lambda_0(\eta/\eta_0)^m$, and examples are given illustrating the results obtained with this equation, and methods for determining the fluidity exponent m are discussed.

The relation $\Lambda = kf^m$ leads to the following expression for the true transference number, n_A, of an ion A in any solution:

$$n_A = n_{0A}(\eta/\eta_0)^{m_A - m}.$$

n_{0A} is the transference number at infinite dilution in pure water, (η/η_0) the relative viscosity of the solution, and m_A and m are the fluidity exponents for the ion and for the salt respectively. Values calculated from this equation are compared with those determined experimentally in the case of potassium, sodium, and lithium chlorides. There is very good agreement in the case of potassium chloride; in the case of the other two salts the change of the transference number with the change in viscosity is in the right direction, but is not large enough.

The above relations do not hold in the case of acids and alkalis, and the equation $\gamma = \Lambda/\Lambda_0'$ is suggested for the degree of ionisation (γ), Λ being the equivalent conductivity of the solution, above which the vapour pressure of the water is p, whilst Λ_0' is the equivalent conductivity of the electrolyte at infinite dilution to which a suitable non-electrolyte has been added, so as to give it the same viscosity and the same vapour pressure, p, as the first solution. T. S. P.

Influence of Pressure and Temperature on the Electrolytic Conductivity of Solutions.

Friedrich Korber (*Zeitsch. physikal. Chem.*, 1911, **77**, 420—422).—The claim for priority made by Lussana (this vol., ii, 462) is not valid. G. S.

Conductivity and Viscosity in Mixed Solvents Containing Glycerol.

J. Sam Guy and Harry C. Jones (*Amer. Chem. J.*, 1911, **46**, 131—197. Compare Jones and Schmidt, Abstr., 1909, ii, 717).—The molecular conductivities in glycerol solution of the following salts have been measured at dilutions varying from 10 to 1600 litres, and at temperatures of 25°, 35°, and 45°: potassium nitrate, chloride and bromide, sodium chloride, bromide, iodide and nitrate, ammonium chloride, bromide and nitrate, barium chloride, bromide and nitrate, calcium bromide, strontium bromide and nitrate, and cobalt chloride and bromide. At 55°, 65°, and 75°, the molecular conductivities in glycerol solution of the following salts were determined: potassium chloride and bromide, sodium bromide and iodide, ammonium nitrate, strontium chloride, barium nitrate, and cobalt chloride and bromide. The molecular conductivities at 25°, 35°, and 45° of potassium chloride, sodium nitrate, and ammonium bromide in aqueous ethyl-alcoholic and methyl-alcoholic solutions containing respectively 25, 50, and 75% of glycerol were also measured, of strontium chloride in aqueous solutions containing 25, 50, and 75% of glycerol, and of ammonium bromide in methyl- and ethyl-alcoholic solution. In addition to the above, the viscosities and fluidities of the above solutions were determined at the respective temperatures.

The conclusions drawn from the results obtained are as follows: Glycerol forms mixtures with water, methyl alcohol, and ethyl alcohol, the properties of which are not additive. The curves representing fluidity and conductivity are very similar to one another over the range of temperature from 25° to 75°. Salts which have the highest power of solvation show the greatest temperature-coefficients of conductivity, and these are greater in the more dilute solutions. In mixed solvents containing glycerol, with water, ethyl and methyl alcohols, the curves representing conductivity and fluidity are strikingly analogous. The molecular conductivities of ternary electrolytes in glycerol at low dilutions are usually smaller than those of binary electrolytes under the same conditions, while at high dilutions the reverse is generally true. While the majority of the salts studied increase the viscosity of glycerol, certain salts of rubidium and ammonium lower its viscosity, a phenomenon which is most readily explained by the hypothesis of Jones and Veazey (Abstr., 1908, ii, 259, 260). It is probable that glycerolates exist in the various solutions. T. S. P.

The Conductivity and Ionisation of a Penta- and a Hexa-ionic Salt.

ARTHUR A. NOYES and ROBERT H. LOMBARD (*J. Amer. Chem. Soc.*, 1911, 33, 1423—1436. Compare Abstr., 1909, ii, 854).—The authors give the results of measurements at 0°, 25°, and 50° of the molecular conductivity (μ), viscosity (η), and density of dilute solutions of the tetrasodium and pentasodium salts of benzenepentacarboxylic acid; also values of their molecular conductivity (μ_0) at zero concentration obtained by graphical extrapolation, and values (calculated from these data) of the ratio $\mu\eta/\mu_0\eta_0$, which expresses the ionisation (γ) of the salts, if it be assumed that intermediate ions are not present.

The following principles, derived from the study of salts of smaller valence-products, are shown to be applicable to these two salts. (1) The exponent n in the function $C(1-\gamma)=K(C\gamma)^n$, which expresses the change of ionisation with the concentration, has approximately the same value ($1·50 \pm 0·05$ at concentrations below $0·02N$) whatever be the number of ions into which the salt dissociates, instead of a value equal to this number of ions, as would be required by the law of mass action. As with salts of smaller valence products, the value which has to be given to n is smaller at higher concentrations, it being 1·20 for the concentration interval 0·01 to $0·1N$. (2) The ionisation of the tetrasodium salt is substantially identical with that of potassium ferrocyanide, a salt of the same valence type. (3) The non-ionised fraction at a given molecular concentration is roughly proportional to the product of the valencies of their ions; thus in a 0·05 molecular solution the non-ionised fraction is $4\times13=52\%$ for the tetrasodium salt, and $5\times12=60\%$ for the pentasodium salt, whilst the average values previously obtained are 13·5 for uni-univalent, 2×14 for uni-bivalent, and 3×13 for uni-tervalent salts. (4) Increase in temperature causes only a slight decrease in ionisation of these salts. Thus the change between 0° and 25° is scarcely appreciable, and that between 25° and 50° amounts to 1·5—2% of the ionisation value in 0·05 molecular solution. At 25° and 50°, the molecular conductivity of the quinquevalent ion $(C_{11}HO_{10})^V$ is 1·5 times that of the quadrivalent ion $(C_{11}H_2O_{10})^{IV}$, whilst if these ions met with the same frictional resistance the larger charge on the former ion would cause its molecular conductivity to be $5^2/4^2=1·56$ times that of the latter ion.

The conductivity of benzenepentacarboxylic acid itself was measured at 25° between the concentrations 0·0006 to 0·02 molecular, and it is shown to be a moderately strong acid with respect to both its first and second hydrogens. T. S. P.

The Hydrolysis of Iodine and of Bromine. A Correction.

WILLIAM C. BRAY and E. L. CONNOLLY (*J. Amer. Chem. Soc.*, 1911, 33, 1485—1487).—In the previous paper (Abstr., 1910, ii, 819) the authors have omitted to allow for the presence of tri-iodide and tri-bromide when calculating the concentrations of the iodide and bromide ions. After making the necessary corrections, the values of the constants are found to be $(H^+)(I^-)(HIO)/(I_2) = 0{\cdot}3 \times 10^{-12}$ and $(H^+)(Br^-)(HBrO)/(Br_2) = 5{\cdot}2 \times 10^{-9}$. T. S. P.

Citrophosphate Solutions. I. Homogeneous Equilibrium in Aqueous Solution Studied by the Cryoscopic Method. U. Pratolongo (*Atti R. Accad. Lincei*, 1911, [v], **20**, i, 812—818).—The author has carried out a series of cryoscopic determinations with solutions of citric acid, of diammonium citrate, and of mixtures of these substances with mono-, di-, and tri-calcium phosphates. Although no general conclusions are drawn from the results hitherto obtained, yet they do not yield any indication of the formation of complex ions from the citric and phosphoric acids, which has been supposed to take place by some authors (compare Barillé, Abstr., 1908, ii, 496; Quartaroli, this vol., i, 176). The indications are more in accord with the occurrence of double decomposition (compare Grupe and Tollens, Abstr., 1880, 825; Zulkowski and Cedivoda, Abstr., 1903, ii, 451).
R. V. S.

The Mechanical Stimulus to Crystallisation. II. S. W. Young and R. J. Cross (*J. Amer. Chem. Soc.*, 1911, **33**, 1375—1388. Compare this vol., ii, 261).—Observations have been made of the freezing point of water containing quartz particles of different sizes in suspension and stirred by the passage of hydrogen at a uniform rate. Assuming that the effect of foreign particles on the freezing point is entirely a kinetic one, and that the stimulus they offer to crystallisation is of an entirely mechanical character, certain conclusions were drawn and tested by experiment.

(1) *The Effect of the Mass of the Particle.*—A liquid charged with particles of large mass should permit of less supercooling than the same liquid charged with particles of small mass, since the disturbance produced by impact of two particles would be proportional to their masses. The experiments confirmed this, the masses of the particles varying from 0·000007 mg. to 0·002 mg.

(2) *The Effect of the Number of Particles.*—At low concentrations the results should be erratic and the amount of supercooling large, since the chances of impact between any two particles occurring within a given interval of time will be relatively small. As the concentrations of the particles increase, the average supercooling should become less, and the results more uniform. When a certain concentration is reached, further increase over a considerable range should not affect the result The experiments confirmed the above conclusions.

(3) *The Effect of Variations in the Viscosity of the Liquid.*—Increase in viscosity of the liquid will affect the smaller particles more than the larger ones, so that to reach the constant maximum effect, there will be required a considerably greater number of small particles than of large ones. Also, increase in viscosity of the water should protect it against the crystallisation stimulus of foreign particles, and this effect should be greater for small particles than large ones.

Experiments in which gelatin was added to the water were in agreement with the above conclusions.

The above principles are used to explain the conduct of supercooled liquids at rest with respect to their spontaneous crystallisation, special reference being made to the work of Jaffé (Abstr., 1903, ii, 469) and Tammann (Abstr., 1898, ii, 330). T. S. P.

Ultra-microscopic Observations. Carl Thomae (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 19—20).—The ultra-microscopic appearance of suspensions of finely-divided coloured substances in water is described, and the whitish appearance presented by particles of gold, platinum, Prussian-blue, and other substances under certain conditions is attributed to the particular size of the particles. This particular size of particle which can thus be identified in a simple optical manner is regarded as a transition stage between the colloidal and suspensoidal conditions. H. M. D.

The Structure of Ultra-microscopic Particles. The Svedberg and Katsuji Inouye (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 49—53).—Measurements have been made of the velocity of the Brownian motion of gold particles of different sizes. The colloidal solutions of gold were obtained in three different ways: (1) by the direct reducing action of hydrogen peroxide or hydrazine; (2) by Zsigmondy's germination method, or (3) by the aggregation method, according to which acid was added to the gold hydrosol obtained by the reducing action of phosphorus.

In the case of the small-sized particles of gold obtained by the first method, the Brownian motion is in good agreement with that calculated from Einstein's formula. For the same sized particles obtained by either of the other methods, the agreement is not satisfactory. In the case of larger particles, still greater deviations are found, the extent of the deviation being approximately the same whatever the method employed in the preparation of the hydrosol.

The observed deviations from the above kinetic equation lead to the conclusion that the larger particles deviate considerably from the spherical form. This deviation may be connected with the aggregation of a number of smaller units to form the larger sized particles.

H. M. D.

Gelatinisation- and Hydration-Capacity. P. P. von Weimarn (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 25—28).—The behaviour of various aqueous salt solutions when rapidly cooled to low temperatures is described and contrasted with the solubility of the salts and their tendency to form crystalline hydrates. The conditions favourable to gelatinisation of such solutions are re-stated. H. M. D.

Properties of Colloidal Systems. II. Adsorption as Preliminary to Chemical Reaction. William M. Bayliss (*Proc. Roy. Soc.*, 1911, **84**, *B*, 81—98. Compare Abstr., 1909, ii, 27).—If a dialysed deep blue colloidal solution of the acid of Congo-red is added to freshly-precipitated and well-washed aluminium hydroxide suspended in water, a dark blue precipitate is obtained, which can be washed by decantation and again suspended in water. This colloidal dark blue substance contains aluminium hydroxide, for on warming it is converted into the red aluminium salt. The same change occurs very slowly at room temperature. It is supposed that the dark blue colloid represents an absorption compound containing acid and base which are chemically uncombined. The change in colour from blue to red is indicative of combination between the two constituents. Similar adsorption compounds are formed when the aluminium hydroxide is replaced by zirconium, thorium, or ferric hydroxide.

Observations made with enzymes seem to show that a similar adsorption compound is formed between an enzyme and its substrate as a preliminary to the particular chemical change brought about by the enzyme in question. In particular, it is found that the influence of neutral salts on the enzyme adsorption is quite similar to that observed in cases of ordinary "electrical" adsorption.

Experiments with trypsin and invertase are also described, in which an attempt was made to determine the relationship between the concentration of the enzyme and its activity. Although the connexion between these can be expressed by an exponential formula, it appears that the value of the exponent varies considerably according to circumstances. H. M. D.

Properties of Colloidal Systems. III. Osmotic Pressure of Electrolytically-dissociated Colloids. William M. Bayliss (*Proc. Roy. Soc.*, 1911, *B*, **84**, 229—254. Compare Abstr., 1909, ii, 648).—No hydrolytic dissociation is to be detected in solutions of Congo-red, but electrolytic dissociation occurs to a large degree, the dye being 80% ionised in a concentration of 500 litres. This value, although large, is less than that of sodium salts of other organic acids of small molecular weight, probably owing to colloidal aggregation of the solutions of the dye-salt.

The osmotic pressure determined experimentally both by direct measurement and by vapour pressure is almost exactly what it would be if no dissociation existed. It should be, however, from one and a-half to three times this value, according to the concentration, an indication of abnormal conditions. The sodium ion is not inactive in the production of osmotic pressure, as shown by the agreement of vapour pressure with direct determinations of the osmotic pressure. Moreover, Chicago-blue, which consists of a single, large non-diffusible anion, like Congo-red, but with four Na ions instead of two, gives double the osmotic pressure of the latter at the same concentration.

The curve expressing the ratio of the conductivity of Congo-red solutions to their osmotic pressure is convex to the axis expressing the conductivity values. The relationship of osmotic pressure and molar concentration is expressed by a straight line. The value of the osmotic pressure per unit increase of conductivity rises with concentration, forming an S-shaped curve.

The possibility of aggregated simple ions carrying the sum of the charges of their components is suggested to explain the experimental results.

The distribution of a salt, such as sodium chloride, between the dye solution and water on opposite sides of the membrane is always such that its concentration is greater in the water. This peculiarity of distribution explains the effect of sodium chloride on the osmotic pressure.

If carbon dioxide has access to the outer water of the osmometer, an even approximately constant osmotic pressure cannot be obtained in the case of colloidal salts with a diffusible cation. This is due to an interchange of hydrogen and sodium ions, and hence the escape of the greater part of the sodium from the interior and precipitation of the acid salt.

Congo-red obeys the gas law so far as the effect of temperature on the osmotic pressure of its solutions is concerned. E. F. A.

The Colour and Degree of Dispersity of Colloidal Solutions. WOLFGANG OSTWALD (*Koll. Chem. Beihefte*, 1911, 2, 409—485).—Available data showing the relationship between the colour of colloidal solutions and the size of the colloidal particles have been subjected to a detailed examination. The colloidal substances involved are gold, silver, platinum, and other metals of the platinum series, mercury, copper, selenium, tellurium, the alkali metals, sulphur, iodine, metallic sulphides and oxides, and organic compounds.

From this comparison it appears that, in general, the absorption maximum is displaced in the direction of smaller wave-lengths as the degree of dispersity of the colloid increases. An apparent exception is found in the case of solutions of iodine in different organic solvents, but this is attributed to chemical changes in the nature of the disperse phase resulting from the combination of the iodine with the solvent to form disperse aggregates, the nature of which is dependent upon the nature of the solvent, the concentration, and the temperature. True colloidal solutions of iodine can only be obtained in presence of a protective colloid like starch, and in these circumstances it appears that the behaviour of iodine is in accordance with the above generalisation.

Various matters which have some bearing on the subject of the paper are discussed incidentally, such as the colour changes involved in the transition from the highly disperse colloidal condition to that represented by molecular disperse systems, and the colour changes exhibited by rock-salt when its temperature is raised. Experimental observations relating to the preparation of violet-blue, blue, green, yellowish-brown, and reddish-brown colloidal solutions of sulphur in glycerol are also described, and the view is put forward that ultramarin represents a solid solution of colloidal sulphur. It is also noted that the behaviour of sulphur is more complex than that of most of the other substances examined, in that it appears to give rise to two series of coloured colloidal solutions. In both these series, however, the variation of colour with the degree of dispersity of the sulphur is in accordance with the above general rule. H. M. D.

The System Gum Arabic–Gelatin. F. W. TIEBACKX (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 61—65. Compare this vol., ii, 378, 591).—Further experiments have been made on the coagulation of solutions containing gelatin and gum arabic, and on the peptisation of the coagulated products. Data are given which show the influence of various acids and salts at different concentrations, of the relative proportions of the gelatin and gum arabic, and of the temperature. It is pointed out that the investigation of a complex colloidal system of this character is of particular interest in connexion with the explanation of the various factors which have an influence on enzyme action, for it is possible that many enzymes may be regarded as complex aggregates comparable with that investigated by the author.

H. M. D.

Indifferent Points. JOUGUET (*Compt. rend.*, 1911, **153**, 346—349. Compare Saurel, Abstr., 1903, ii, 15).—A theoretical discussion. Given the pressure, temperature, and concentration of a component in one phase only, these are sufficient to define, not a single system, but a class of systems. The indifferent points for such a class are shown to form a continuum dependent on a single variable.

W. O. W.

Polarimetric Determination of Avidity of Weak Bases in Non-aqueous Solutions. EBERHARD RIMBACH and H. VOLK (*Zeitsch. physikal. Chem.*, 1911, **77**, 385—410. Compare Skraup, Abstr., 1895, ii, 259).—The activity of ammonia and a number of optically inactive fatty and aromatic amines has been determined in solution in methyl and ethyl alcohols by finding the extent to which they displaced cinchonidine from combination as the nitrate. The position of equilibrium was determined by polarimetric measurements. Corrections were applied for the influence of the free inactive base and of the nitrate of the inactive base on the rotation of the cinchonidine and cinchonidine nitrate respectively. In most of the experiments the ethyl alcohol used as solvent contained 97·5 vol. % of alcohol; the methyl alcohol contained 99·5% by weight of pure alcohol.

From the results the dissociation constants of the bases are calculated, and are represented in tabular form; the relative activities are also referred to ammonia as unit. On the whole the relationships between the strength of the bases and their constitution are similar to those observed in aqueous solution. The activity increases on substituting alkyl groups for hydrogen in ammonia. The strength of the bases increases from methylamine to ethylamine, falls to butylamine, and then increases with increasing complexity of the substituting group. In contrast to piperidine, formylpiperidine is a very weak base, as in aqueous solution.

The most marked difference between the results in aqueous and alcoholic solution is that the activity diminishes regularly when the remaining hydrogen atoms in a primary amine are successively displaced by alkyl groups, whereas in aqueous solution dimethylamine is a stronger base than ethylamine or triethylamine. This result appears to support the suggestion of Walker (compare Abstr., 1906, ii, 735) that the abnormal behaviour of the alkylamines in aqueous solution is due to differences of hydration. G. S.

The System Hydrogen Sulphide–Water. F. E. C. Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 195—201. Compare this vol., ii, 264).—The equilibrium relationships of the system hydrogen sulphide–water have been further investigated, and data are recorded showing the composition of the two liquid phases, which are in equilibrium with vapour and the solid compound, at different temperatures. At the quadruple point, the one liquid contains about 1·3 mols. % of water, and the other 3·4 mols. % of hydrogen sulphide. From these values it is evident that the region of non-miscibility extends almost completely over the width of the concentration diagram.

Analyses of the solid hydrate have been made, from which the author draws the conclusion that its composition is represented by $H_2S,5H_2O$. The greater proportion of water indicated by the analyses of previous workers is attributed to the readiness with which water becomes enclosed in the solid hydrate. H. M. D.

The System Water–Phenol. Andreas Smits and J. Maarse (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 192—195).—The behaviour of liquid mixtures of water and phenol when cooled has been investigated, and a freezing-point diagram constructed. From this it appears that a definite compound, $2C_6H_5{\cdot}OH,H_2O$, is formed, which melts at 16°, as described by Calvert (*Zeitsch. Chem.*, 1865, 1, 530). The inability of Paternò and Ampola (Abstr., 1897, ii, 476) to observe the formation of this compound is probably due to the readiness with which metastable conditions make their appearance. The following significant equilibrium temperatures were determined: solid phenol in metastable equilibrium with two liquid phases, 1·70°; ice, solid phenol, and liquid, 1·2°; ice, solid hydrate, and liquid, −1·0°; solid hydrate, solid phenol, and liquid, 15·8°; stable equilibrium between solid phenol and two liquid phases, 12·2°. H. M. D.

The System Acetaldehyde–Ethyl Alcohol. H. L. de Leeuw (*Zeitsch. physikal. Chem.*, 1911, **77**, 284—314).—The densities, boiling points, heats of reaction, viscosities, refractivities, and melting points of mixtures of ethyl alcohol and acetaldehyde in different proportions have been measured. The results show that under certain conditions two compounds exist containing 1 mol. of aldehyde to 1 and 2 mols. respectively of alcohol. The existence of the first compound is proved by the occurrence of distinct maxima in the curves representing the variation of the different physical properties with composition; the existence of the second compound is shown most definitely by the freezing-point curve.

When acetaldehyde and alcohol are mixed, there is at first a slight cooling effect, and then the temperature gradually rises. It follows that the heat of mixing is negative, whereas the heat of reaction is positive. The latter attains its maximum value when the components are mixed in equivalent proportions, and amounts to about 1000 cal. per mol.

The boiling-point curves were determined at pressures of 9·7, 40, and 70 cms. At the two lower pressures, the form of the curves indicates the existence of a highly dissociated compound, but at the higher pressure the curves are normal, showing that at the corresponding temperature the compound is completely dissociated.

In connexion with the freezing-point determinations, a very accurate resistance thermometer is described. Acetaldehyde melts at −123·3°, ethyl alcohol at −114·9°.

In the presence of anhydrous copper sulphate, the double compound of alcohol and aldehyde slowly loses water, acetal being formed.

G. S.

The Course of the P.T.-Lines for Constant Concentration in the System Ether–Anthraquinone. ANDREAS SMITS and J. P. TREUB (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 183—188. Compare Abstr., 1909, ii, 987).—The changes which occur in the form of the pressure-temperature curves as the molar proportion of anthraquinone is gradually increased are discussed in detail.

H. M. D.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. V. Fluorene and Polynitrobenzenes. ROBERT KREMANN [with DISCHENDORFER, FRANKOVIC, HAUSER, HÖNEL, SCHOULZ, and VALENTA] (*Monatsh.*, 1911, **32**, 609—617. Compare Abstr., 1906, ii, 268; 1909, ii, 28).—Freezing-point curves of mixtures of fluorene with nitro-compounds show that fluorene does not form compounds with any of the dinitrobenzenes or with 2 : 4-dinitrotoluene or 2 : 4-dinitrophenol. On the other hand, trinitrobenzene, trinitrotoluene, and picric acid yield compounds with fluorene, giving rise to maxima on the freezing-point curve. Fluorene resembles benzene and phenanthrene in this respect, whilst naphthalene can also combine with compounds containing two nitro-groups in an ortho-position.

C. H. D.

Homogeneous Allotropy in a Pseudoternary System. The Termolecular Pseudoternary System Acetaldehyde–Paracetaldehyde–Metacetaldehyde. ANDREAS SMITS and H. L. DE LEEUW (*Zeitsch. physikal. Chem.*, 1911, **77**, 269—283).—The equilibrium in the system acetaldehyde–paracetaldehyde–metacetaldehyde has been determined. It is shown that although the equilibria in the homogeneous pseudobinary systems acetaldehyde–metacetaldehyde and paracetaldehyde–metacetaldehyde must be in the region where metacetaldehyde is present in the supersaturated state, at the equilibrium point in the pseudoternary system the mixture is not supersaturated with regard to metacetaldehyde. Further, the pseudoternary equilibrium is a closed one; in other words, the three components are in complete equilibrium with each other. It is shown that these assumptions account for all the observed phenomena. For example, when a homogeneous mixture at its boiling point, 41·6°, is suddenly cooled to 18°, a little metacetaldehyde separates, showing that all three forms were present at the higher temperature. From the magnitude of the heats of combustion, the conclusion is drawn that the dissociation should be increased by raising the temperature, and this is borne out by the experimental results.

On the basis of these and other observations, the equilibria in the system are represented on a projected space diagram. Metacetaldehyde melts under the pressure of its own vapour at 246·2°.

G. S.

Speed of Propagation of Chemical Reactions. W. SREBNITSKY

(*J. Russ. Phys. Chem. Soc.*, 1911, **43**, *Phys. Part*, 148—156).—The author has studied the rate at which the reaction

$$5H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 = 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

is propagated through the liquid when one part of the latter is brought into contact with a solution in which the reaction has already taken place, that is, one represented by the right-hand side of the equation, this acting as a catalyst. The catalytic liquid was poured carefully on to the surface of the other solution in a test-tube immersed in a thermostat, and the passage of the reaction down the tube followed by the decolorisation of the liquid.

The rate of propagation is accelerated with lapse of time; in one experiment the vertical distances covered by the reaction in equal successive intervals of time being, 0·5, 0·6, 0·75, 1·0, 1·5, and 2·5 mm.

The rate of propagation of the reaction diminishes markedly with increase in the diameter of the tube, for example, from 4·5 mm. per ten minutes in a 3 mm. tube to 1·6 mm. for a 9·5 mm. tube and to 1·4 mm. for a 14·5 or 30 mm. tube. The conclusion is drawn that the adsorption of the walls of the tubes has a decided influence on the propagation.

Increasing amounts of quinol cause an increase of the rate of propagation, represented by a quadratic parabola with the axis of velocity of propagation as its axis. The rate of propagation is proportional to the concentration of the reacting solution, and is increasingly accelerated with rise of temperature; for example, 0·3 mm. at 16·4°, 0·4 at 17·8°, 0·7 at 20°, 1·2 at 22°, and 1·9 at 25°.

T. H. P.

Theory of Platinum Catalysis with Reference to the Oxidation of Hydrogen by Sulphuric Acid. JAROSLAV MILBAUER

(*Zeitsch. physikal. Chem.*, 1911, **77**, 380—384).—The effect of platinum in different forms on the rate of oxidation of hydrogen by sulphuric acid at 174° has been determined. The measurements were made by the method already described (Abstr., 1907, ii, 252). The results show that the maximum catalytic effect is obtained when the sulphuric acid is saturated (not supersaturated) with a soluble platinum salt, probably platinum sulphate. The saturation occurs most readily when the platinum is used in the form of platinum-black. The reaction is retarded to some extent by arsenious oxide. G. S.

Action of Acids on the Catalytic Oxidation of Phenols by Ferric Salts. H. COLIN and A. SÉNÉCHAL

(*Compt. rend.*, 1911, **153**, 282—283).—The formation of complex ferric compounds referred to in a previous communication (this vol., ii, 795) cannot be the only cause of the retarding action exerted by organic acids on artificial peroxydase systems, since addition of sugars, glycerol, or acetylacetone has little effect on the rate of oxidation of quinol by such systems. W. O. W.

Grading of the Intensity in the Properties of Chemical Compounds and Additive Products. Basil B. Kuriloff (*Chem. Zeit.*, 1911, **35**, 1005).—A chemical compound is characterised by a large number of properties, which, however, can be referred to comparatively few types. One series of properties is necessitated by the law of constant proportions, another by the valency of the elements, a third by the law of mass action (for example, constant dissociation pressure, definite solubility, etc.), and, finally, a fourth by the phase rule. A typical chemical compound possesses the properties of all the above classes, but additive products do not necessarily belong to all four classes.

In the light of the above principles, the author shows how various compounds and additive products can be classified. T. S. P.

Ionogenic Atomic Groups and Atoms. Oscar Hinsberg (*J. pr. Chem.*, 1911, [ii], **84**, 169—193).—This paper contains an extension of the views of Vorländer (Abstr., 1899, i, 309, 312; ii, 250; 1901, ii, 444; 1902, ii, 250) and Henrich (Abstr., 1899, i, 469, 794; 1900, i, 429) on the nature of radicles. In developing his ideas, the author was guided by the difference in the activity of the extra-nuclear hydrogen atoms of benzaldehyde, benzoic acid, and perbenzoic acid. Whilst the hydrogen atom in benzaldehyde is very reactive but not ionisable, that of benzoic acid, although very readily ionised, shows little chemical activity. In the case of perbenzoic acid, the hydrogen atom is neither reactive nor ionisable. From these considerations the conclusion is drawn that the carbonyl group exerts a two-fold influence on hydrogen atoms in the molecule; firstly, a "reactivating" influence, as in the case of benzaldehyde, and, secondly, an acidifying action, which is restricted to hydrogen atoms in the β-position. This double influence is not confined to the carbonyl group, but is shared by all unsaturated groups, for example, $O{:}\dot{S}{:}O$, $O{:}\dot{P}{:}O$, $\cdot CN$, $\cdot NO$. According to the author, the reactivating influence is due to intramolecular attractions and repulsions. The acidifying or ionogenic action, on the other hand, is a special characteristic of unsaturated groupings, and is confined in all cases to atoms in the β-position. All unsaturated groups and atoms causing ionisation of other atoms or groups in the β-position are termed ionogens of the second order; the strongly negative elements, such as the halogens and sulphur, are ionogens of the first order, for these elements bring about the ionisation of atoms (hydrogen or metals) only when in direct combination with them.

The author further distinguishes between negative and positive ionogenic radicles and atoms; negative ionogens give rise to acids, positive ionogens to bases.

Chlorine is an ionogen of the first order, and therefore should have no effect on atoms not in direct combination with it. A comparison of the acidic properties of acetic and trichloroacetic acid shows, however, that the chlorine atom exerts a strongly negative influence on the hydroxylic hydrogen. This is referred to the hydrogen atom being under the simultaneous ionogenic influence of the carbonyl group.

Atoms or groups of this kind which intensify or weaken an ionogenic valency already present in the molecule are termed "commutating" atoms or groups. The commutating effect of the sulphur atom affords an explanation of the greater reactivity of the methylene hydrogen atoms in ethyl thioacetate, $S(CH_2{\cdot}CO_2Et)_2$, as compared with the methyl hydrogen atoms of ethyl acetate.

The basic properties of triphenylcarbinol, distyryl ketone, and of the iodoso- and iodonium compounds are referred to the presence of the vinylene group, $\cdot CH{:}CH\cdot$, which functions as a positive ionogen of the second order when attached to a carbon or iodine atom.

a-Thiocinnamic acid, $S(CHPh{:}C{\cdot}CO_2H)_2$, prepared by condensing ethyl thioacetate with benzaldehyde by means of methyl-alcoholic sodium methoxide, crystallises in small, colourless needles, m. p. 228—230° (decomp.). F. B.

Dr. Johnstone Stoney's Logarithmic Law of Atomic Weights.

LORD RAYLEIGH (*Proc. Roy. Soc.*, 1911, *A*, **85**, 471—473).—Extracts are given from a paper communicated by Dr. Stoney to the Royal Society in 1888, and published in part in *Proc. Roy. Soc.*, 1888, **44**, 115.

By taking a series of spheres the volumes of which are proportional to the atomic weights of the elements, and using the radii of these spheres as radii vectors of a polar diagram, a curve is obtained which closely resembles the positive branch of the logarithmic spiral of the second order corresponding with the equation $\tau = \kappa \log(q\theta)$. The author claims that this spiral affords the same information as a Mendeléeff's table, and, in addition, furnishes an intelligible representation of the atomic weights.

The absence of elements on a particular sesqui-radius is referred to, and the vacant places pointed out are now occupied by the since-discovered inert gases. In Lord Rayleigh's opinion, this anticipation goes far to justify the high claims made for the diagram by the author.

H. M. D.

The Significance of the Periodic Law.

FERNANDO SANFORD (*J. Amer. Chem. Soc.*, 1911, **33**, 1349—1353).—Since the disintegration products of uranium seem to fall into their proper positions in the periodic series, it would seem to follow that the other elements of these groups must in the same way be formed by adding alpha particles and electrons to elements of lower atomic weight. The atomic weights of successive elements do not, however, increase by four or multiples of four, but this difficulty is largely overcome for a considerable part of the series, by assuming two parallel lines of development, one line starting from helium (Gl, C, and O) and one from lithium (B, N, and F). These two series have, in fact, long been separated on the basis of their chemical valency, the elements of the helium series having zero valency or even valencies, whilst the elements of the lithium series have odd valencies. They have likewise been separated on the basis of their spectra, the elements of the helium series having their spectral series made up of single lines or groups of three, whilst the elements of the lithium series have their spectral lines arranged in pairs.

The author then discusses a possible cause of radioactivity, and the possibility of artificially changing one element into another, based on the idea that as the electropositive charges on the elements increase, their hold upon the α-particles must decrease, and the heavier elements must accordingly become more and more unstable, since the positive charges carried by many of the elements are proportional to the square roots of their atomic weights (Sanford, *Phys. Review*, 1911, 32, 512). T. S. P.

A Handy Burette Holder. NORMAN ROBERTS and F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1911, 33, 1402—1404).—A piece of board (50 × 8 × 2·2 cm.) is bored, a little in front of the middle, with a row of holes about 2·5 cm. in diameter and 5 cm. between the centres. The holes are then connected with the front of the board by slots about 1·7 cm. wide. The bored holes are filed out so as to be slightly conical, with the base up. Conical corks to fit the holes are then bored with borers slightly smaller than the burette they are to carry, and split longitudinally into two equal parts. When the two halves of the cork are placed round a burette and then wedged in one of the holes, the burette will be held firmly, but at the same time may be easily slid up and down. A further improvement is to cut a shallow groove round the upper end of the cork and place in it two or three light rubber bands, so as to keep the two parts of the cork in position.

The perforated board is supported in a bracket, and then forms a convenient holder for several burettes. It may also be used as a funnel support. T. S. P.

An Electrically-heated Sealed Tube Furnace. RAYMOND C. BENNER (*J. Amer. Chem. Soc.*, 1911, 33, 1402).—The tubes of an ordinary bomb furnace are covered with a layer of thin asbestos paper and then wound, each with 55 feet of No. 22 B.S. asbestos-covered nichrome resistance wire, the winding being rather closer at each end of the tube than in the centre. The space within the box and around the tubes is filled with asbestos fibre and magnesium oxide. The tubes are then connected with the 110 volt circuit, about two amperes flow when they are in parallel, and one ampere when in series, the temperatures attained being respectively about 240° and 440°. When no packing is put in the box, the respective temperatures are about 150° and 250°. T. S. P.

Apparatus for Maintaining the Level of a Liquid. EUGEN NOGA (*Chem. Zeit.*, 1911, 35, 997).—The liquid to be evaporated is contained in a large bottle fitted with a two-hole bung, through the one hole of which passes a siphon tube leading to the bottom of the bottle, and through the other hole passes a short right-angled tube. The siphon tube is connected, by means of rubber tubing, with a vertical tube which opens on to the evaporating dish (or on to a funnel in the case of filtration), and which is sealed, at the upper end, into a wider tube, the bottom of which is flush with the narrow tube. Near the seal, the wider tube contains a side-tube which is connected by rubber tubing with the right-angled tube in the bottle.

By means of this arrangement, the level of the liquid in the evaporating dish is automatically maintained constant. T. S. P.

Automatic Filtering of Solutions by Maintaining a Constant Level. Fr. C. Bellaire-Wörschweiler (*Chem. Zeit.*, 1911, **35**, 880).—The principle of the apparatus is as follows: The liquid to be filtered is contained in a large bottle placed on a shelf. A siphon tube leads from the bottle and opens on a filter funnel placed in the neck of another large bottle. A stopcock is inserted in the siphon tube, and is so regulated that the rate of flow of the liquid on to the filter funnel equals the rate of filtration. T. S. P.

Improvements in Receivers for Vacuum Distillations. E. John (*Chem. Zeit.*, 1911, **35**, 943).—To an upright rod inserted in a plate base are soldered six pairs of thin metal strips which can be used to hold receivers of any shape and size. This arrangement replaces the ordinary one in the well-known Brühl's receiver, where all the vessels are of the same size and shape. T. S. P.

Apparatus for Continuous Fractional Distillation. M. M. Tichwinsky (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 806—808).—This apparatus is so constructed that each drop of liquid is virtually distilled separately, the thermometer standing automatically at a definite temperature during the whole of the distillation.

The liquid is placed in a separating funnel which stands on a shelf, and is connected with a tube passing through the stopper in the top of the fractionating column. The latter is filled with metallic beads, these being also placed in the side-tube which carries the thermometer nearly up to the bulb of the latter. The column is fitted to a short-necked round-bottomed flask, which together with the burner and the lower portion of the column is protected from draughts by asbestos.

When a little of the liquid is boiled in the flask, distillation soon sets in, and the thermometer becomes stationary. Fresh liquid is then introduced, drop by drop, into the top of the column. With this procedure, the temperature remains surprisingly constant, and there is no difficulty in obtaining a fraction for every two degrees.

Into such a column, made of Bohemian glass, it is safe to drop cold liquid if the temperature is not above 130°. For higher temperatures the liquid is not dropped, but is passed down a tube open at the bottom and enclosed in a wider tube sealed at the bottom, and provided with a lateral orifice at some distance from the bottom; the liquid thus becomes warmed before it issues through the orifice into the column.

By means of this apparatus, a sample of Grosny light petroleum, b. p. 134—137°, was separated into the following fractions: (1) 110 c.c., b. p. 129—130°, D^{19} 0·7631; (2) 40 c.c., b. p. 129—130·5°, D^{19} 0·7634;

(3) 120 c.c., b. p. 132—133°, D^{19} 0·7661; (4) 173 c.c., b. p. 135—136°, D^{19} 0·7675. Nononaphthene has b. p. 135—136° and D^{20} 0·7652.

T. H. P.

New Water Decomposition Apparatus with a Dividing Wall. KARL WOYTAČEK (*Chem. Zeit.*, 1911, **35**, 943).—Instead of the two separate decomposition tubes of an ordinary Hofmann voltameter, one tube is used with a dividing wall down the centre. At the top of the tube each compartment is provided with a tap, and the bottom of the tube below the partition connects with the levelling tube. The electrodes placed in each compartment just above the bottom of the partition are thus fairly close together, and the electrical resistance of the apparatus is small. Being very compact it is not easily breakable. T. S. P.

An Improved Soxhlet Condenser. OSWALD SILBERRAD (*Chem. News*, 1911, **104**, 54).—In order to do away with the cork joint between the top of a Soxhlet extractor and the lower end of the reflux condenser, the author simply inserts a bulbous Walters condenser into the open end of the Soxhlet tube, which is somewhat lengthened for the purpose. This, at the same time, does away with the necessity of clamps, etc., for supporting the condenser.

T. S. P.

A New Extraction Apparatus. G. A. QUINCKE (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 171—172).—The apparatus consists of a glass cylinder, at the bottom of which is placed a flask containing the solvent; the substance to be extracted is placed in a syphon-vessel fitted above the flask and held in position by means of springs which press against the sides of the cylinder, and a suitable glass condenser fits into the top of the cylinder. The latter is heated by means of a water-, oil-, or sand-bath, according to the boiling point of the solvent employed. The apparatus is readily taken apart for cleaning, and the use of corks or rubber stoppers is rendered unnecessary.

W. P. S.

Two New Forms of Apparatus for Extraction of Liquids with Organic Solvents. F. C. TEN DOORNKAAT KOOLMAN (*Biochem. Zeitsch.*, 1911, **34**, 481—484).—Both forms are figured, and both are constructed on the principles generally adopted for apparatus of this class. The essential modification of one form consists in the connexion of the apparatus with an air blast, so that the liquid is kept in constant agitation during extraction. In the other form, the liquid to be extracted is kept in a long spiral tube, through which the bubbles of the solvent pass. S. B. S.

Inorganic Chemistry.

Apparatus for the Evolution of Large Quantities of Hydrogen Sulphide and Partial Recovery of the Waste Gases from Precipitation Reactions. A. GWIGGNER (*Chem. Zeit.*, 1911, **35**, 891).—The apparatus is similar in principle to that described by the author for the evolution of hydrogen chloride (Abstr., 1901, ii, 93). The waste gases from precipitation reactions are led up a tube filled with glass beads and down which water trickles, and thereby recovered as hydrogen sulphide water. T. S. P.

Action of Thionyl Chloride on Metallic Oxides. GEORGES DARZENS and FRANÇOIS BOURION (*Compt. rend.*, 1911, **153**, 270—272. Compare Abstr., 1909, ii, 229; Matignon, Abstr., 1905, ii, 459).—When passed over heated metallic oxides below 400°, the vapour of thionyl chloride behaves like the mixture of chlorine and sulphur chloride previously used as a chlorinating agent (Abstr., 1907, ii, 690), producing either the anhydrous chloride, as in the case of thorium oxide, or an oxychloride, as in the case of tungstic oxide. Thionyl chloride is less advantageous in practice than the mixture mentioned, owing to the difficulty in obtaining it free from phosphorus compounds. W. O. W.

The Reduction of Nitrosylsulphuric Acid by Mercury. O. WENTZKI (*Zeitsch. angew. Chem.*, 1911, **24**, 1468).—Polemical against Divers (this vol., ii, 596). T. S. P.

Apparatus for the Generation of Carbon Dioxide. C. PURRMANN and P. VERBEEK (*Chem. Zeit.*, 1911, **35**, 927—928).—Hydrochloric acid contained in a reservoir of special construction is allowed to run into a bottle filled with acid, causing the same to enter a bottle filled with pieces of marble. The gas evolved first passes through an empty bottle, where it deposits any foam; it then passes through a tall wash-bottle containing, besides water, a number of pieces of marble to absorb any hydrochloric acid fumes. For full details, the illustration in the original article should be consulted. L. DE K.

Colloidal Sulphur. M. RAFFO and J. MANCINI (*Zeitsch. Chem. Ind. Kolloide,* 1911, **9**, 58—61. Compare Abstr., 1908, ii, 683).—The colloidal sulphur obtained by the slow addition of a concentrated solution of sodium thiosulphate to cooled concentrated sulphuric acid has been subjected to dialysis with the object of determining the dependence of the stability of the solution on the presence of sulphuric acid and sodium sulphate. From measurements of the quantities of sulphur, acid, and sodium sulphate present after different periods of dialysis, the authors draw the conclusion that the presence of definite amounts of electrolyte are necessary for the stability of a colloidal sulphur solution of given concentration. As the electrolytes are progressively removed by dialysis, more and more sulphur separates from the solution in amorphous form.

The coagulation of colloidal sulphur by different electrolytes has also been examined. It is found that potassium salts are much more active than the corresponding sodium salts, whilst these are a little less effective than magnesium and zinc salts. H. M. D.

Reversible Light Reaction of Sulphur. ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1911, **77**, 423—471. Compare Abstr., 1908, ii, 676; 1909, ii, 228).—When soluble sulphur (S_λ) is exposed to light, it changes slowly into insoluble sulphur. It is now shown that the reaction in question is reversible in light, and a true photochemical equilibrium is attained, both in the case of liquid and dissolved sulphur. The position of equilibrium and the rate of change depends on a number of factors, such as the temperature, rate of stirring, nature of solvent, extent of surface exposed to light, etc., and the effect of each of these factors is described in detail.

In most of the experiments, a mercury-vapour lamp was used as the source of illumination. The principal solvents were carbon tetrachloride and benzene. The relative proportions of S_λ and S_μ were determined by evaporating off the solvent in a vacuum, and extracting the soluble S_λ from the residue; after repeating this process twice, the clear solution was evaporated and the S_λ weighed. In the case of liquid sulphur, the position of equilibrium was determined from the results of freezing-point experiments. When liquid or dissolved sulphur is exposed to light, the S_μ first separates in the colloidal form, and this process has been followed (in the case of solutions) by means of the ultra-microscope.

The absorption of light in sulphur solutions and in liquid sulphur was measured by means of the spectrophotometer.

The heat of solution in carbon disulphide, measured with the ice calorimeter, is for rhombic sulphur, −12·3 cal., and for soluble amorphous sulphur, −1·0 cal. per gram. When 1 gram of S_μ is precipitated from a carbon disulphide solution under the influence of light, 15·8 cal. are absorbed; when carbon tetrachloride and benzene are used as solvents, rather less energy is absorbed. For the last two solvents it was found that the energy absorbed in the same interval of time is equal to the product of amount of S_μ precipitated and the work done in the transition. Of the energy absorbed, about 0·24% is used up in bringing about the transformation. G. S.

Relation between the Three Triple Points of Sulphur. Hugo R. Kruyt (*Chem. Weekblad*, 1911, 8, 643—648).—No striking proof has been put forward of van't Hoff's expression for the relation of the triple points of sulphur $\frac{Q\longrightarrow}{T\longrightarrow} - \frac{Q_{rh}}{T_{rh}} + \frac{Q_{mon}}{T'_{mon}} = 0$, in which Q_{rh} is the heat of fusion of rhombic sulphur, Q_{mon} that of monoclinic sulphur, $Q\longrightarrow$ the transition heat of the conversion of the rhombic into the monoclinic form, and T_{rh}, T_{mon}, and $T\longrightarrow$ the corresponding equilibrium temperatures. The author points out that the most recent results support van't Hoff's views. For $Q\longrightarrow$ Brönsted (Abstr., 1906, ii, 339) obtained the value 3 28; for Q_{rh} Lewis and Randall's (this vol., ii, 371) value recalculated for the corresponding temperature was 15·4; for Q_{mon} the author obtained 12·1 by combining the two values, and for $T\longrightarrow$ 273 + 95·6; for T_{rh} Smith and Holmes (Abstr., 1903, ii, 284) found 273 + 110·5; and Reicher's (*Diss. Amsterdam*, 1883) old, hitherto unchecked, value for T_{mon} was 273 + 114·5. A. J. W.

Some Alloys of Metals with Silicon and the Density of Alloys. R. Frilley (*Rev. de Métallurgie*, 1911, 8, 457—559).—A large number of alloys of different metals with silicon have been prepared, and their densities determined by means of a specific gravity bottle. By plotting the specific volumes against the percentage composition, curves are obtained showing certain discontinuities, which are rendered more obvious by plotting the molecular volumes. The silicides assumed from these results to exist are much more numerous than those indicated by thermal methods. The method is also applied to alloys of copper with aluminium and with tin, and to alloys of cadmium with mercury. C. H. D.

The Structure of the Gel of Silicic Acid. The Theory of Dehydration. RICHARD ZSIGMONDY (*Zeitsch. anorg. Chem.*, 1911, **71**, 356—377).—The moist silicic acid gel is transparent, as in the dry, glassy mass obtained on dehydration, but during the evaporation of the water an intermediate stage is passed through, in which the mass is white and opaque. This has been attributed to the porosity of the gel, and the diameter of the pores has been calculated to be 1—1·5μ. This is improbable in view of the transparency of the gel, and it is now shown by ultramicroscopical investigation of a dry silicic acid gel saturated with benzene that the true size of the particles is very small, and that the observed coarse structure is due to the accumulation of liquid in some parts, separated by air.

The peculiarities of the curves of dehydration obtained by van Bemmelen (Abstr., 1897, ii, 137) may be explained by assuming that the vapour pressure of the retained water is diminished by the presence of fine capillaries. Assuming the capillary formulæ to hold for such small dimensions, the diameter of the pores is calculated to be 5$\mu\mu$ for a depression of vapour pressure of 6 mm. The difference between the curves of dehydration and subsequent re-hydration may be explained as caused by the liquid failing to wet the walls completely in the second case, owing to the presence of adsorbed air. The irreversible changes are due to the union of amicronic particles of silica to form larger particles, probably crystalline.

When silicic acid gel is immersed in a hydrosol of silver, ferric hydroxide, benzopurpurine, or carmin, it acts as an ultra-filter, water penetrating into the gel, whilst a layer of colloid is formed on its surface. C. H. D.

Determination of the Absolute Value of the Viscosity of Molten Silicates. CORNELIUS DOELTER and H. SIRK (*Monatsh.*, 1911, **32**, 643—653).—The absolute viscosity of molten silicates may be measured by the method employed by Arndt (Abstr., 1907, ii, 745) for borates and phosphates. A platinum sphere, 6 mm. in diameter, is partly balanced, and the time taken by it to fall through a given distance is measured. Synthetic diopside, melted in a crucible of Marquardt's mass, has been used for the preliminary experiments. The specific gravity of the molten mass, which must be known, is determined by weighing the platinum sphere when immersed, and also by the floating method, using meionite, quartz, and anorthite. Diopside has D^{1290} 2·8.

Castor oil is used as a standard substance for calibrating the apparatus. The absolute viscosity of diopside, in C.G.S. units, is found to be 106 at 1280°, diminishing rapidly with use of temperature, and reaching 33 at 1300°. C. H. D.

The Hydration and Hardening of Cement. PAUL ROHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 21—22).—Keisermann's statement (compare Abstr., 1910, ii, 848) that the author regards the hardening of cement as due to the combination of silicic acid with free lime is refuted. In the author's opinion the hardening consists in the formation of solid solutions or adsorption compounds. A microphotograph by Ambronn, showing the appearance of cement during the hardening process, is given as evidence in support of the colloido-chemical theory of the process. H. M. D.

The Melting of Carbon. O. P. WATTS and C. E. MENDENHALL (*Ann. Physik*, 1911, [iv], **35**, 783—789).—The deformation of carbon rods at very high temperatures has been examined in continuation of experiments of La Rosa (Abstr., 1909, ii, 399, and *Ann. Physik*, 1911, [iv], **34**, 95). Comparative observations with samples of American and German carbon rods and of Acheson graphite showed that the lowest temperatures at which deformation took place were respectively 1800°, 1900°, and 2150°. The mechanical properties and the effect of applied stress on the heated rods as well as the appearance of slowly and rapidly heated rods in cross section after cooling are described in some detail. From the experiments, the authors draw the conclusion that the observed deformation is due to gradually increasing plasticity of the carbon, and not to the commencement of melting. The changes in the structural appearance are attributed to volatilisation and subsequent condensation. H. M. D.

Catalytic Preparation of Ammonia from Compounds Containing Nitrogen and Carbon. F. SCHREIBER (*Chem. Zeit.*, 1911, **35**, 943).—When carbon or carbohydrate compounds containing nitrogen are heated at 350° with hydrated iron oxide, the nitrogen is transformed into ammonia and carbon dioxide is formed. Experiments in which pyridinesulphonic acid, albumin, potassium ferrocyanide, or Prussian-blue were heated at 350° with excess of an ore containing 32·95% Fe_2O_3, 22·07% FeO, and 10·83% H_2O showed that 47—73·7% of the total nitrogen was converted into ammonia. When gas from coke ovens and containing 40·4 grams of hydrogen cyanide per 100 cubic metres was led over the iron oxide heated at 350°, 32·7—47·6 grams of ammonia per 100 cubic metres were obtained. T. S. P.

The Ratio of the Molecular Weights of Potassium Chlorate and Potassium Chloride. ARTHUR STAHLER and FRIEDRICH MEYER (*Zeitsch. anorg. Chem.*, 1911, **71**, 378—402).—Potassium chlorate cannot be fused or dried at 350° without slight decomposition. The salt is repeatedly recrystallised, dried at 100°, and weighed. It is then fused in a quartz vessel, and the water evolved is collected and weighed, the weight of the dry potassium chlorate being thus calculated. The salt is then covered with water, and decomposed by means of purified hydrogen chloride at 0°, quartz vessels being used. The mixture of chlorine and chlorine oxides evolved is condensed by means of a mixture of alcohol and liquid air, a further vessel being cooled directly by liquid air. The water is removed from the decomposition vessel by slow evaporation in a current of dry air, and the residual potassium chloride is then heated to 200—300°, and finally fused in a stationary atmosphere of pure nitrogen and cooled in dry air.

The contents of the condensing vessels are dissolved in water and slowly evaporated in a quartz basin. A minute residue, consisting chiefly of potassium perchlorate, is obtained. It is evaporated with pure perchloric acid and weighed. The final results give, as a mean of five determinations, the ratio $KClO_3 : KCl = 1{\cdot}643819$. For $O = 16$ and $K : Cl = 1{\cdot}102641$, this gives $K = 39{\cdot}097 \pm 0{\cdot}0004$ and $Cl = 35{\cdot}458 \pm 0{\cdot}0004$. C. H. D.

Deformation in Mimetic Crystals. Paul Fischer (*Jahrb. Min.*, 1911, *Beil-Bd.*, **32**, 1—48).—Crystallographic descriptions are given of the following salts: ammonium sulphate, potassium sulphate, triammonium hydrogen sulphate $[(NH_4)_3H(SO_4)_2]$, tripotassium hydrogen sulphate $[K_3H(SO_4)_2]$, and potassium chlorate. A detailed study was made of the twin lamination produced by pressure or by changes of temperature. As indicated by changes in the optical properties with increasing temperature, the last three salts are dimorphous. L. J. S.

The Liquidus Surface of the Ternary System Composed of the Nitrates of Potassium, Sodium, and Calcium. Alan C. W. Menzies and N. N. Dutt (*J. Amer. Chem. Soc.*, 1911, **33**, 1366—1375).—The freezing points of seventy-one different binary and ternary mixtures of the nitrates of potassium, sodium, and calcium have been determined, and from the results the isotherms representing the contour lines of the liquidus surface have been plotted for each 10° interval to 300°, and for each 50° interval above that temperature.

The freezing points of sodium and potassium nitrates were found to be 315·1° and 346·3° respectively. The freezing point of the mixture represented by $NaNO_3,KNO_3$ was 228·1°; that of the mixture $NaNO_3,Ca(NO_3)_2$ was 261° (by interpolation), whereas Maumené (1883) found 235°. T. S. P.

Lithium Amalgams. G. J. Schukoffsky (*Zeitsch. anorg. Chem.*, 1911, **71**, 403—418; *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 708—725). —In the preparation of lithium amalgams, the dried lithium is rapidly introduced into an iron vessel containing some mercury. The vessel is closed and heated until combination has taken place, and, after cooling, mercury is added as required. For the thermal analysis, a protecting layer of paraffin, or for higher temperatures eutectic mixtures of potassium and lithium chlorides, m. p. 352°, or of lithium and rubidium chlorides, m. p. 312°, are used.

The freezing-point curve indicates the existence of five compounds, Li_3Hg, $LiHg$, $LiHg_2$, and $LiHg_3$, the formula of the fifth being uncertain; it lies between Li_3Hg and $LiHg$. The compound LiHg melts at 600·5°, and is represented by a conspicuous maximum on the curve; the other compounds are only indicated by breaks. The compound LiHg crystallises in cubes, the remaining compounds in needles.

The heat of formation of the amalgams containing from 50 to 75 atomic % Hg has also been determined by comparing the heat of solution in dilute sulphuric acid with that of lithium. The existence of the compounds $LiHg_2$ and $LiHg_3$ is thus confirmed. The molecular heat of formation of LiHg is 20·2 cal.

The behaviour of lithium in its intermetallic compounds approaches that of magnesium rather than of the other alkali metals.

C. H. D.

The Action of Nitrogen on Lithium Carbide. SAMUEL A. TUCKER and HERBERT R. MOODY (*J. Amer. Chem. Soc*, 1911, **33**, 1478—1485).—The preparation of lithium carbide in the electric furnace from a mixture of lithium carbonate and carbon is attended with difficulty, owing probably to the small interval of temperature between its formation and decomposition. The best results were obtained with a mixture of 60 parts of lithium carbonate and 48 parts of carbon, to which 4% of manganese dioxide had been added. With a granular carbon furnace, 210 amperes at 18 volts, gradually increasing to 700 amperes at 30 volts after sixteen minutes, were used. The time of heating never exceeded seventeen minutes, otherwise decomposition of the carbide occurred. The product obtained was for the most part black, and the best results gave a carbide content of 53%. Moissan's claim (Abstr., 1896, ii, 419) to have prepared a nearly pure carbide in the electric furnace could not be confirmed.

The carbide product obtained by the authors gave a maximum absorption of nitrogen at about 925°, this maximum absorption being reached in about one hour; longer heating decreases the absorption. The most efficient reaction takes place with nitrogen at a pressure of about 50 lbs. to the square inch.

The product obtained by the action of nitrogen on lithium carbide differs considerably from the corresponding calcium product, or "nitrolime," nitrogen being present as cyanamide, dicyanamide, and cyanide. The proportion of nitrogen fixed does not differ greatly from that fixed by calcium carbide, but the time taken to fix it is much less.

T. S. P.

Constitution of the Compound of Silver Chloride with Ammonia. JAN STRAUB (*Zeitsch. physikal. Chem.*, 1911, **77**, 331—338).—Bodländer and Fittig (Abstr., 1902, ii, 248) have shown that solutions of silver chloride in ammonia contain the silver almost exclusively as the complex $Ag(NH_3)_2Cl$, although the solid in contact with the solution has the formula $2AgCl,3NH_3$. The author has repeated these measurements in order to find whether under certain conditions the presence of other complexes in solution can be detected, but the results merely serve to confirm those of Bodländer and Fittig. The method of calculating the results is given in detail.

G. S.

Method for Determining the Uniformity or the Phase-Number of a Substance. Application to Silver Mercuric Iodide. HENRIK WEGELIUS (*Zeitsch. physikal. Chem.*, 1911, **77**, 587—590).—Silver mercuric iodide, Ag_2HgI_4, alters in colour from yellow to red when the temperature is raised, but there is no sharp transition point, and there is a difference of opinion as to whether the red substance represents the compound itself or a mixture of the components (compare Ostwald, *Lehrbuch* II, 2, 407). The author has settled this point by shaking the solid compound and mercuric iodide with potassium iodide solutions of varying concentrations until equilibrium is reached at a temperature above the transition point, and analysing the mixtures. It was found that there is no relationship between the mercuric iodide and potassium iodide concentration, as should be the case if mercuric iodide is present in the solid in equilibrium with the solution; hence the red substance is a definite compound. G. S.

Silver Fluoride and Silver Subfluoride. LUDWIG VANINO and PAULA SACHS (*Zeitsch. anal. Chem.*, 1911, **50**, 623—629).—Historical. The authors agree with Marignac that the formula of hydrated silver fluoride is AgF,H_2O. The brownish colour of some specimens is not due to metallic silver, but to silver oxide.

The substance supposed to be silver subfluoride is, according to the authors, not a true compound, but a mixture of silver fluoride and silver (and silver oxide) in varying proportions. L. DE K.

The Extraction of Silver from its Ores by means of Cyanides. E. KÜHN (*Metallurgie,* 1911, **8**, 399—404, 421—436, 464—472, 481—492).—In the extraction of silver sulphide by means of potassium cyanide, the reaction $Ag_2S + 6KCN = 2AgK_2(CN)_3 + K_2S$ occurs, the constants for which have been determined by Lucas (Abstr., 1904, ii, 715). The equilibrium is further complicated by the hydrolysis of the cyanide and the sulphide. Taking this into account, formulæ are arrived at from which a three-dimensional diagram is constructed, the co-ordinates of which are the concentrations of KCN, KSH, and Ag respectively. Silver sulphide is only dissolved within a region forming a limited part of the equilibrium surface. It is found, however, that in very dilute solutions (below $0{\cdot}05N$-KCN) the reaction is not in accordance with Lucas's equation.

In practice, the quantity of silver dissolved is increased by removal of the alkali sulphide produced, by means of lime in presence of air, or by addition of lead acetate, or, better, of lead oxide. C. H. D.

The Ternary System Silver–Zinc–Lead. The Theory of the Parkes Process. ROBERT KREMANN and F. HOFMEIR (*Monatsh.*, 1911, **32**, 563—595).—As silver and zinc form four well defined compounds (Petrenko, Abstr., 1906, ii, 284), whilst lead does not form compounds with either silver or zinc, the ternary system may be broken up into five ternary systems, $Pb–Zn–Ag_2Zn_5$; $Pb–Ag_2Zn_5–Ag_2Zn_3$; $Pb–Ag_2Zn_3–AgZn$; $Pb–AgZn–Ag_3Zn_2$, and $Pb–Ag_3Zn_2–Ag$. On the triangular diagram these systems occupy five triangles having a common apex. The primary crystallisation of lead is restricted to a very small area, and the ternary eutectic contains about 97·5% of lead, and melts at 305°.

In the technical extraction of silver from lead by the Parkes process, the quantity of zinc added is so small that the region of two immiscible liquid phases is not usually entered. The crystals which separate on cooling are then solid solutions of zinc and the compound Ag_2Zn_5. A small proportion of the binary eutectic, of which the other constituent is lead, also separates. Repetition of the process brings the system nearer to the line Pb–Zn, the silver passing almost exclusively into the crystalline phase. C. H. D.

Bolognian Stones. III. LUDWIG VANINO and EMILIE ZUMBUSCH (*J. pr. Chem.*, 1911, [ii], 84, 305—317. Compare Abstr., 1909, ii, 731 ; 1910, ii, 847).—In the earlier papers it was pointed out that in Bolognian stones exhibiting a marked phosphorescence, only a portion of the barium, strontium, or calcium exists in combination in the form of sulphides. The object of the present communication is to ascertain more exactly the relationship existing between the luminosity of the stones and their sulphur content.

In good calcium stones the total amount of sulphur may vary between 12% and 33%, but with a slightly greater sulphur content the luminosity is considerably impaired. Stones in which polysulphides could not be detected were always found to be feebly luminous. That this lack of phosphorescence is really due to a deficiency of polysulphides is proved by the fact that stones, prepared by igniting calcium sulphate with carbon, and therefore free from polysulphides, are non-luminous. Moreover, whilst the addition of fusible salts and traces of metals to these non-luminous calcium monosulphide stones produces only a very feeble phosphorescence, the addition of a small quantity of sulphur results in the formation of more strongly luminescent stones. The presence of polysulphides thus appears to be essential for the production of good stones, but the amount of sulphur in the form of polysulphides is always comparatively small, varying from ½% to 2½%.

The phosphorescence also depends on the texture of the stones. Those consisting of monosulphides are always obtained in the form of hard, stony, non-luminous or, at most, very feebly luminous masses. Addition of calcium oxide to these monosulphide stones produces a less compact mass, and at the same time a marked increase in their luminosity. The quality of the lime used in the preparation of the stones is also of importance, but no essential difference could be detected in the composition of feebly luminous stones prepared from unsuitable specimens of lime, and stones showing an intense luminescence. Partial replacement of calcium oxide by strontium carbonate or oxide in the preparation of the stones exercises no influence on their sulphur content, although the mixed stones thus obtained are characterised by an intense phosphorescence.

The effect of reducing agents has also been investigated; whilst the addition of 4% of starch is advantageous, larger quantities completely destroy the phosphorescence ; good results are also obtained with cane sugar, but not with lamp black. With respect to the influence of pressure, it is found that the previously-observed diminution in the intensity of the luminescence is accompanied by a change in the colour of the stones. When ground in the dark, all stones lose their original colour and acquire a more or less greyish tint. A further change of colour is observed on exposure to light, the stones in this case acquiring a reddish or even a reddish-brown tint. This secondary coloration depends on the metallic content and percentage of sulphur; increase of the latter produces a marked increase in the intensity of the colour. Stones acquiring a strong secondary colour sometimes exhibit very feeble luminosity, so that there appears to be no connexion between the two phenomena.

Admixture of the phosphorescent masses with photo-sensitisers, or exposure to chlorine, ammonia, hydrogen sulphide, and other gases has no effect on their luminosity.

Further attention has also been directed to the influence of metallic salts on the phosphorescence. Addition of silver, gold, or platinum salts, arsenic sulphides, or of coloured substances, such as ultramarine or Thenard's blue, has either little or a deleterious effect on the luminosity. Partial replacement of calcium oxide by calcium tungstate in a mixed strontium–calcium stone produces a magnificent sea-green luminescence.

With stones of high metallic content and simple composition, the time of exposure necessary to excite the maximum luminescence is shorter, and the rate of decay more rapid, than in the case of stones of a low metallic content and complex composition. F. B.

Transformation of Aragonite into Calcite. P. N. Laschtschenko (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 793—803).—The results of previous investigators have shown that between the ordinary temperature and one not lower than corresponds with a red heat, calcite is undoubtedly a more stable form of calcium carbonate than aragonite. But discord exists in regard to the magnitude of the heat-change accompanying the transformation of the latter into the former modification; thus, Favre and Silbermann, whose results are stated by Abegg (*Handbuch der anorg. Chem.*, 1905, II, **2**, 155) to be clearly erroneous and are not mentioned by Tammann (*Krystallisiren und Schmelzen*, 1903, 113), found the heat of transformation of aragonite to calcite to be +2·36 Cals. per gram-mol., whilst Le Chatelier (Abstr., 1893, ii, 259) obtained the value −0·300 Cal. per gram-mol. Widely different temperatures have also been given by various authors as that at which the above transformation occurs.

The author has investigated this change by determining calorimetrically the amounts of heat given out on cooling by aragonite and calcite (marble and Iceland spar) heated to various temperatures.

In the case of aragonite, the curve expressing the relation between the amount of heat evolved and the temperature is composed of three portions. In the first (up to about 400°) the curve cannot, by the method used, be distinguished from that for calcite. At 445°, however, a distinct separation occurs, the heat of cooling of aragonite increasing rapidly until the temperature reaches 465—470°. The third portion of the curve again coincides with that for calcite, although above 600° there appears to be some divergence.

A sudden change also takes place in the specific gravity of aragonite at about 465—470°, the values of $D_{16\cdot5}$ found by the author being as follows: 16·5°, 2·9219; 400°, 2·9278; 410°, 2·9209; 445°, 2·9217; 450°, 2·9218; 460°, 2·9231; 465°, 2·9215; 475°, 2·7691; 525°, 2·7711; 650°, 2·7800.

These results show that the turbidity and brittleness of aragonite crystals observed by Boeke (Abstr., 1906, ii, 753) to appear at 445° are not connected with the transformation into calcite.

Taking the temperature of the transformation as 465—470°, the difference between the heats of cooling of calcite and aragonite gives the value about +2·72 Cals. per gram-mol. for the heat-effect of the change; this number is in fair agreement with that given by Favre and Silbermann (*loc. cit.*). T. H. P.

Electrical Conductivity and Hardness of Magnesium-Cadmium Alloys. G. G. URAZOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 752—771).—The electrical conductivity and hardness of alloys of magnesium and cadmium confirm Grube's view (Abstr., 1906, ii, 355) that, at the ordinary temperature, these alloys contain two series of solid solutions: (1) of the compound β-CdMg and (2) of α-MgCd, in their components. With the compound α-CdMg correspond a maximum of conductivity and a minimum of hardness (compare Schemtschuschny, Abstr., 1906, ii, 539; Kurnakoff and Schemtschuschny, Abstr., 1908, ii, 932; Smirnoff and Kurnakoff, Abstr., 1909, ii, 402). The following temperature-coefficients of resistance have been determined: Mg, 0·00438; Cd, 0·00425, and α-CdMg, 0·00586.

On addition of cadmium to magnesium, the specific conductivity diminishes rapidly until 20 atom. % Cd is present; this part of the curve corresponds with the formation of solid solutions of β-CdMg with magnesium. At the 20% Cd point, the conductivity suddenly rises, the curve subsequently falling, rising to a maximum for the composition corresponding with the compound CdMg, then falling again, and rising until the atom. % of cadmium reaches 82·5; this part of the curve corresponds with solid solutions of α-MgCd in its components. At 82·5% Cd, the curve exhibits a sudden fall, and then rises rapidly to the pure cadmium point; this branch corresponds with solid solutions of β-CdMg with cadmium.

As the temperature is raised, the region in which solid solutions of α-CdMg exist continually decreases, until at 255° it vanishes altogether. At this and higher temperatures, an uninterrupted series of solid solutions of β-CdMg is formed, and the conductivity curve consists of two continuous branches meeting in a maximum at the CdMg point.

The micro-structures of alloys of various compositions confirm these results. T. H. P.

Definite Compounds with Variable Composition of the Solid Phase. I. Electrical Conductivity and Hardness of the System Magnesium–Silver. WLADIMIR I. SMIRNOFF and NICOLAI S. KURNAKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 725–752; *Zeitsch. anorg. Chem.*, 1911, **72**, 31—54).—In the first part of this paper the authors discuss the forms of the conductivity and hardness curves of compounds with varying composition of the solid phase and melting (1) without and (2) with decomposition.

The general form of the conductivity curve resembles that of the freezing point curve (compare Schemtschuschny, Abstr., 1906, ii, 539), the maximum corresponding with the composition MgAg being clearly marked. The results show that all the substances formed in the system magnesium–silver show varying composition of the solid phase. The temperature-coefficients of the conductivity are important and characteristic magnitudes, and for the compounds MgAg and Mg_3Ag they approximate to the corresponding values for the component metals.

The third part of the paper, dealing with the hardness of these alloys, has been already published (Abstr., 1909, ii, 402).

T. H. P.

Differences of Potential between Cadmium and Alcoholic Solutions of Some of its Salts. FREDERICK H. GETMAN (*Amer. Chem. J.*, 1911, **46**, 117—130. Compare Jones, Abstr., 1894, ii, 374; Kahlenberg, Abstr., 1899, ii, 624; 1901, ii, 81, and Jones and Smith, Abstr., 1900, ii, 467).—The author has measured the potential at 20° of the cadmium electrode against solutions of cadmium iodide and cadmium chloride in methyl alcohol, ethyl alcohol, and water respectively, the normal calomel electrode being used as the standard. In alcoholic solution the potential becomes more strongly negative (with reference to the solution) as the concentration of the solution increases, whereas in aqueous solution the opposite is the case. When cadmium is immersed in solutions of cadmium iodide in ethyl alcohol of concentrations less than 0·06 molar, there is a reversal of the polarity of the system, and the current flows outside of the cell from cadmium to mercury instead of from mercury to cadmium, as in methyl alcohol and aqueous solutions. The behaviour of the electrode in alcoholic solutions is contrary to what one would expect from Nernst's theory of the voltaic cell, unless the improbable assumption is made that the degree of ionisation increases with dilution more rapidly than the dilution increases, so that at present the theory cannot be extended to non-aqueous solutions.

The solution pressure of cadmium is calculated to be $5{\cdot}64 \times 10^5$, $1{\cdot}68 \times 10^6$, and $1{\cdot}64 \times 10^6$ atmos. respectively from measurements on 0·01, 0·05, and 0·1 molar aqueous solutions of cadmium iodide, and $3{\cdot}45 \times 10^5$ and $1{\cdot}07 \times 10^6$ atmos. from measurements on 0·01 and 0·05 molar aqueous solutions of cadmium chloride. There are no data on which a calculation of the solution pressure of cadmium in the alcohols can be based.

Boiling-point measurements showed that cadmium iodide is partly polymerised in both methyl- and ethyl-alcoholic solution. T. S. P.

Persulphates of Bivalent Metals. GUISEPPE A. BARBIERI and F. CALZOLARI (*Zeitsch. anorg. Chem.*, 1911, **71**, 347—355).—The only persulphates of bivalent metals hitherto prepared are those of barium and lead (Marshall, Trans., 1891, **59**, 771). These salts are in general very unstable. It is now found that the persulphates form crystalline compounds with ammonia, pyridine, and hexamethylenetetramine. The last of these compounds furnishes the only means of preparing manganous and cobaltous persulphates (compare this vol., i, 268). The hexamethylenetetramine compounds contain water, and their properties indicate that the central atom is not in contact with molecules of the base, but is surrounded by water molecules.

The ammonia compounds may be prepared by adding a concentrated solution of ammonium persulphate (2 mols.) to a concentrated, strongly ammoniacal solution of the metallic sulphate (1 mol.). The crystalline products are washed with ammonia and dried with filter paper. They lose ammonia readily, and explode on heating or percussion. The following ammine persulphates have been prepared: *zinc*, $ZnS_2O_8,4NH_3$; *cadmium*, $CdS_2O_8,6NH_3$; *nickel*, $NiS_2O_8,6NH_3$, and *copper*, $CuS_2O_8,4NH_3$.

The following pyridine persulphates have been prepared: *zinc*, $ZnS_2O_8,4C_5NH_5$; *cadmium*, $CdS_2O_8,4C_5NH_5$; *nickel*, $NiS_2O_8,4C_5NH_5$, light blue, and *copper*, $CuS_2O_8,4C_5NH_5$, bluish-violet.

The hexamethylenetetrammine persulphates are precipitated, separated as rapidly as possible from the mother liquor, and washed with alcohol. The *magnesium, manganese, cobalt*, and *nickel* salts all have the composition $MS_2O_8,8H_2O,2C_6H_{12}N_4$. The manganese and cobalt salts are shown to be isomorphous. The cobalt and nickel salts resemble in colour the ordinary hydrated salts of those metals. C. H. D.

The Nature of the Transformation of Lead-Tin Alloys in the Solid State. DOMENICO MAZZOTTO (*Internat. Zeitsch. Metallographie*, 1911, **1**, 289—352).—The transformation occurring in solid lead-tin alloys at about 150° has been attributed by Degens (Abstr., 1909, ii, 888) to the formation of a compound of the two metals, and by Rosenhain and Tucker (Abstr., 1908, ii, 1038) to an allotropic change in the solid solution of tin in lead. Cooling curves of the alloys have now been taken after annealing for different periods below, at, or slightly above the eutectic temperature. Mercury is used as a standard of comparison. The conclusion is drawn from the curves that it is unnecessary to assume either combination or allotropic change, the heat developed during cooling being merely due to the separation of tin from solid solution with falling temperature. Annealing increases the saturation of the solid solution. The transformation occurs at 150° in alloys containing 18% Sn or more, but below that temperature at lower concentrations.

Similar transformations are observed in alloys of tin with bismuth, thallium, and cadmium, in all of which solid solutions are formed.

C. H. D.

Action of Seltzer Water on Lead, Tin, and Antimony. Causes of Poisoning by Chemical Alteration. A. BARILLÉ (*Compt. rend.*, 1911, **153**, 351—353).—Alloys of lead or antimony with tin are more soluble in seltzer water than either metal separately, even when an alloy contains only 0·5% of lead. A litre of Seltzer water gave 0·0905 gram of lead sulphate and 0·0381 gram of stannic acid when allowed to act for six months on the head of a syphon containing 19·47% of lead. An alloy containing 10% of antimony gave 0·153 gram of antimonious oxide after two months. The use of porcelain or silicious linings for syphon heads is recommended.

W. O. W.

Crystallographic (Isomorphous) Relations of Indium and Thallium. R. C. Wallace (*Zeitsch. Kryst. Min.*, 1911, **49**, 417—454).—Detailed crystallographic determinations were made for several salts in the following isomorphous series:

1. The ditetragonal-bipyramidal series, $R_3MX_6,2H_2O$:

$K_3TlCl_6,2H_2O$. $(NH_4)_3TlCl_6,2H_2O$. $K_3InCl_6,2H_2O$.
$Rb_3TlBr_6,2H_2O$. $K_3InBr_6,2H_2O$.

2. The rhombic-bipyramidal series, R_2MX_5,H_2O:

Rb_2TlCl_5,H_2O. Cs_2TlCl_5,H_2O. $(NH_4)_2InCl_5,H_2O$.
Rb_2InCl_5,H_2O. Cs_2InCl_5,H_2O. $(NH_4)_2InBr_5,H_2O$.
Rb_2InBr_5,H_2O. Cs_2InBr_5,H_2O.

Isomorphous with these are K_2FeCl_5,H_2O and $(NH_4)_2FeCl_5,H_2O$.

3. The cubic series, RMX_4,xH_2O:

$KTlBr_4,2H_2O$. $(NH_4)TlBr_4,2H_2O$. $RbTlBr_4,H_2O$.
$CsTlBr_4$.

4. The ditetragonal-bipyramidal salt, $K_3Tl_2Br_9,3H_2O$.

The effect of the various replacements on the crystallographic constants is discussed. The alkalis stand in the order K, (NH_4), Rb, Cs, there being very little interval between (NH_4) and Rb. With Fe, In, Tl, the intervals are approximately proportional to the differences in the atomic weights.

L. J. S.

Decomposition of the Cerium Earth Double Sulphates with the Alkali Sulphates by Fusion with Charcoal. Philip E. Browning and Philip L. Blumenthal (*Amer. J. Sci.*, 1911, [iv], **32**, 164—166).—One part of the double sulphate is heated with four parts of charcoal in a covered porcelain crucible over a Bunsen flame for about an hour. The mass then dissolves readily in dilute hydrochloric acid with evolution of hydrogen sulphide. From the filtrate the cerium may be recovered by precipitation with oxalic acid and then ignited to oxide.

L. de K.

Sulphides of the Rare Earths. II. Lanthanum and Praseodymium Sulphides. Wilhelm Biltz (*Zeitsch. anorg. Chem.*, 1911, **71**, 427—438. Compare Abstr., 1908, ii, 1037).—Like cerium, lanthanum and praseodymium yield normally only trisulphides (Muthmann and Stützel, Abstr., 1900, ii, 142), but higher polysulphides are obtainable.

Lanthanum disulphide, LaS_2, prepared by heating lanthanum sulphate in hydrogen sulphide at 580—600°, behaves as a polysulphide, and decomposes when more strongly heated at about 650°. A comparison of the heat of solution of the two sulphides in hydrochloric acid gives the result $4LaS_2 = 2La_2S_3 + S_2(\text{gas}) - 43{\cdot}4$ cal. This gives a theoretical dissociation temperature of 670°, about 100° lower than that of cerium disulphide.

The action of hydrogen sulphide on anhydrous praseodymium sulphate only results in the formation of *praseodymium oxysulphide*, Pr_2SO_2. Sulphides free from oxygen are only obtained in the presence of some cerium. In the same way, cerium is known to assist the formation of praseodymium peroxide. *Praseodymium disulphide*, PrS_2, dissociates at a temperature near that of the lanthanum compound. C. H. D.

Thulium. I. CHARLES JAMES (*J. Amer. Chem. Soc.*, 1911, **33**, 1332—1344. Compare Abstr., 1910, ii, 412).—The best sources for thulium were found to be ytterspar, euxenite, and a columbate, resembling sipylite, from an island in the north of Norway, and having the following composition:

Cb_2O_5(trace Ta_2O_5).	SiO_2.	WO_3,SnO_2.	ZrO_2.	Cu group.	U_3O_8.	Fe_2O_3,Al_2O_3.
42·42	4·27	0·37	0·41	1·38	1·40	1·55

Yttrium earths.	Cerium earths.	ThO_2.	CaO.	MgO.	Loss on ignition.
39·91	3·57	1·10	1·25	0·07	2·00

The preliminary treatment in the various cases was as follows: *Euxenite.*—The finely powdered material was evaporated to dryness with excess of sulphuric acid. The residue was powdered, well agitated with water, and the metallic acids allowed to settle, after which the rare earths were precipitated as oxalates from the supernatant fluid. *Fergusonite and Samarskite.*—These were treated similarly to euxenite, except that potassium sulphate was added to the sulphuric acid so as to increase the temperature. In some cases the hydrofluoric acid method of treatment was adopted. *Columbates.*—The mineral was first ignited, then powdered, and fused with sodium hydroxide. The cold fusion was made into a mud with water and then heated on the water-bath with hydrochloric acid. The columbic acid, etc., was filtered off, and the rare earths precipitated as oxalates. *Yttrotitanite* was attacked with hydrochloric acid, filtered, and the rare earths obtained as oxalates. *Ytterspar* (impure Norwegian xenotime) was treated in much the same way as the columbates, while *gadolinite* was decomposed by heating with hydrochloric acid, the rare earths being obtained in the usual way.

The ytterspar earths were converted into the bromates by igniting the oxalates, dissolving in hydrochloric acid, filtering, and reprecipitating as oxalates, which were then converted into the sulphates. The anhydrous sulphates were dissolved in water, and the solution heated on a water-bath with barium bromate. After collecting the barium sulphate, the bromates were fractionally crystallised.

The earths from euxenite, gadolinite, etc., were first subjected to the sodium sulphate treatment, since they contained members of the cerium group. After separating the insoluble double sulphates, the solution was precipitated with oxalic acid, the oxides obtained, and converted into the bromates in a manner similar to that described for the ytterspar earths.

Thulium was then concentrated by fractional crystallisation of the bromates (compare Abstr., 1908, ii, 190, 498), collecting in the fractions between erbium and ytterbium, and being more soluble than erbium. The fractions in which the thulium bands were intense were finally submitted to a long series of recrystallisations, as they consisted mainly of ytterbium and lutecium, with some erbium and traces of scandium. The thulium was gradually concentrated in the fractions next to the least soluble erbium, and when free from erbium the solutions possessed a bluish-green colour. The presence of a little erbium turns the colour yellowish-green, a little more renders it colourless, and further addition changes it to pink. The various colours so obtained were made use of in collecting the fractions. It was found that the thulium fractions did not change in colour, always retaining a greenish tint when in solution.

Other methods of fractionation were tried, but none could be compared with the bromate method.

Spectroscopic examination (by Sir William Crookes) of the purest thulium fraction obtained showed it to contain a trace of ytterbium and a very faint trace of calcium.

The results show that the element giving the characteristic absorption bands of thulium cannot be separated into simpler substances. After 15,000 operations the absorption spectrum underwent no change.

The following compounds are described: *Thulium oxide*, Tm_2O_3, prepared by igniting the oxalate, forms a dense white powder with a faint green tint. It gives a carmine glow when carefully made to incandesce. *Thulium hydroxide* is best precipitated by means of ammonium hydroxide. *Thulium bromate*, $Tm_2(BrO_3)_6,18H_2O$, was obtained as pale bluish-green, hexagonal prisms from thulium sulphate and barium bromate. *Thulium chloride*, $Tm_2Cl_6,14H_2O$, was prepared from the oxide and hydrochloric acid. It forms crystals with a green tint. The *sulphate*, $Tm_2(SO_4)_3,8H_2O$, was obtained from the chloride and sulphuric acid by precipitating the solution with alcohol. It loses $8H_2O$ at a temperature near to redness. The *oxalate*,

$$Tm_2(C_2O_4)_3,6H_2O,$$

possesses a greenish tinge. It forms double salts with potassium and ammonium oxalates. *Thulium acetylacetonate*, $Tm_2(C_5H_7O_2)_6,2H_2O$, was obtained by dissolving the hydroxide in a warm mixture of absolute alcohol and acetylacetone, and the *phenoxyacetate*,

$$Tm_2(CO_2{\cdot}CH_2{\cdot}OPh)_6,6H_2O,$$

from the hydroxide and phenoxyacetic acid. *Thulium nitrate*,

$$Tm_2(NO_3)_6,8H_2O,$$

was obtained from the oxide and nitric acid. T. S. P.

New Rare Earth Compounds. L. A. PRATT and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1911, **33**, 1330—1332).—The following compounds were prepared by solution of yttrium oxide in the corresponding acid and evaporation of the solution to dryness. The residue was then dissolved in alcohol and the salt precipitated with ether.

Yttrium methylsulphonate, $(MeSO_2\cdot O)_3Y,4H_2O$. *Yttrium methanedisulphonate*, $[CH_2(SO_2\cdot O)_2]_3Y_2,2\frac{1}{2}H_2O$. *Yttrium methanetrisulphonate*, $[CH(SO_2\cdot O)_3]Y,3\frac{1}{2}H_2O$. *Yttrium ethanesulphonate*, $(EtSO_2\cdot O)_3Y,4H_2O$. *Yttrium camphorsulphonate*, $(C_{10}H_{15}O\cdot SO_2\cdot O)_3Y,7H_2O$. *Yttrium methoxysulphonate* [?] could not be obtained crystalline. The above salts are all very soluble.

Yttrium salicylate, $(OH\cdot C_6H_4\cdot CO_2)_3Y,3\frac{1}{2}H_2O$, and *yttrium phthalate*, $[C_6H_4(CO_2)_2]_3Y_2,3H_2O$, were obtained by first preparing yttrium formate and then adding the required amount of the respective acids. These salts are both practically insoluble. *Yttrium phenylacetate*, $(CH_2Ph\cdot CO_2)_3Y,3H_2O$, and *yttrium glycollate*, $[CH_2(OH)\cdot CO_2]_3Y,2H_2O$, were obtained as insoluble salts from the respective acids and yttrium hydroxide, whilst *yttrium phenoxyacetate*, $(Ph\cdot O\cdot CH_2\cdot CO_2)_3Y,3\frac{1}{2}H_2O$, was prepared by precipitating a solution of yttrium chloride with phenoxyacetic acid, it being only slightly soluble in cold water.

The *phenoxyacetates* of *samarium, neodymium, praseodymium, lanthanum*, and *cerium* were prepared in the same manner as the yttrium salt, but they are much less soluble than the latter. They have the compositions $SmX_3,3\frac{1}{2}H_2O$, $NdX_3,2\frac{1}{2}H_2O$, $PrX_3,1\frac{1}{2}H_2O$, $LaX_3,2\frac{1}{2}H_2O$, and CeX_3, where $X = Ph\cdot O\cdot CH_2\cdot CO_2$.

Thorium is almost quantitatively precipitated from neutral solutions by the addition of excess of phenoxyacetic acid, a reaction which may be used for the separation of this element from the other rare earths, which are not thus precipitated. T. S. P.

Europium. CHARLES JAMES and J. E. ROBINSON (*J. Amer. Chem. Soc.*, 1911, **33**, 1363—1365).—The materials worked up by the authors comprised: oxides from insoluble double sodium sulphates obtained from about 200 kilos. of yttrium minerals; all the samarium and gadolinium oxides derived from about 200 kilos. of Brazilian monazite; and about 110 kilos. of oxides obtained from the more soluble double potassium sulphates coming from very large amounts of Carolina monazite.

These crude oxides were converted into the double magnesium nitrates (compare Demarçay, Abstr., 1901, ii, 511), which were recrystallised several times. When the mother liquors began to crystallise indefinitely, they were diluted and precipitated with oxalic acid. The oxalates so obtained were converted into oxides, and found to contain small quantities of lanthanum, cerium, and praseodymium, much neodymium and fair amounts of samarium, gadolinium, and yttrium earths. This material was again converted into the double magnesium nitrate, and recrystallised from 30% nitric acid. The neodymium, lanthanum, cerium, and praseodymium collected rapidly in the least soluble portion; the intermediate fractions consisted chiefly of the pale yellow samarium compound, while the most soluble portions were rich in gadolinium, and were coloured very pale pink by the erbium metals. When crystals of the simple nitrates of the yttrium elements made their appearance, fractionation was proceded with according to the bismuth magnesium nitrate method (Urbain and

Lacombe, Abstr., 1904, ii, 340). By this means all samarium and europium were rapidly eliminated from the most soluble fractions. With regard to the yttrium earths, it was found that erbium and yttrium separated first, holmium next, and lastly dysprosium and terbium.

As soon as the fractions containing lanthanum, cerium, praseodymium, and neodymium had been freed from samarium, it was considered that all the europium had passed further along the series.

As the work proceeded, the europium band was seen to become stronger in the fractions between samarium and gadolinium, and when nearly all the samarium had been separated, bismuth was removed from the fractions containing europium by means of hydrogen sulphide, the fractions having been previously mixed according to their absorption spectra. The europium was then precipitated as oxalate, about 100 grams of this salt being obtained after two years' work. Some samarium was still present in the fractions nearest to that element, so the whole material was again fractionated with bismuth magnesium nitrate; when free from samarium, it was again converted into europium oxalate, which is to be further investigated.

About 5 kilos. of pure samarium oxalate and 4 kilos. of nearly pure gadolinium oxalate were also obtained. T. S. P.

The Action of Hydrogen Fluoride on Certain Oxides. WALTER K. VAN HAAGEN and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1911, **33**, 1504—1506).—The material to be tested was contained in a platinum boat placed in a platinum combustion tube, and hydrogen fluoride was then passed over it.

At a white heat aluminium oxide was quantitatively converted into the fluoride. Yttrium oxide at a red heat gave non-volatile fluoride or oxyfluoride. Lanthanum oxide was quantitatively converted into the non-volatile fluoride. Finely divided quartz was completely volatilised without the action of heat, whilst with titanium oxide a red heat was necessary.

Zirconium oxide and zircon mineral were completely converted into volatile fluoride at a red heat, as were also columbium and tantalum pentoxides. Tantalum fluoride is less volatile than columbium fluoride.

Cerium dioxide was changed quantitatively into non-volatile fluoride; tin stone gave a small quantity of a fluoride or oxyfluoride which was only volatile at a white heat, and thorium dioxide underwent a slight alteration only, without any volatilisation.

Columbium and tantalum were expelled from powdered columbite, and the metallic acids were completely volatilised from fergusonite. Potassium dichromate lost nearly all its chromic acid, whilst sodium tungstate was attacked with difficulty, and the tungstic acid not completely expelled. Phosphoric acid was expelled quantitatively from sodium pyrophosphate. T. S. P.

Metallographic Notes. HENRI LE CHATELIER (*Rev. de Métallurgie*, 1911, **8**, 367—376).—Several specimens of alloys prepared by Moissan in the electric furnace have been examined microscopically. Aluminium carbide crystallises from aluminium in large plates, which disintegrate in air. C. H. D.

Constitution of the Alloys of Aluminium and Zinc. WALTER ROSENHAIN and SYDNEY L. ARCHBUTT (*Phil. Trans.*, 1911, *A*, **211**, 315—343; *Proc. Roy. Soc.*, 1911, *A*, **85**, 389—392. Compare Shepherd, Abstr., 1905, ii, 588).—Thermal and microscopic methods were employed in the investigation of the alloys. In the thermal experiments, cooling and heating curves were taken, large masses of alloy (300 grams) and slow rates of cooling being used. Further cooling curves were obtained with specimens of certain alloys which had been exposed to prolonged heating to allow of the completion of slow chemical changes. In the microscopic portion of the work specimens were examined which had been (*a*) slowly cooled from fusion, (*b*) annealed at certain definite temperatures and slowly cooled, and (*c*) annealed at certain temperatures and then quenched.

From the results obtained, an equilibrium diagram has been constructed which differs materially from that given by Shepherd. The liquidus and solidus curves are interpreted by reference to this diagram. Evidence has been obtained of the existence of a definite compound Al_2Zn_3, the micro-structure of which exhibits characteristic dendritic crystals which possess a marked habit of assuming six-rayed forms. H. M. D.

Solubility of Hydrogen in Copper, Iron, and Nickel. ADOLF SIEVERTS (*Zeitsch. physikal. Chem.*, 1911, **77**, 591—613).—The solubility of hydrogen in copper, iron, and nickel has been determined for pressures up to 1½ atmospheres and at intervals of temperature from 400° to 1600°. The solubility is independent of the extent of surface of the metal, so that the phenomenon is one of true solution and not of adsorption. At constant temperature the solubility in the solid and fused metals is proportional to the square root of the pressure, but below 100 mm. pressure the amount of hydrogen taken up diminishes rather more rapidly with the pressure than the above rule would indicate. At constant pressure the solubility increases with the temperature, and there is a sudden increase in solubility when the metal melts. The temperature-coefficient of the solubility is greater in fused than in solid copper. The change of α- to β-iron is not recognisable on the solubility curve, but there is a rapid increase in solubility between 850° and 900°, connected with the transition from β- to γ-iron. All three metals give up hydrogen accompanied by "spitting" when they solidify in an atmosphere of the gas. At the respective melting points copper gives up 2 volumes, iron 7 volumes, and nickel 12 volumes of the gas.

At 930°, 100 grams of solid copper dissolve 0·108 mg.; at 1420° the fused metal takes up 1·097 mg. of hydrogen. At 930°, 100 grams of solid iron dissolve 0·431 mg.; at 1550° the fused metal takes up 2·5 mg. of hydrogen. At 923°, 100 grams of solid nickel dissolve 0·86 mg. of hydrogen. In each case the gas was corrected to 760 mm. pressure. G. S.

Passivity of Metals. Ernst Grave (*Zeitsch. physikal. Chem.*, 1911, 77, 513—576).—There are serious objections to the oxide theory of passivity and to the suggestion that the passive and active metals have different valency. The only theory of passivity in accordance with the facts is that of Le Blanc (*Boltzmann Festschrift*, 1904, 183), who has pointed out that the solution pressure of iron in the passive state is much smaller than that in the active state. On this basis there are two possibilities: either pure iron is the active form and a negative catalyst is produced which renders it passive, or pure iron is the passive form and is rendered active by some positive catalyst which greatly increases its solution pressure. The author's results (described below) lend support to the latter view, the positive catalyst being $H^{\cdot}$ ions.

The ordinary impurities in iron and nickel have no effect on the passivity. Neither hydrogen peroxide nor ozone renders iron or nickel passive, although they render them less readily attacked, and the passive condition is retained longer in the presence of hydrogen peroxide. Further, the nature of the change from the passive to the active state is different from the fall of potential after polarisation by oxygen.

The main evidence in favour of the view that the activity of these metals is due to the presence of $H^{\cdot}$ ions is as follows. Iron and nickel become active when heated in hydrogen, but become passive when heated strongly in air, nitrogen or a vacuum. Molecular hydrogen, after being in contact with iron and nickel, does not alter the potential, but ionised hydrogen renders the metals active and ionised nitrogen renders them passive. Hydrogen ions are given off when a metal changes from the active to the passive state. When iron is saturated with $H^{\cdot}$ ions, the charge given off on heating is greatly increased. When iron is rendered active at one point by bringing it in contact with $H^{\cdot}$ ions, other parts of the metal are rendered active by diffusion. G. S.

A New Method for Determining the Extent of Rusting. Hugo Jacob and R. Kaesbohrer (*Chem. Zeit.*, 1911, 35, 877—878).—The rusted article, which has been carefully weighed before rusting was allowed to take place, is made the cathode to an anode of platinum or carbon, preferably the former, in a suitable electrolyte. On the passage of a weak current, the gas which forms on the cathode detaches the rust from the surface, or else makes it so loose that it is easily brushed off. The article in question is thus very readily cleansed from all particles of rust, and after drying may be weighed to determine the extent of rusting. The best electrolyte is a 0·25—1% solution of sodium sulphate, and the current is so regulated that there is a vigorous evolution of gas from the electrodes. The time necessary for the cleansing process varies considerably, but the results obtained with this method are much more accurate than those got with the ordinary method of cleansing. T. S. P.

The Influence of Surface Condition on the Rusting of Iron. Kurt Arndt (*Metallurgie*, 1911, 8, 353—358).—Whilst cast iron rusts uniformly over the surface, the rusting of wrought iron and mild steel is confined to local areas. The difference is due to the adherent character of the protective oxide film on cast iron, which is not readily dislodged by rust, whilst the film on wrought iron and steel readily scales off and allows the spongy rust to form. Alternations of wetness and dryness are better resisted by cast iron for the same reason. C. H. D.

The Rusting of Iron in Reinforced Concrete. EDUARD DONATH (*Zeitsch. angew. Chem.*, 1911, **24**, 1398—1402).—It is known that rusty iron or steel, embedded in concrete, gradually loses its rust. It is found that calcium hydrogen carbonate readily dissolves the ferrous hydroxide from rust, causing it to separate from the iron surface. The solvent action is accelerated by the presence of sulphates. Small quantities of nitrites and nitrates are formed in the action of lime on iron rust, the nitrogen being derived from ammonia contained in the rust. It has been suggested by Michaelis that the ferric oxide partly reacts with the lime of the concrete, forming a calcium ferrite. This is found to be the case. A mixture of iron rust with slaked lime is much more readily dissolved by dilute acetic acid or by alkaline sugar solution than the rust alone, and this reaction is probably, in part, the cause of the removal of rust by the concrete. C. H. D.

The Solubility of Carbon in Iron. OTTO RUFF and OTTO GOECKE (*Metallurgie*, 1911, 8, 417—421. Compare Ruer and Iljin, this vol., ii, 494).—Iron is melted in a graphite crucible, enclosed in a carbon tube resistance vacuum furnace. The temperature is read by means of a Wanner optical pyrometer. The iron is kept molten until saturated with carbon, and the crucible is then, by means of a special device, allowed to fall through the furnace into a closed vessel of ice-cold water. The quantity of dissolved carbon is estimated analytically. The experiments have been carried as far as 2620° without any separation into two layers.

The solubility of graphite in iron increases with the temperature from 1130°, the solubility curve having an abrupt change of direction at 1837° and 6·6% C, and a very distinct maximum at 2220° and 9·6% C. These two points correspond with the carbides Fe_3C and Fe_2C respectively. The rapidly quenched specimens show the structure of the metastable eutectic, with the excess of graphite in the form of plates parallel with the octahedral faces. C. H. D.

The Equilibrium Diagram of the Iron–Carbon Alloys. OTTO RUFF (*Metallurgie*, 1911, 8, 456—464. Compare preceding abstract). —Although the freezing-point curve of the iron–carbon alloys has critical points corresponding with the carbides Fe_3C and Fe_2C, the equilibrium point $3Fe + C \rightleftarrows Fe_3C$ is always below the saturation point for the carbide, so that the only solid phase in contact with the solution is graphite. The carbides are endothermic compounds at temperatures above 700°. The diminished solubility of graphite in iron above 2220° is due to dissociation of the carbide Fe_2C. Below 2220° the reaction $3Fe_2C = 2Fe_3C + C$ takes place, and at 1837° the reaction $Fe_3C = 3Fe + C$.

The boiling point of iron saturated with carbon is 2750°/10 mm., whilst pure iron boils at about 2220° under the same conditions. The vapour of the alloys contains both iron and carbon.

In the process of solidification, the quantity of solid carbide formed is determined by its velocity of dissociation and the difference between its equilibrium concentration and its solubility, whilst the rate of cooling, by determining the extent of the supersaturation, also affects the result. Formulæ are given for calculating the quantity of carbide formed under given conditions. C. H. D.

Influence of Thermal Treatment on the Properties and Structure of Hypereutectoid Steel. A. JUNG (*Internat. Zeitsch. Metallographie*, 1911, 1, 209—255).—In steels containing from 1·0 to 1·5% of carbon, a martensitic structure gives the greatest hardness, and a pearlitic structure the greatest ductility, whilst troostite and sorbite give toughness. The limits of temperature between which the steel can be safely hardened by quenching become closer and also lower as the carbon is increased. C. H. D.

The Alloys of Iron and Antimony. A. PORTEVIN (*Rev. de Métallurgie*, 1911, 8, 312—314).—The temperature at which pearlite is formed in alloys of iron and carbon is not appreciably altered by the presence of 1—9% of antimony. The antimony is retained in solid solution up to 6·5%; richer alloys show distinct crystals of an antimonide (compare Kurnakoff and Konstantinoff, Abstr., 1908, ii, 391; Goerens and Ellingen; Abstr., 1910, ii, 298). C. H. D.

The Structure of Galvanised Iron. W. GUERTLER (*Internat. Zeitsch. Metallographie*, 1911, 1, 353—376).—Sections cut obliquely through the outer layers of galvanised iron show that the zinc and iron are separated by an intermediate layer of crystals of the compound $FeZn_3$. This compound is more electronegative than either iron or zinc, and thus accelerates corrosion if exposed. The zinc layer contains isolated crystals of the compound FeZn, which is also electronegative.

Zinc deposited from vapour by the dry process, or from solution by the electrolytic process, is porous, and also contains minute crystals.
C. H. D.

The System CrO_3–H_2O. ROBERT KREMANN [with J. DAIMER and E. BENNESCH] (*Monatsh.*, 1911, 32, 619—622).—The ice-curve of the system CrO_3–H_2O has been determined down to $-74°$. It was not found possible to measure the eutectic temperature, but extrapolation of the ice curve and the solubility curve of chromium trioxide gives a eutectic point at $-105°$ and 57·2% CrO_3. Analysis of the crystals separating from more concentrated solutions shows that the only solid phase formed is the trioxide, no hydrate being found. C. H. D.

The Action of Acetic Anhydride on Uranium Nitrate. LUDWIG VANINO (*Chem. Zeit.*, 1911, 35, 1005—1006).—When uranium nitrate (5 grams) is treated with an excess (20 c.c.) of acetic anhydride, a solution is first formed, from which, after a short time, copious fumes of nitrogen peroxide are evolved. At the same time anhydrous uranyl acetate, UO_2Ac_2, is deposited as a yellow, crystalline powder. For the above reaction to take place in the cold, it is necessary that the acetic anhydride should contain a little acetic acid, or that another acid, for example, hydrochloric acid, be added to liberate some nitric acid from the uranium nitrate. If pure acetic anhydride is used, heat is necessary before the reaction commences.

If excess of the anhydride is not used, the only product obtained is a deep yellow liquid.

Thorium nitrate does not react as vigorously as uranium nitrate, and there is scarcely any action with lead or thallium nitrate.

Concentrated nitric acid reacts vigorously with excess of acetic anhydride in a short time, even in the cold. T. S. P.

Melting Point of Tantalum. M. VON PIRANI and ALFRED R. MEYER (*Ber. deut. physikal. Ges.*, 1911, **13**, 540—551).—An electrical method of measuring the melting point is described, which involves the use of an optical pyrometer. This method allows the determination to be made in a vacuum, and enables the metal to be completely isolated from other substances, which is a necessary condition because of the great reactivity of the metal at high temperatures. In these circumstances tantalum is found to melt at 2850° ± 40°.

H. M. D.

The Atomic Weight of Tantalum. WILLIAM H. CHAPIN and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1911, **33**, 1497—1504).—The method used was the transformation of tantalum pentabromide into the oxide.

Tantalum oxide was obtained from recrystallised potassium tantalifluoride by treatment with sulphuric acid, subsequent hydrolysis, washing, and ignition. The pentabromide was prepared by conducting bromine vapours over a red-hot mixture of the oxide with sugar-carbon. To purify it, it was repeatedly sublimed in a vacuum, whereby very small quantities of a yellow residue were obtained, the analysis of which indicated the existence of a *tantalum oxybromide*, $TaOBr_3$. The pure pentabromide so obtained was then hydrolysed by water, and the acid and water evaporated off, the last traces of bromine being removed by evaporation with 10% nitric acid; the residue was then ignited to constant weight.

As a mean of eight experiments the atomic weight is found to be 181·80, the values varying from 181·68 to 181·91 ($O = 16$).

T. S. P.

Metallography of Selenium–Antimony Systems. HENRI PÉLABON (*Compt. rend.*, 1911, **153**, 343—346).—Microscopic examination of selenium–antimony systems leads to the same conclusions as the previous study by the cryoscopic and electrical methods (this vol., ii, 575). Mixtures containing more selenium than the compound Sb_2Se_3 show large crystals of this substance in a matrix of selenium. This is the only definite compound obtainable by fusion of the elements.

Mixtures containing 16—50% atomic proportions of selenium show two phases having almost the same density. The less dense contains the smaller amount of antimony and crystallises in long needles, whilst the other appears as irregular leaflets. W. O. W.

Mineralogical Chemistry.

New Synthesis and New Occurrences of Covellite. AUSTIN F. ROGERS (*School of Mines Quarterly, New York*, 1911, **32**, 298—304).—Pseudomorphs of bluish-black covellite after zinc-blende from Big Coon mine, Galena, Kansas, gave analysis I; deducting unaltered zinc sulphide, this agrees with the covellite formula CuS. The covellite was no doubt produced by the action of copper sulphate solution on zinc-blende, $ZnS + CuSO_4 = CuS + ZnSO_4$. When finely-powdered zinc-blende was heated with copper sulphate solution in a sealed tube at 150—160° for some hours, the material became largely converted into bluish-black covellite (analysis II).

	Cu.	Zn.	Fe.	S.	SiO_2.	Total.
I.	18·80	43·68	1·17	31·37	4·47	99·49
II.	60·10	5·98	0·74	33·75	—	100·75

Other occurrences of covellite are described from California, Colorado, Nevada, and Wyoming. The mineral occurs in the oxidised zone of ore-deposits, and is a product of decomposition of copper-pyrites, bornite, tetrahedrite, enargite, malachite, etc., and it also occurs as pseudomorphs after zinc-blende or galena. L. J. S.

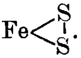
Minerals from the Lead and Zinc District of Galena-Joplin (Kansas-Missouri). AUSTIN F. ROGERS (*Zeitsch. Kryst. Min.*, 1911, **49**, 370—374; from *Univ. Geol. Survey, Kansas*, 1904, **8**, 445—509).—Descriptions are given of thirty-nine species collected in this mining district. Analyses are given of the following: Covellite pseudomorphous, after zinc-blende (preceding abstract). I, Zinc-blende (wurtzite?) from near Joplin: massive with botryoidal or stalactitic surface, of a dark brown colour, and under the microscope showing a granular structure and birefringence. In the cavities it contains small hemimorphic crystals of wurtzite. The results of the analysis are calculated to 100% after deducting SiO_2 and PbS. II, Hydrozincite, white, opaque encrustation on smithsonite and hemimorphite, from Granby, Missouri; formula $ZnCO_3,2Zn(OH)_2$.

	Zn.	Fe.	S.	ZnO.	CO_2.	H_2O.	SiO_2.	Total.
I.	64·09	2·73	33·18	—	—	—	—	100·00
II.	—	—	—	72·80	14·94	12·12	0·14	100·00

L. J. S.

The Constitution of Marcasite and Pyrites. George W. Plummer (*J. Amer. Chem. Soc.*, 1911, 33, 1487—1492).—When marcasite or pyrites was heated at 250° with carbon tetrachloride in a sealed tube, the results indicated that about 75% of the iron in each mineral remained in the ferrous state. Sulphur monochloride was formed, however, and the results obtained are probably vitiated by the establishment of an equilibrium. With a 10% solution of cadmium sulphate instead of carbon tetrachloride, about 20% of the iron was found to be in the ferrous state. With arsenic trichloride instead of arsenic trisulphide, a colloidal solution of arsenic was obtained.

When either marcasite or pyrites is heated with excess of bismuth chloride at the fusion point of the latter and in an atmosphere of dry carbon dioxide, the mineral is completely decomposed within five minutes, and all the iron is found to be in the ferrous state. Only about 91% of the sulphur is in the form of bismuth sulphide, however, some of it being transformed into sulphur monochloride.

The authors draw the conclusion that in both marcasite and pyrites the iron is in the ferrous state, the formula being  $Fe\!\left\langle\begin{matrix}S\\|\\S\end{matrix}\right.$.

T. S. P.

Chemical Composition of a Telluride of Gold and Silver from Nagyag. Carlo Gastaldi (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iiia], 17, 24—26).—Very different results have been obtained by different observers for the composition of krennerite, a rare telluride of silver and gold found in Transylvania and at Cripple Creek, Colorado. The author now shows that two different minerals have been known under this name, and proposes to retain the name krennerite for the compound, $AuTe_2$, occurring in rhombic crystals, whilst for the other mineral, of the formula $(Au,Ag)Te$, the name *muthmannite* is suggested. G. S.

Chemical Composition of Goldschmidtite. Carlo Gastaldi (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iiia], 17, 22—24).—A rare mineral obtained from Cripple Creek in Colorado has been shown by Hobbs (Abstr., 1899, ii, 493) to contain gold, silver, and tellurium, and was termed by him goldschmidtite. Palache, on the other hand (Abstr., 1901, ii, 109), regarded the new mineral as identical with sylvanite. The author now shows that goldschmidtite is a new mineral of the approximate composition $(Au,Ag)_2Te_5$, whereas sylvanite has the formula $(Au,Ag)Te_2$. G. S.

Neocolemanite, a Variety of Colemanite, and Howlite from California. Arthur S. Eakle (*Bull. Dep. Geol. Univ. California*, 1911, 6, 179—189).—A workable deposit of calcium borate, with seams 6—10 feet in thickness, occurs interbedded with black carbonaceous shales near Lang, Los Angeles Co., California. The material consists mainly of neocolemanite (anal. I), with embedded nodules of howlite (anal. II) and a little calcite. The neocolemanite is identical with colemanite in chemical composition, and in many of its physical characters, but it shows slight differences in the angles of the monoclinic crystals ($a : b : c = 0·7771 : 1 : 0·5492$; $\beta = 111°40'$), and in the optical properties (optic axial plane perpendicular to the plane of symmetry, as in colemanite, but $\mathfrak{c} : \acute{c} = -42°30'$).

	B_2O_3.	CaO.	SiO_2.	H_2O.	Total.	Sp. gr.
I.	49·45	27·76	—	22·48	99·69	2·423
II.	45·56	28·26	14·81	11·37	100·38	2·531

L. J. S.

Barytes from the Freiberg Mining District. M. Henglein (*Jahrb. Min.*, 1911, *Beil-Bd.*, **32**, 71—100).—A crystallographic description of barytes from the mineral-veins of the Freiberg district. Brownish-yellow crystals from the Himmelsfürst mine contained only about 0·1% CaO; the colour is due to the presence of bitumen. Reddish platy barytes from the Kurprinz mine gave:

Ba.	Ca.	Fe.	SO_4.	Total.
58·17	0·28	0·57	41·04	100·06

L. J. S.

Synthesis of Smithsonite and Anglesite. Giuseppe Piolti (*Atti R. Accad. Sci. Torino*, 1911, **46**, 783—788).—A rhombohedron of calcite was suspended by a platinum wire in 20% zinc sulphate solution contained in a closed vessel. After about seventeen and a-half years, the rhombohedron was found to be coated with needles of gypsum, and with a white mamillary incrustation which proved to be smithsonite. A solution of potassium nitrate left for about twenty years in contact with a fragment of zinc-blende was found to give the reactions for sulphates. The author, therefore, draws the conclusion that the formation of smithsonite in the superficial layers of the earth's crust (in calcareous rocks containing zinc-blende) is due to the oxidation of the blende to zinc sulphate, and the subsequent interaction of the latter with the calcium carbonate.

Similarly, a piece of galena left in potassium nitrate solution for seventeen and a-half years became covered with minute anglesite crystals, whilst the solution contained nitrite: $4KNO_3 + PbS = PbSO_4 + 4KNO_2$ (compare Abstr., 1910, ii, 621). T. H. P.

Mineralogical Notes [Cuprodescloizite, etc.]. F. N. Guild (*Zeitsch. Kryst. Min.*, 1911, **49**, 321—331).—Crystallographic descriptions are given of various minerals—vanadinite, wulfenite, linarite, caledonite, etc.—from Arizona and California. The following analyses (previously published in "The Mineralogy of Arizona" by the same author, 1910) are given: I, Cuprodescloizite, occurring as a black crystallised crust, 1—2 mm. thick, on large crystals of vanadinite, from the Old Yuma mine, near Tucson, Arizona; the colour of the powdered mineral is pale olive-green. II, Descloizite, occurring as small, black crystals with yellowish-green streak, from Argentina. Both analyses agree with the usual formula

$$R_3(VO_4)_2,R(OH)_2.$$

	PbO.	CuO.	FeO.	ZnO.	MnO.	V_2O_5.	As_2O_5.	Cl.	H_2O.	Insol.	Total.
I.	52·26	11·64	—	6·71	—	23·02	—	—	2·52	—	98·31
II.	53·36	1·21	0·56	13·15	4·56	23·05	0·11	0·08	2·27	0·78	99·13

L. J. S.

Ferritungstite, a New Mineral. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1911, [iv], **32**, 161—162).—The sample of tungstic-ochre described is from the Germania tungsten mine, Deer Trail mining district in the north-eastern part of the State of Washington, where it occurs as an alteration product of wolframite in massive quartz. It is a pale yellow or brownish-yellow ochre, but under the microscope is seen to consist of minute, hexagonal plates, which are optically isotropic on the base. Analyses of small quantities of material gave:

WO_3.	Fe_2O_3.	Ignition (H_2O).	Insol. (Quartz).	Total.
37·1	26·6	18·6	14·7	97·0
35·8	27·3	20·9	[16·0]	100 0

These results agree with the formula $Fe_2O_3,WO_3,6H_2O$. The mineral thus differs from ordinary tungstic-ochre, or tungstite, and it is named ferritungstite. L. J. S.

Some Presumed Chemical Effects of Pressure in Mineral Metamorphism. GIORGIO SPEZIA (*Atti R. Accad. Sci. Torino*, 1911, **46**, 682—698).—The author has submitted to experimental examination the statements of van Hise (*Treatise on Metamorphism*, *Monographs U.S. Geol. Survey*, 1904, **47**) on the effect of pressure in causing chemical change. This writer supposes that under the influence of high pressure (1) silicates are formed from silicon dioxide and carbonates; (2) combined water may be squeezed out of hydrated minerals; (3) combined oxygen may be removed in the same way. In regard to the first statement it has been shown that hydrated silicon dioxide and calcium carbonate do not react under a pressure of 6000 atmospheres for one year (*Atti. R. Acad. Sci. Torino*, 1905, **40**, 698). The author has subjected samples of limonite, alum, and alabaster to a pressure of 8000 atmospheres for eight months at 15—24° without effecting any dehydration. Crystals of göthite maintained under a pressure of 9500 atmospheres for twenty-six days at 15° showed no loss of water, although crystals of the substance were almost dehydrated after having remained in water in an autoclave for seven days at 320—330° (corresponding with a pressure of 135 atmospheres). It has also been impossible to obtain evidence of the occurrence of deoxidation at high pressures. When a mixture of cupric oxide and potassium (or magnesium) was kept under a pressure of 9500 atmospheres at 18° for thirty days, no oxidation of the metal occurred, although pressure might be expected to favour the reaction, because it would be attended by a diminution of the molecular volume.

Calcite (D 2·73) and aragonite (D 2·92) when kept under a pressure of 7000 atmospheres at 15—25° for six months both remain unchanged, so that van Hise's statement that high pressure favours the production of the densest form of minerals lacks confirmation. R. V. S.

Physiological Chemistry.

The Chemical Regulation of Vascular Tone as Studied on the Perfused Blood-vessels of the Frog. DONALD R. HOOKER (*Amer. J. Physiol.*, 1911, **28**, 361—367).—Vascular tone is increased by calcium ions and oxygen, and decreased by sodium and potassium ions, carbon dioxide, and urea. The musculatures of the vascular system and of the intestine give opposite results under the influence of carbon dioxide and oxygen. W. D. H.

The Behaviour of Acetone Substances in Intermediary Metabolism. H. CHR. GEELMUYDEN (*Zeitsch. physiol. Chem.*, 1911, **73**, 176—191).—Acetoacetic acid and β-hydroxybutyric acid administered to phloridzinised rabbits on a constant cabbage diet produced in all cases a decided increase in the sugar excreted in the urine. It is considered that these "acetone-substances" are first synthesised into glycogen in the liver. W. D. H.

Mucic Acid and Intermediary Carbohydrate Metabolism, WILLIAM C. ROSE (*J. Biol. Chem.*, 1911, **10**, 123—138).—Mucic acid in large doses is only, in part, excreted in the urine; a very small increase occurs in the oxalic acid of the urine, and so mucic acid is hardly a percursor of oxalic acid. Large doses of galactose and lactose do not lead to mucic acid in the urine. Mucic acid is therefore not an intermediary product in the metabolism of galactose-yielding sugars. The experiments were made on dogs and rabbits.
W. D. H.

Protein Metabolism. II. FRANZ FRANK and ALFRED SCHITTENHELM (*Zeitsch. physiol. Chem.*, 1911, **73**, 157—175).—Two dogs were fed on a diet containing the necessary amount of fat and carbohydrate; nitrogen was supplied in the form of dog's flesh, ox flesh, and other forms of meat in the dried state, as well as in casein, blood albumin, peptone, and the abiuretic products of complete digestion of fish, beef, egg albumin, and milk. Each article mentioned was employed alone for periods of from seven to twenty-six days. Two results of importance stand out: (1) nitrogenous metabolism was practically the same whatever form of protein food was given; dog's flesh for the dog has no special value; (2) the abiuretic products maintained metabolism as well as the undigested protein.
W. D. H.

Velocity of Decomposition of Food-protein and Body-protein. HEINRICH VON HOESSLIN and E. J. LESSER (*Zeitsch. physiol. Chem.*, 1911, **73**, 345—364).—The relative value of protein from dog's and ox flesh in feeding dogs after inanition has been pointed out by Michaud. The present observations, although they show small differences in favour of Michaud's view that an animal utilises best protein obtained from another animal of the same kind, do not prove that the advantage is a great one. W. D. H.

Formation of Proline in the Digestion of Gliadin. Emil Fischer and E. S. London (*Zeitsch. physiol. Chem.*, 1911, **73**, 398—400).—In the dry residue of the chyme obtained from about the middle of the intestine by a fistula in a dog fed on gliadin, the amount of free proline found was approximately that obtained by Abderhalden and Samuely after complete hydrolysis by acids. W. D. H.

A Mode of Resorption of Reserve Fat. Maurice Piettre (*Compt. rend.*, 1911, **153**, 487—490).—The fat of sheep suffering from distomatosis, in which the liver has become invaded by the embryos of *Fasciola hepatica*, undergoes a change in appearance and acquires a peculiar farinaceous consistence. Determination of the iodine number and other constants shows that no chemical change has taken place. The subject has been investigated histologically.
W. O. W.

Histo-chemistry of Spermatozoa. II. Hermann Steudel (*Zeitsch. physiol. Chem.*, 1911, **73**, 471—477. Compare this vol., ii, 626).—The heads of herring spermatozoa washed with water and freed from fat by alcohol and ether should theoretically yield 71·8% nucleic acid and 28·2% protamine. By phosphorus estimation, supposing all the phosphorus to be in the form of nucleic acid, only 65·4% of nucleic acid is present. By extraction with 1% sulphuric acid, the loss of protamine is even greater, 19·78 instead of 28·2%. By estimating the yield of arginine, there is still a loss of the protamine reckoned therefrom of 5·9%. Evidence is adduced that the spermatozoa heads contain a small quantity of a protein which gives Millon's reaction. W. D. H.

The Relation between the Physical, Chemical, and Electrical Properties of Nerves. V. The Action of Cinchonamine Hydrochloride on Frog's Nerves. F. O'B. Ellison (*J. Physiol.*, 1911, **43**, 28—33).—Cinchonamine hydrochloride increases the injury current, and abolishes the action current of a nerve. It does not abolish excitability or conductivity. W. D. H.

The Oxidation of Isolated Animal Tissues. Arthur Harden and Hugh Maclean (*J. Physiol.*, 1911, **43**, 34—45).—An apparatus for estimating the post-mortem gaseous metabolism of minced organs is described and figured. Such organs have no more power of producing carbon dioxide from sugar in an atmosphere of oxygen than they have in one of nitrogen or hydrogen. Tissue juices prepared by the aid of kieselguhr and aqueous or saline extracts of tissues possess little or no respiratory activity. Oxidation in minced tissue is markedly lowered by grinding with sand, mixing with kieselguhr, or by the use of antiseptics. The figures obtained throughout are considerably lower than those given by Battelli and Stern. W. D. H.

The Indophenol Oxydase of Mammalian and Avian Tissues. Horace M. Vernon (*J. Physiol.*, 1911, **43**, 96—108).—In twelve mammals, the heart muscle is richest in this oxydase, and with the exception of the hedgehog, the liver is the poorest. The harvest mouse has more than the common mouse, and that more than the rat, but the amount in each tissue in the larger mammals from the guinea-pig upwards is nearly constant. These results roughly correspond with the degree of oxygen saturation as determined by Ehrlich. In birds the oxydasic power of the tissues and the respiratory exchange run parallel. The oxydasic power depends largely on the power a tissue possesses of sustained activity. Cold-blooded animals have very little oxydase, and the same is true for embryonic tissues, the liver excepted. W. D. H.

The Composition of the Heart of Man and Dog. Richard Lederer and Karl Stolte (*Biochem. Zeitsch.*, 1911, 35, 108—112).—The following estimations were made: Water content, amount of substance extractable by ether, glycogen, potassium + sodium chlorides, sodium, potassium, chlorine, phosphorus, sulphur, nitrogen, and total ash. No appreciable difference could be detected between normal hearts and hearts pathologically affected. Dogs' hearts contain less sodium, chlorine, and sulphur than the human heart, whereas the phosphorus and nitrogen content is higher. The results are tabulated. S. B. S.

Action of Various Salts on Isolated Muscle. I. Sodium, Potassium, and Ammonium Salts. P. G. Ward (*Proc. physiol. Soc.*, 1911; *J. Physiol.*, 43).—The abolition of response to direct excitation in the frog's sartorious is most readily produced by potassium salts; ammonium and sodium salts follow in the order named. The recovery in saline solution is rapid in the case of potassium salts, and that from the other salts is much less pronounced. W. D. H.

The Formation of Glycine in the Animal Body. I. The Synthesis of Hippuric Acid in the Liver of the Rabbit. Ernst Friedmann and Hermann Tachan (*Biochem. Zeitsch.*, 1911, 35, 88—103).—It has been shown that in the excretion of hippuric acid more glycine can be removed from the body than is ingested, and, furthermore, that young animals can have combined in their proteins more glycine than is contained in the ingested proteins. Investigations were therefore undertaken with the view of throwing light on the method of synthesis of glycine in the animal body. For this purpose, the formation in the rabbit's liver was studied, the method of experiment adopted being the perfusion of this organ in Friedmann's apparatus with defibrinated rabbit's blood to which benzoic acid had been added, and the estimation of the hippuric acid formed under various conditions. From a large series of experiments, it was found that the hippuric acid quantities formed varied greatly in different livers, but that the addition of glycine or its homologues, or of the lower fatty acids (as sodium salt), did not increase the amount. It was concluded therefore that glycine is directly formed in the liver when the latter is perfused with blood containing benzoic acid. S. B. S.

Uric Acid Formation. VII. (1) Failure of Regeneration of Uric Acid in Hunger. (2) Destruction and Formation of Uric Acid in Birds. (3) Uric Acid Synthesis in Mammals and Birds. Guido Izar (*Zeitsch. physiol. Chem.*, 1911, **73**, 317—334).—The livers of dogs in a state of inanition have only a feeble uricolytic power, and they do not produce regeneration of the uric acid on the addition of the blood of fasting animals. A considerable amount of uric acid is, however, formed if the blood of a well-fed animal is used. The bird's liver freed from blood has the power of decomposing uric acid. Livers of birds killed two hours after feeding are able to re-form (in the absence of oxygen) the uric acid which has disappeared; in the latter phenomenon, an enzyme (thermolabile) in the blood, and a co-enzyme (thermostable) in the liver are concerned; the co-enzyme is soluble in alcohol and is not present in the kidneys. Uric acid synthesis from dialuric acid and urea occurs, not only *in vitro*, but in artificial perfusion of the liver in both mammals and birds. The addition of lactic, sarcolactic, tartronic, acrylic, oxalic, and mesoxalic acids leads in the absence of oxygen to no formation of uric acid. Among the substances which are uric acid formers in birds, only ammonium carbonate and urea in the presence of carbon dioxide lead to an increase of uric acid. W. D. H.

Probable Formation of Adrenaline in the Animal Body. Casimir Funk (*Proc. physiol. Soc.*, 1911, iv.; *J. Physiol.*, **43**).—3 : 4-Dihydroxyphenylalanine (Trans., 1911, **99**, 554) has no action on blood-pressure, and is not toxic; when incubated with suprarenal glands, or with a mixture of these glands with liver and pancreas, no adrenaline is formed. It is, however, still possible that the first stage of adrenaline formation may occur in the intestine, and may be of a similar nature to the transformation in the intestine of tyrosine into *p*-hydroxyphenylethylamine. W. D. H.

Calcium Resorption and Calcification. Masahiko Tanaka (*Biochem. Zeitsch.*, 1911, **35**, 113—133).—The solvent effect of liquids (water, 0·9% sodium chloride solution, or ox-serum) saturated with carbon dioxide on bone and allied material, such as teeth and ivory, was studied, and the rate of solution per day per 100 sq. mm. noted. In all cases the solution was found to be quite appreciable. The solvent action of the tissues was also studied by embedding weighed pieces of ivory in the various tissues of living animals and estimating the rate of absorption by weighing. This was found to vary from 0·00070 (in the kidneys) to 0·00118 gram (in the spleen) per sq. mm. per day. The formation of calcium deposits in the living organism after injection of calcium salts was also studied. It was found that in rabbits, dogs, guinea-pigs, and mice, deposits were formed after injection both of soluble and insoluble calcium salts, the formation commencing after two days when the injected dose was not too small. The deposits do not form at the point of injection, but in the neighbouring tissues. Attempts to produce calcium metastases, such as are met with pathologically, were not successful under the varying conditions of experiment tried (including simultaneous injection of phosphates). Analyses of calcium deposits formed after introduction of carbonates and phosphates were made. From the results the conclusion is drawn that the constancy of the composition of calcium deposits and of bone is not due to the existence of a definite chemical compound, but to the practically constant proportions of carbonates and phosphates in the blood-plasma and lymph. The results confirm the conclusions arrived at by Wells and Benson. S. B. S.

Melanin. II. The Pigmentation of the Adult Periodical Cicada (Tibicen septendecim). Ross A. Gortner (*J. Biol. Chem.*, 1911, **10**, 89—94).—The "seventeen year" locust pupa spends seventeen years in subterranean regions, and on emerging from the ground is fully matured in from twenty to sixty minutes. At first it is white, and then in a few hours develops black and orange patches; it then becomes deep black, except the eyes, which are red, and the wing veins, which are orange. This is due to the interaction of a chromogen and an oxydase of the tyrosinase group; the latter is secreted with the new cuticle; it is soluble in water, and rendered inactive by alcohol and by prolonged dialysis in collodion bags.

W. D. H.

Melanin III. The Inhibitory Action of Certain Phenolic Substances on Tyrosinase. A Suggestion as to the Cause of Dominant and Recessive Whites. Ross A. Gortner (*J. Biol. Chem.*, 1911, **10**, 113—122).—If albinos are crossed with a coloured variety, the first generation are all coloured. Other forms of white animals differ from the true albino in giving white offspring. In the former case, the white is a recessive, in the latter a dominant, characteristic to adopt Mendelian nomenclature. The difference must ultimately be due to the interaction of chromogens and oxydases in the skin. Aromatic compounds with two hydroxyls in the meta-position inhibit the action of tyrosinase on tyrosine and other chromogens If tyrosine is converted in the body into either 3-hydroxy-α-anilinopropionic acid (that is, the hydroxyl is shifted from 4 to 3), or if an additional hydroxyl is added ortho to the alkyl chain, a compound is secured which would be incapable of pigment formation under the influence of tyrosinase, and would inhibit pigment formation even if tyrosine and tyrosinase were both present. Such a condition would produce dominant whites. Albino whites lack either the enzyme, the chromogen, or the inhibiting factor. W. D. H.

Composition of the Secretion of Timarcha tenebricosa. E. Wace Carlier and C. Lovatt Evans (*Premier Congrès Internat. d'Entomol. Brussels*, 1910).—The red secretion of the bloody-nosed beetle issues from between the jaws. The ash contains calcium, iron, magnesium, potassium and sodium, phosphoric acid, and chlorine. The most abundant salt is calcium phosphate. The secretion contains albumin and globulin, the pigment is mainly lipochrome, and is soluble in alcohol and ether. The fluid bubbles with sodium hypobromite, and contains a copper-reducing substance in small quantities. No enzymes were found. No quantitative analysis was made owing to the paucity of material. W. D. H.

Some Energy Factors of the Urine Excreted After Severe Muscular Exercise. HAROLD L. HIGGINS and FRANCIS G. BENEDICT (*Amer. J. Physiol.*, 1911, **28**, 291—300).—Urea and ammonia (C : N ratio 0·43 and 0 respectively) tend to keep this ratio in the urine low; uric acid, creatinine, and other carbonaceous compounds raise this ratio. The value of a study of the C : N and calorie : N ratios in the urine is very great in nutrition experiments and in pathology. The ratios (methods for determining which are given) were estimated in eighteen urines after a long-distance running race. In twelve cases the values were normal; the remaining six gave high ratios, probably due to perverted protein metabolism. In view of the fact that the calorie : carbon ratio is constant, the advantage is pointed out of the development of either a volumetric method or a wet process by which estimations of carbon in urine can be rapidly and accurately made.

W. D. H.

Differences in the Urine of Health and Carcinoma. KENJI KOJO (*Zeitsch. physiol. Chem.*, 1911, **73**, 416—433).—The amount of nitrogen which is precipitable by metallic salts (zinc and barium) is about twice as great in the urine of carcinoma as in health. The disturbance of metabolism to which this is attributable is unknown; nor is it known if it is characteristic of cancer. W. D. H.

The Degradation of the Naphthalene Ring in the Animal Body. T. KIKKOJI (*Biochem. Zeitsch.*, 1911, **35**, 57—87).—After ingestion of β-1-naphthylalanine by a dog, a nitrogenous substance was excreted in the urine, of which the composition has not yet been definitely determined. After ingestion of the corresponding β-2-compound a similar substance was also excreted (with the probable formula $C_{15}H_{16}O_3N_2$), but in relatively smaller quantities. In addition, β-naphthylacetic acid and somewhat larger quantities of hippuric acid were excreted. After ingestion of β-naphthylpyruvic acid, β-naphthylacetic and hippuric acids were also excreted. A nitrogen derivative was not in this case isolated. These results indicate the influence of the position of the side-chain on the degradation of the naphthalene ring in the animal body, which is discussed theoretically in some detail by the author, and compared with the various known degradations of the benzene ring, such as is found both in alcaptonuria and in normal cases.

The naphthylalanines were prepared by condensing the naphthaldehydes with hippuric acid to the lactimides of the α-benzoylaminonaphthylacrylic acids. The benzoylaminonaphthylacrylic acids obtained from this by hydrolysis with potassium hydroxide were reduced by sodium amalgam to benzoylnaphthylalanines, from which, by scission of the benzoyl group with acid, the naphthylalanines were obtained in the form of the hydrochlorides. The author gives improved methods for preparing the naphthaldehydes, and obtained the following substances in the course of the research:

α-Benzoylamino-β-1-naphthylacrylic acid,

$$C_{10}H_7\cdot CH{:}C(NHBz)\cdot CO_2H,$$

yellow needles, m. p. 221°; the *lactimide*, $C_{20}H_{13}O_2N$, reddish-yellow needles, m. p. 168—169°. *β-1-Naphthylalanine*, $C_{10}H_7\cdot CH_2\cdot CH(NH_2)\cdot CO_2H$, colourless leaflets, m. p. 240° (decomp.); the *hydrochloride* forms colourless needles, and the *benzoyl* derivative rosettes of colourless, glistening leaflets, m. p. 192—193°.

a-Benzoylamino-β-2-naphthylacrylic acid, pale yellow, stout needles, m. p. 229—230° (decomp.); the *lactimide*, yellow needles, m. p. 147—148°. *β-2-Naphthylalanine*, radiating spheres, m. p. 263—264° (decomp.); the *hydrochloride* was not obtained pure; the *benzoyl* derivative forms glistening leaflets, m. p. 164°.

β-Naphthylpyruvic acid, $C_{10}H_7\cdot CH_2\cdot CO\cdot CO_2H$, prepared from a-benzoylamino-β-2-naphthylacrylic acid by boiling with potassium hydroxide solution, crystallises in colourless, wide needles and irregular leaflets, m. p. 192° (decomp.). S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XIII. The Behaviour of Furylacrylic and Furoylacetic Acids in the Animal Body. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1911, **35**, 40—48. Compare Abstr., 1910, ii, 977).—Furylacrylic acid after subcutaneous injection into the body of the dog is excreted unchanged to the extent of 29%; in addition, pyromucic acid (22·4%) is excreted and furyl methyl ketone. The results might indicate that furoylacetic acid is formed as an intermediate product, although direct evidence of its formation was wanting. When, however, this substance was injected, either as ester or sodium salt, neither pyromucic nor pyromycuric acids could be detected. It is therefore concluded that a β-keto-acid is not formed as an intermediate stage in the degradation of furylacrylic or furylpropionic acids, thus confirming an opinion formerly expressed by the author that aβ-unsaturated acids can be degraded to acids with two less carbon atoms without the intermediate formation of keto-acids. S. B. S.

The Degradation of Carboxylic Acids in the Animal Body. XIV. The Removal of Hydrogen in the Animal Body. ERNST FRIEDMANN (*Biochem. Zeitsch.*, 1911, **35**, 49—56).—In view of the various observations on the formation of unsaturated acids from saturated in the animal body, and to throw light on the processes involved in the removal of hydrogen, the author tried the effect of feeding dogs with the following hydrogen-rich substances: *cyclo*hexanecarboxylic acid, hexahydroanthranilic acid, *cyclo*hexaneacetic acid, and *cyclo*hexanolacetic acid. The two former only caused a notable increase in the amount of hippuric acid excreted. A method for isolating this substance from the urine is described. S. B. S.

Carbohydrate Metabolism. I. The Influence of Hydrazine on the Organism with Special Reference to the Blood Sugar Content. FRANK P. UNDERHILL (*J. Biol. Chem.*, 1911, **10**, 159—168).—Hydrazine sulphate subcutaneously injected in dogs and rabbits in doses of 0·1 gram per kilo. of body-weight causes death. Half this quantity is usually followed by recovery, and lowers the amount of

sugar in the blood of dogs; this effect is not constant in rabbits. During a short period of inanition, assimilation of dextrose after hypodermic administration is as good as in normal well-fed dogs. Dextrose in subcutaneous doses of 5 grams per kilo. promptly causes death if the dogs had previously been treated with non-fatal doses of hydrazine. Hydrazine introduced into the blood stream causes no appreciable immediate influence on arterial blood-pressure.
W. D. H.

Action of an Oxazine (3:5:9-Triaminophenoxazonium Chloride) on Trypanosomes. A. LAVERAN and ROUDSKY (*Compt. rend.*, 1911, **153**, 226—230. Compare Kehrmann and Sager, Abstr., 1903, i, 279).—The experiments were conducted on mice by intramuscular injection, using a 0·1% aqueous solution of the substance. Both *in vivo* and *in vitro* the centrosomes show a marked affinity for the dye, which also brings about morphological changes. In *T. Brucei* the centrosomes disappear, and the new modification is transmissible by heredity. Other species of trypanosomes show the same behaviour in variable degrees; in general, their virulence is diminished, but often only temporarily.
W. O. W.

The Physiological Effects of Alkaloids of Zygadenus Intermedius. PHILIP H. MITCHELL and GEORGE SMITH (*Amer. J. Physiol.*, 1911, **28**, 318—329).—An alkaloidal preparation from *Zygadenus intermedius* (one of the death camas, which is so destructive to sheep) causes slowing of the heart by acting on the cardio-inhibitory centre, slowing of the respiration by acting on the respiratory centre, vasodilatation, purgation, and emesis. In quantities approaching the fatal dose (5 mg. per kilo. of guinea-pig) the heart is rapid and irregular, and the respiration convulsive. In fatal doses the heart stops before respiration.
W. D. H.

Pharmacology of Substances Behaving Like Digitalis. ALBERTUS SLUYTERMAN (*Zeitsch. Biol.*, 1911, **57**, 112—134).—The action of antiarin, helleborein, oleandrin, infusion of Folia Digitalis, barium chloride, and methyl-violet on the ventricle of the frog's heart was examined. The general effect of all is the same, so that the author classes them as digitalis substances. Examination of the curves, however, reveals certain differences; a scale of activity for different dilutions can be drawn up for antiarin, digitalis infusion, and barium chloride, but not for the others.
E. J. R.

***p*-Iodophenylarsinic Acid and Some of its Derivatives. II. Pharmacological Action.** EFISIO MAMELI and ALDO PATTA (*Arch. Farm. sperim. Sci.*, 1911, **11**, 475—484. Compare Abstr., 1909, i, 543; 1910, i, 531).—From experiments with guinea-pigs, rabbits, and dogs, the authors find that *p*-iodophenylarsinic acid is much more toxic than atoxyl, so that the displacement of NH_2 by iodine increases toxicity. The absorption of the substance requires considerable time: iodine does not appear in the urine until three to five hours after administration of the drug. The absorption of the iodide of the acid is even slower. After administration of the acid, all the iodine of the urine is in organic combination, but the iodide yields also ionic iodine in the urine. In both cases arsenic is present in inorganic combination, and the appearances found in the animals coincide with those of arsenic poisoning. R. V. S.

p-Iodophenylarsinic Acid and Some of its Derivatives. III. Action on Metabolism, on the Circulation, and on Trypanosomes.

Efisio Mameli and Aldo Patta (*Arch. Farm. sperim. Sci.*, 1911, **12**, 1—7. Compare preceding abstract).—In rabbits, *p*-iodophenylarsinic acid appears to diminish the rate of the metabolism of the albumins. The substance does not affect the pulse or the arterial pressure. Neither the acid nor its iodide has any action on *Trypanosoma Brucei*. R. V. S.

Mercurial Therapeutics of Experimental Syphilis in the Rabbit and of Brazilian Spirollosis.

L. Launoy and G. Levaditi (*Compt. rend.*, 1911, **153**, 304—306).—The mercury derivative of the dithiocarbamate of potassium methylaminoacetate,

$$(CO_2K\cdot CHPh\cdot NMe\cdot CS_2)_2Hg,$$

(Fourneau, this vol., i, 528), has a distinct curative action in syphilis of rabbits and spirollosis of fowls when administered by intravenous injection. Instances of complete cure are recorded. W. O. W.

Action of Senecio Alkaloids and the Causation of Hepatic Cirrhosis in Cattle.

Arthur R. Cushny (*Proc. Roy. Soc.*, 1911, *B*, **84**, 188—190).—Whilst the various species of Senecio in this country are usually considered harmless, in Canada and New Zealand the species *Senecio Jacoboea*, apparently identical with the common ragwort, is associated with hepatic cirrhosis in cattle, and in S. Africa this disease is associated with *Senecio Burchellii* and *S. latifolius*, from which Watt (Trans., 1909, **95**, 466) obtained two alkaloids, senecifoline and senecifolidine.

The results of experiments with these two alkaloids showed that they are equally toxic and produce the same symptoms. Very large amounts have an effect on the central nervous system resembling that seen in many convulsive poisons, whilst with smaller quantities the chief effect is hæmorrhage, which may occur in almost any organ and is constant in the liver and nearly always present in the stomach and bowels.

Experiments with extract of English ragwort and of *S. silvaticus* collected in Yorkshire gave negative results. *S. vulgaris* (common groundsel) collected in England proved poisonous, the animals dying from symptoms resembling those produced by senecifoline, but with diarrhœa. N. H. J. M.

The Combination of Tetanus Toxin [with other Substances]. II.

Siegfried Loewe (*Biochem. Zeitsch.*, 1911, **34**, 495—511. Compare this vol., ii, 638).—The tetanus toxin, in varying concentrations, was shaken with brain substance, and the coefficient of distribution between the two phases ascertained by determining the number of minimal lethal doses in the aqueous phase at the end of the experiment. The results indicate that there can be no question of a chemical combination between the brain substance and the toxin; they indicate rather a distribution of the latter between the two phases in the sense of Henry's law. S. B. S.

The Action of Crotalus Poison. IVAR BANG and E. OVERTON (*Biochem. Zeitsch.*, 1911, 34, 428—461).—A solution of the dried crotalus poison in pure water acts toxically on tadpoles only when the solution reaches a concentration of 1%. By the addition, however, of small quantities of hæmolysed blood-corpuscles, the toxicity is increased three hundred-fold, and is then about one-third of that of cobra poison. Within certain limits the toxicity of the crotalus poison increases with increasing quantity of blood-corpuscles, an addition of less than 0·1 c.c. to 25 c.c. of the toxin solution exerting no action, whereas 1 c.c. exerts the maximal action. This is probably due to the action of the phosphatides, Merck's "lecithin" exerting a similar action. The toxic action of crotalus is diminished by momentarily boiling the solution. A solution of the poison in blood serum is four to five times stronger than the correspondingsolution in water. The serum must be rendered innocuous to the tadpoles by previously heating it to 50°. The crotalus poison differs from the cobra poison, in that in concentrations sufficient to paralyse the central nervous system it also causes stoppage of the circulation. The solution in water (but not in serum) injures the skin epithelium. In consequence of these two last actions, the toxic action, unlike that of cobra poison, is not reversible when the tadpoles are transformed to a toxin-free medium. The addition of calcium chloride to a crotalus toxin solution activated by blood-corpuscles diminishes or destroys the toxicity. The antivenin preparation (from the Pasteur Institute of Lille) as strongly diminishes the toxic action as it does that of cobra poison. The toxic action from the crotalus bite appears to come into play when the secretion of the poison glands exerts its action on the blood-corpuscles. S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Electrical Effects Accompanying the Decomposition of Organic Compounds. M. C. POTTER (*Proc. Roy. Soc.*, 1911, *B*, **84**, 260—275).—Experiments performed with yeast and dextrose, invertase, diastase, and *B. coli communis* all show that the disintegration of organic compounds by micro-organisms is accompanied by the liberation of electrical energy. The electrical effects express the activity of the micro-organisms, and are influenced by the factors temperature, concentration of the nutrient, and the number of organisms present. They take place only within the ordinary temperature limits of biological activity.

A special type of galvanic cell with platinum electrodes is described. The charge was found to correspond with an *E.M.F.* of 0·3 to 0·5 volt between the fermenting and non-fermenting fluids. E. F. A.

The Significance of Dihydroxyacetone as an Intermediate Product of Alcoholic Fermentation. S. KARAUSCHANOFF (*Ber. Deut. bot. Ges.*, 1911, **29**, 322—327).—Jensen states that dihydroxyacetone is fermentable by yeast, and argues that it is an intermediate product in the fermentation of sugar. The author does not consider that Jensen's methods were sufficiently refined; the small amounts of carbon dioxide supposed to arise from fermentation may in reality have come from the animal charcoal. E. J. R.

Alteration in the Fermentative Properties of Yeast Cells on Killing by means of Acetone. REGINALD O. HERZOG and O. SALADIN (*Zeitsch. physiol. Chem.*, 1911, **73**, 263—283).—A comparison is made of the relative velocities of fermentation of dextrose, lævulose, mannose, and galactose by living yeast and by the same yeast after killing with acetone. Action was stopped by mercuric chloride and the change determined polarimetrically. The velocity constants K and V were calculated by means of the formulæ $K=\frac{1}{t}\log\frac{C_o}{C_t}$ and $V=\frac{1}{t}\log\frac{C_o+(C_o-C_t)}{C_t}$, in which C_o and C_t are the optical rotations at the beginning and after a time t. The values given by V were more constant. The quantity of dead yeast selected was such as to give about the same rate of fermentation of dextrose as the living yeast.

Doubling the quantity of either dead or living yeast doubles the rate of fermentation. Galactose was not fermented by the yeast chosen. The relative velocities of fermentation of dextrose, lævulose, and mannose by the living yeast are 1 : 0·63 : 0·52, and by the acetone yeast, 1 : 1·06 : 0·81, indicating that the killing of yeast alters its relative fermentative activity towards the three sugars. The change may be attributed to an alteration in the permeability of the cell membrane or to the presence of different zymases within the cell. Adopting Harden and Young's view, the treatment with acetone and ether damages a substance which is important for the rapid fermentation of dextrose, but relatively less important for that of lævulose.

E. F. A.

Phosphorus Assimilation of Aspergillus Niger. ARTHUR W. DOX (*J. Biol. Chem.*, 1911, **10**, 77—80).—Raulin's medium was used with the ammonium phosphate omitted, and an equivalent amount of phosphorus in another form added. Excellent growth was obtained with anhydrous sodium orthophosphate, pyrophosphate, and metaphosphate. Sodium hypophosphite led to germination, but not growth, and sodium phosphite was not utilised at all. Excellent results were also obtained with various organic phosphorus compounds, namely, phytin, sodium glycerol phosphate, and nucleinate, lecithin, casein, and ovovitellin. W. D. H.

Behaviour of Certain Mould Fungi towards Organic Acids. I. Reginald O. Herzog and O. Ripke (*Zeitsch. physiol. Chem.*, 1911, **73**, 284—289).—*Mycoderma cerevisae*, *Monilia candida*, and *Oidium lactis* were grown for six weeks in solutions containing from 0·5 to 3% of a number of organic acids. They caused from 30% to 95% of the acid to disappear, being very selective in their behaviour. Mycelium killed with acetone and ether when kept under water through which a stream of air was passed developed more carbon dioxide in presence of acids, the acid being used up in the process. Mycelium treated with liquid air behaved quite similarly to the dead mycelium, although it had remained alive. E. F. A.

Behaviour of Certain Mould Fungi towards Organic Acids. II. Reginald O. Herzog, O. Ripke, and O. Saladin (*Zeitsch. physiol. Chem.*, 1911, **73**, 290—301. Compare preceding abstract).—*Mycoderma cerevisiae*, killed by acetone, when kept in solutions of acetic or lactic acid causes a disappearance of the acid, which is not oxidised, however, since the production of carbon dioxide is less in acid than in pure aqueous solution. Mandelic acid behaves similarly; the acid used up is not bound by the fungus, either by salt formation or by absorption, or converted into an ester, but it is chemically changed. There is no difference in behaviour between the two optical isomerides in the case of mandelic and tartaric acids. Living fungi give similar results with acids. E. F. A.

Behaviour of Certain Mould Fungi towards Amino-acids. Reginald O. Herzog and O. Saladin (*Zeitsch. physiol. Chem.*, 1911, **73**, 302—307. Compare preceding abstracts).—The addition of leucine to a mycelium of *Penicillium glaucum*, previously kept in water until the respiratory daily output of carbon dioxide was steady. caused a definite increase in the daily production of carbon dioxide. This increase amounted to considerably more than was to be accounted for by the leucine which had disappeared. An exactly parallel behaviour was shown by a mycelium previously killed with acetone. Other amino-acids behave similarly in causing an increased production of carbon dioxide. E. F. A.

A Ferment Causing Bitterness in Wines, Acting as a Dehydrating Agent towards Glycerol. E. Voisenet (*Compt, rend.*, 1911, **153**, 363—365. Compare Abstr., 1910, ii, 738, 909).—A pure culture of the bacillus causing bitterness in wine has been obtained in a Laurent peptone medium. This has previously been shown to produce acraldehyde during fermentation. It appears to effect a direct, irreversible transformation of glycerol into acraldehyde without the formation of intermediate compounds. The organism is incapable of producing acraldehyde from butyric, lactic, or succinic acids, glyceraldehyde or dihydroxyacetone. The acids formed during fermentation have an inhibitory effect on the production of acraldehyde, but this proceeds further on the addition of calcium carbonate.

W. O. W.

The Erepsins of Glomerella Rufomaculans and Sphæropsis Malorum. HOWARD S. REED and H. S. STAHL (*J. Biol. Chem.*, 1911, **10**, 109—112).—Erepsins have previously been found by others in saprophytic fungi, but not in parasitic fungi. The two fungi named are parasitic and infest apples. The presence of erepsin was shown in both. The extracts of the mycelia also liquefy gelatin.

W. D. H.

Chemistry of Tuberculin. GEORG LOCKEMANN (*Zeitsch. physiol. Chem.*, 1911, **73**, 389—397).—Various purified forms of tuberculin do not give the protein reaction. The bacilli were grown in a medium containing only one organic substance, namely, asparagine. The culture fluids were found to contain protein. The same is true for glycerol-bouillon media; but the preparation known as *endotin* did not give a single protein reaction, and therefore does not contain the protein substances which pass during growth into the culture fluid.

W. D. H.

Action of Nitrogen on Wines. PHILIPPE MALVEZIN (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **29**, 73—75).—When nitrogen is passed through wine contained in a test-tube for a second, and the wine inoculated with *Mycoderma vini*, a turbidity is produced after about thirty-six hours. No turbidity is produced in wine merely inoculated.

Red wine which has been decolorised with animal charcoal, inoculated with *Mycoderma*, treated with nitrogen, and then heated for five minutes at 70—80°, acquires a blue colour when a few drops of tincture of guaiacum are added. When treatment with nitrogen is omitted, either no blue coloration is produced, or else a paler blue than in the nitrogen-treated wine.

If an excessive amount of nitrogen is employed, the oxidising action is checked, and the *Mycoderma vini* fails to develop.

When fermenting wines rich in sugar are saturated with nitrogen, left for a day or two, and filtered, fermentation is completely checked. The amounts of nitrogen employed were 20 grams per hectolitre.

N. H. J. M.

The Assimilation of Atmospheric Nitrogen by Thermophilic Bacteria. HANS PRINGSHEIM (*Centr. Bakt. Par.*, 1911, ii, **31**, 23—27).—Cultures of these organisms were obtained by inoculating Winogradsky's solution with a little garden soil, and incubating under anærobic conditions at 61°. Active fermentation set in after six days, and microscopical examination showed the presence of long bacilli and some plectridium forms. Sub-cultures could not be obtained until media containing soil extracts were used. In such media and with impure cultures, considerable quantities of nitrogen were assimilated; where 5 and 2·5 grams of dextrose per litre of nutrient solution were supplied, the respective amounts of nitrogen assimilated for each gram of sugar fermented were 3·0 and 6·2 mg. H. B. H.

The Formation of Oxides of Nitrogen during Denitrification. SHIGEHIRO SUZUKI (*Centr. Bakt. Par.*, 1911, ii, **31**, 27—49).—An account of experiments carried out to throw light on some discordant results obtained by Beyerinck and Minkman (Abstr., 1909, ii, 1043), and to ascertain whether a production of nitrous oxide occurred when nutrient solutions other than nitrate bouillon were used.

It was found that accurate results could be obtained when the mixture of gases produced by fermentation was collected over mercury instead of calcium chloride solution, the oxygen absorbed by means of pyrogallol instead of by phosphorus, and the remaining gas burnt with pure oxygen and carbon monoxide in a Drehschmidt's platinum capillary tube. The percentage of nitrous oxide in the gas produced during denitrification was found to vary at different periods of the same fermentation, and to be dependent to a large extent on the composition of the nutrient solution. In all cases nitrous oxide, but not nitric oxide, was formed. High percentages of nitrate and high temperatures were favourable to the production of the former gas. H. B. H.

The Formation of Nitric Oxide by B. Hartlebi during Denitrification. A. J. Lebedeff (*Ber. Deut. bot. Ges.*, 1911, **29**, 327—329).—Nitric oxide is evolved during the growth of *B. Hartlebi* under anærobic conditions, and with the following culture solution: 1% of potassium sodium tartrate or sodium lactate, 0·3% of potassium nitrate, 0·05% of potassium dihydrogen phosphate, 0·02% of magnesium sulphate, and a trace of ferric chloride rendered slightly alkaline with potassium hydroxide. After three or four days at 26°, it is found that a considerable quantity of carbon dioxide is evolved, and a volume about one-twentieth as great of nitric oxide. On leading air into the flasks, brown fumes are seen. E. J. R.

Plant Chemistry. P. Q. Keegan (*Chem. News*, 1911, **104**, 109—110).—From the results of analyses of about fifty wild plants, the conclusion is drawn that sugar is a highly important product of assimilation, that it is independent of starch, and is not a respiratory material and not convertible into acids. Sugar migrates in the plant, whilst starch does not.

An alcoholic extract of dried leaves of *Alliaria officinalis*, previously extracted with benzene, was found to contain a tannoid or a glucoside of a flavone derivative, which differs from all others by its reaction with iodine, indicating some form of hydroxybenzoic acid. It has no catechol or quinol nucleus, but probably a phloroglucinol complex.

Plants of the order *Compositæ* were found to contain a tannoid which contains a catechol nucleus, and, perhaps, a quinol nucleus. Other plants of the same order contain coffee tannin. The sub-order *Corymbiferæ* seems to have most tannoid, and the *Cynarocephalæ* most tannin.

In connexion with the statement of Pichard (Abstr., 1899, ii, 788) that the presence of chlorides in the soil and the absorption by plants is antagonistic to the absorption of nitrates, it was found that seven micorhyza plants which contain no nitrates contained 9·8—28% of chlorine in the crude ash, whilst the same number of nitrate plants contained only 1·2—4% On the other hand, some micorhyza plants were found to contain very small, and some nitrate plants considerable, amounts of chlorine. N. H. J. M.

Formation of Nitrous Acid in the Vegetable and Animal Cell.

Pierre Mazé (*Compt. rend.*, 1911, **153**, 357—360. Compare this vol., ii, 643).—The fresh juice from pea-stalks was precipitated with alcohol and filtered through a Chamberland filter. The sterile liquid thus freed from the organisms which produce nitrous acid described in a previous paper, still developed traces of this substance when allowed to remain, but was free from nitric acid. Etiolated plants furnished more nitrous acid than green ones, in one case 0·0093 gram per litre was obtained after twenty-four hours.

Washed blood-corpuscles when submitted to hæmolysis yield a liquid giving a distinct reaction with potassium iodide. Bence Jones' discovery of nitrous acid in normal urine was confirmed, but urine from a patient in an advanced stage of tuberculosis gave a negative result. W. O. W.

The Relationship between Tanning Substance and Another Colloid in Ripening Fruits, Especially Phœnix, Achras, and Diospyros.

Francis E. Lloyd (*Zeitsch. Chem. Ind. Kolloide,* 1911, **9**, 65—73).—It has been found that certain tannin cells, especially those of the pericarp of certain fruits, contain a second colloidal substance in addition to tannin. This appears to absorb the tannin during the process of ripening, and as a result of this absorption the tannin cannot be removed from the cells by extraction processes. The active colloid appears to be a carbohydrate which resembles the pectoses, and on hydrolysis yields a sugar.

In the unripe fruit the colloid is present in a mucous condition, which changes, however, during the ripening until a stiff gelatin-like mass is obtained. The structure of the tannin-colloid aggregate, is much more nearly like that of the colloid than that of tannin. It is supposed that this aggregate is of the nature of a solid solution, and that its formation is of primary importance in connexion with the ripening of fruits. H. M. D.

Origin of Osmotic Effects. IV. The Differential Septa in Plants with Reference to the Translocation of Nutritive Materials.

Henry E. Armstrong and E. Frankland Armstrong (*Proc. Roy. Soc.*, 1911, *B*, **84**, 226—229. Compare this vol., ii, 642).—In water, laurel or *Aucuba* leaves remain unchanged for many days. When a substance, such as toluene, which can penetrate the leaf is added to the water, not only does the leaf change, but reducing sugar and other substances diffuse out of it. In a solution of hydrogen cyanide, however, although similar changes take place inside the leaf, no reducing sugar passes out into the solution.

Most leaves become brown and some black when exposed to water containing a little toluene; in a cyanide solution such coloration is very much less marked. These differences are interpreted as proof that differential septa which breakdown under the influence of most hormones remain intact when hydrogen cyanide is used, and it is suggested that the septa remain intact because the oxydase effect is eliminated in presence of hydrogen cyanide.

Oxidation processes are at a maximum in plants during the period when light is inactive, and growth takes place chiefly during this period; the translocation of nutritive materials may take place because the septa are broken down and rendered permeable by oxidation; they may be repaired subsequently when assimilatory processes become ascendant. E. F. A.

The Action of Anæsthetics on the Osmotic Properties of the Plasma Membrane. W. W. LEPESCHKIN (*Ber. Deut. bot. Ges.*, 1911, **29**, 349—355).—Treatment of a plant cell with an aqueous solution of an anæsthetic lowers the permeability of the plasma membrane; thus the isotonic coefficients of potassium nitrate for *Tradescantia discolor* were: after immersion in water, 2·95; in 0·1% chloroform water, 3·04, the corresponding permeability factors being 0·127 and 0·100 respectively. Immersion in 2·5% ether solution caused a still further lowering of permeability. In other words anæsthetics lead to an increase in osmotic pressure of the cell sap.

The bearing of these results on Nathanson's hypothesis of the Mosaic structure of the plasma membrane is indicated. E. J. R.

Absorption of Arsenic by Beetroots. HANS REMMLER (*Chem. Zeit.*, 1911, **35**, 977—979).—The author has carried out a number of experiments in order to ascertain whether the spraying of beetroots with arsenical preparations for the destruction of parasites (*Silpha atrata*) leads to the absorption of appreciable quantities of arsenic by the beetroots. After removal of soil from beetroots which had been sprayed with a solution of Schweinfurt-green, the roots were found to contain 0·08 mg. of As_2O_3 per kilogram. Other specimens contained less, the quantity appearing to depend on the amount of arsenical solution which reached the soil during the spraying. The beetroot leaves contained 0·25 mg. of As_2O_3 per kilogram.

W. P. S.

The Action of Methylene-blue on the Respiration and Alcoholic Fermentation of Living and Killed Plants. WLADIMIR I. PALLADIN, ELISE HÜBBENET, and MARIE KORSAKOFF (*Biochem. Zeitsch.*, 1911, **35**, 1—18).—In the presence of air, etiolated stem tips of *Vicia faba*, which have been coloured with methylene-blue, excrete considerably more carbon dioxide than do uncoloured control tips. The tips from *Pisum sativum* are similarly effected by the dye, but to a less degree. Quinine has a similar action. On the seeds, however, the action in the two plants differs, in that methylene-blue stimulates slightly the respiration of the seeds of *Pisum sativum*, whereas quinine slightly diminishes it. The difference of action is explained by the difference in the amounts of respiratory chromogen, those materials containing small quantities of these substances being only slightly stimulated by methylene-blue, and being readily poisoned by quinine. The stimulating action of methylene-blue on *Vicia faba* ceases if the plant is killed by subjecting it to a low temperature. Other differences between the action of the methylene-blue on ærobic and anærobic respiration are demonstrated. The ratio carbon dioxide/alcohol is about 1 in coloured plants, but less than 1 in the control plants.

Disodium hydrogen phosphate paralyses the injurious action of methylene-blue on the etiolated stem tips of *Vicia faba*. S. B. S.

Direct Assimilation of Inorganic and Organic Forms of Nitrogen by Higher Plants.

Henry B. Hutchinson and Norman H. J. Miller (*Centr. Bakt. Par.*, 1911, ii, **30**, 513—547. Compare Abstr., 1909, ii, 923).—Water-culture experiments, under sterilised conditions, with the apparatus previously described (*loc. cit.*), in which peas were supplied with nitrogen in various forms.

Of the substances employed, urea showed the greatest assimilation, one plant taking up 18·2 mg. of nitrogen. Barbituric acid (with calcium carbonate) was readily assimilated, being possibly converted in the plant into urea and malonic acid. Acetamide and alloxan were also readily assimilated, the former producing more growth than ammonium sulphate without calcium carbonate, whilst formamide, glycine, alanine, guanidine hydrochloride, cyanuric acid, and oxamide, although assimilated, were taken up in smaller amounts. The results obtained with trimethylamine, *p*-urazine [1 : 2 : 4 : 5-tetrazine], and hexamethylenetetramine were doubtful, as although one of the two plants showed a slight gain of nitrogen (especially with *p*-urazine and hexamethylenetetramine), there was no gain in dry produce. Hydroxylamine hydrochloride, ethyl nitrate, propionitrile, and methyl carbamate gave negative results, whilst tetranitromethane is toxic.

Soluble humus was readily assimilated, producing considerable growth. Peptone was also assimilated, but the dry produce was a good deal less than with humus. N. H. J. M.

Constituents of Apples.

Carl Thomae (*J. pr. Chem.*, 1911, [ii], **84**, 247—248).—By the distillation of apple-skins in steam and extraction of the resulting aqueous liquid, a soft mass is obtained, which yields a crystalline substance when moistened with alcohol; the alcoholic filtrate contains a yellow oil, having a refreshing odour of apples.

When treated with dilute sodium carbonate and extracted with ether, the skins yield a colourless, odourless, powdery substance, m. p. above 200°. This substance is not readily wetted by water, and in conjunction with a little plant-fat or gum, forms the covering which prevents the fruit from drying. F. B.

Chemistry of Polyporus frondosus.

Max Bamberger and A. Landsiedl (*Monatsh.*, 1911, **32**, 641—642).—The alcoholic extract of the fungus contains a basic nitrogenous substance which forms a colourless, granular powder. It dissolves readily in mineral acids, with which it gives crystalline salts. The *hydrochloride* and *hydrobromide* crystallise in transparent, rectangular columns and quadratic plates. The *sulphate* is specially characteristic, crystallising in glass-like needles. The *nitrate*, *picrate*, and *platinichloride* have been prepared. The salts do not become brown until heated above 300°.

E. F. A.

Loss of Hydrocyanic Acid from Cherry-laurel Water on Keeping and on Treatment with Animal Black. A. ASTRUC (*J. Pharm. Chim.*, 1911, [vii]. 4, 5—13).—This paper is mainly of pharmaceutical interest. The results obtained show that to avoid loss of hydrogen cyanide from the cherry-laurel water of the French codex, the water should be stored in the dark in well-stoppered bottles holding from 125 to 150 c.c., and that the supply should be renewed frequently and its content of hydrocyanic acid determined from time to time.

Cherry-laurel water, which has become coloured, due to the action of air and light, should not be decolorised by animal charcoal, as this occasions large losses of hydrogen cyanide. The amount of acid absorbed by the charcoal varies with the quality of the latter, the strength of the water in acid, and the quantity of charcoal used, but is scarcely affected by the time the charcoal is left in contact with the water or the temperature (up to 80°) at which the operation is conducted. T. A. H.

The Sugar in the Nodules of Nephrolepis hirsutula, Presl. G. DIETHELM LIEBER (*Ber. Deut. bot. Ges.*, 1911, 29, 375—380).—The nodules contained 4·3% of dry matter, of which 1·6 was sugar. Beyond the fact that the sugar is a hexose or mixture of hexoses, nothing more could be determined. E. J. R.

Chemical Examination of Œnanthe Crocata. FRANK TUTIN (*Pharm. J.*, 1911, [iv], 33, 296—298).—The investigation was undertaken to ascertain the nature of the substance to which the well known toxic action of this plant is due. Poehl (*Arch. exp. Path. Pharm.*, 1895, 34, 258) has attributed this property to "œnanthotoxin," a neutral, amorphous product soluble in ether, and the author confirms this observation, but points out that the toxic material is ill-defined and amorphous, so that no formula can be assigned to it. In addition a number of physiologically inactive substances were isolated.

A concentrated alcoholic extract of the whole plant deposited sucrose on keeping. On steam-distillation the extract yielded (1) a volatile oil, b. p 100—200°/100 mm., D_{15}^{15} 0·9381, α_D +1°16′ in a 25 mm. tube, which was yellow, had an unpleasant odour, and gave the furfuraldehyde reaction; (2) a dark-coloured aqueous liquid, and (3) a brown resin. From the aqueous liquid salicylic acid, a crystalline substance, m. p. 83°, amorphous products, and a mixture of dextrose and lævulose, probably resulting from inversion of sucrose, were obtained. The brown resin was resolved into its constituents by extraction successively with light petroleum, ether, chloroform, ethyl acetate, and alcohol. The portion soluble in light petroleum contained triacontane, hentriacontane, ipuranol, a phytosterol, probably sitosterol, $C_{27}H_{48}O$, palmitic acid, and a mixture of unsaturated fatty acids, chiefly linoleic acid. The portion dissolved by ether was a brown, sticky solid, of which about half was soluble in alkalis, the residue being a dull green, viscid mass, which became reddish-brown when heated with potassium hydroxide in alcohol.

The portions of the crude resin finally dissolved in turn by chloroform, ethyl acetate, and alcohol were black, amorphous solids, devoid of physiological activity when given to guinea-pigs in doses of 1 gram. This was also the case with the aqueous liquid, but similar doses of the light petroleum and ether extracts of the resin rendered guinea-pigs hyper-excitable, and marked convulsions with trismus soon appeared. Of the two portions of the ether extract, the neutral part was more active than the acidic portion, and the former probably corresponds with Poehl's "œnanthotoxin." No alkaloid or enzyme could be detected in any part of the plant. T. A. H.

Algerian Oleander Bark. ALBERT LEULIER (*J. Pharm. Chim.*, 1911, [vii], 4, 157—161).—Dubigadoux and Durieu have shown already that the latex of this apocynaceous shrub contains a strophanthin-like glucoside, and the author confirms this and further characterises the glucoside.

The bark of the plant, which contains the latex, was used as a raw material, and Fraser's process was employed for the isolation of the glucoside (Abstr., 1887, 1115; 1888, 606; 1890, 262). It crystallises in minute, brilliant, pale yellow, irregular lamellæ, is intensely bitter, dissolves in water, alcohol or glycerol, is precipitated by tannin solutions, and becomes pasty at about 165°. It is hydrolysed by boiling with mineral acids, forming a reducing sugar and an amorphous bitter substance, m. p. 92° (approx.). A number of colour reactions of the parent glucoside are described. It is regarded as possibly a ψ-strophanthin (compare Feist, Abstr., 1900, i, 555).

T. A. H.

Pot-culture Experiments. JOHN A. VOELCKER (*J. Roy. Agric. Soc.*, 1910, 71, 343—350. Compare Abstr., 1908, ii, 622).—Small amounts of lithium salts (Li = 0·0018%) seem to have a stimulating effect on wheat; no injurious action was observed when the amount of lithium does not exceed 0·002%. Cæsium salts may be employed in larger amounts (0·0036%) without injurious effects. Zinc salts are injurious to wheat when the soil contains 0·04% of zinc.

Experiments in which barley was grown in soil containing 0·02% of iron sulphate and varying amounts of manganese sulphate (0·005 to 0·06%) showed a slightly stimulating effect, but no clear differences due to the different amounts of manganese. Similar results were obtained when 0·02% of manganese sulphate and varying amounts of iron sulphate were applied to the soil. N. H. J. M.

Production of Nitrates in Arable Soils. ALFRED KOCH (*J. Landw.*, 1911, 59, 293—315).—Drain-pot experiments on nitrification in different soils and subsoils, both alone and with addition of ammonium sulphate.

Comparing the amounts of nitrates produced in the surface soil (20 cm.) and in the subsoil (20—40, 40—60, and 60—80 cm.), it was found that the amounts of nitrates decreased with the depth more than the percentages of total nitrogen. When ammonium sulphate was added to the soils, somewhat less nitrate was formed in the subsoils than in the surface soil during the first three months, whilst later on there was less difference.

Ammonium sulphate (2 grams per kilo. of soil) applied in November was nitrified to the extent of one-half by the following March, and completely nitrified by June.

As regards losses of nitrogen during the nitrification of ammonium salts, the results obtained with two different soils showed that 83—85% of the nitrogen applied was nitrified. In the case of subsoil (60—80 cm.) the amount of nitrogen recovered as nitrate amounted to only 78%. In addition to loss of nitrogen applied as ammonium salt, there was also a loss of soil nitrogen.

Application of lime to soils containing ammonium sulphate checks nitrification as long as an odour of ammonia is perceptible. Lime added to soil alone increased nitrification until converted into carbonate. N. H. J. M.

Behaviour of Manganese in the Soil Towards Some Agricultural Plants. PAUL LEIDREITER (*Bied. Zentr.*, 1911, **40**, 531—535; from *Inaug. Diss.*, Rostock).—The results of pot experiments in which oats were manured with various manganese compounds showed in every case an increased yield as compared with plants which received no manganese. The highest gain was obtained with manganese carbonate; pyrolusite and manganese phosphate gave the next highest results, whilst the least gain was obtained with the nitrate. Similar results were obtained with beans with small amounts of manganese, whilst larger amounts were injurious.

In experiments with mustard in sandy, loam, and humus soils, it was found that the effect of the different forms of manganese varies according to the nature of the soil. In sandy soil, pyrolusite and manganese carbonate gave the greatest gains. In loam the greatest and least gains were obtained with manganese hydroxide and pyrolusite respectively.

Further experiments with sugar-beet and mangolds grown in sandy loam showed increased yields of leaf and roots when manganese was applied. In the case of potatoes, manganese sulphate increased the yield both of tubers and starch.

Water-culture experiments with oats showed that manganese is injurious when 25 mg. per litre is present, and that the plants fail altogether in solutions containing 0·5 gram per litre.

Oats take up most manganese when applied in the form of nitrate whilst beans take up more as phosphate than as nitrate.

N. H. J. M.

Dihydroxystearic Acid in Good and Poor Soils. OSWALD SCHREINER and ELBERT C. LATHROP (*J. Amer. Chem. Soc.*, 1911, **33**, 1412—1417).—The authors have isolated dihydroxystearic acid from soil by extraction with 2% sodium hydroxide solution. Examination of a number of soils shows it to be an almost invariable acccompaniment of infertility; the soil conditions in which it is found are generally poor drainage, poor æration, too great compactness, deficiency in lime, lack of good oxidation, and tendency for fungus development. It does not appear to be connected with any special crop.

The authors have already shown that the acid is harmful to plants in water cultures; they consider therefore that it is a direct factor in causing infertility, but it is not necessarily the only factor; it is, however, symptomatic of poor soil conditions. E. J. R.

The Availability of Nitrogenous Materials as Measured by Ammonification. JACOB G. LIPMAN, PERCY E. BROWN, and IRVING L. OWEN (*Centr. Bakt. Par.*, 1911, ii, 31, 49—85).—The value of many organic fertilisers is determined, not so much by the actual amount of nitrogen as shown by chemical analysis, as by the rate at which the substance is broken down in the soil, that is, its availability. The present paper is an attempt to ascertain whether this availability can be gauged by ammonification, and how far the results so obtained agree with vegetation experiments.

Definite quantities of dried blood, tankage, and ground fish from different sources were mixed with 100 grams of loam and quartz sand, and, after being moistened, were incubated at 27° for several days. The ammonia was then estimated, and the results when calculated as percentages of the total nitrogen supplied showed, in many cases, close agreement with those obtained from pot experiments.

The ammonification of substances of vegetable origin depends largely on the carbon-nitrogen ratio. In the presence of substances rich in carbon there appears to be re-assimilation of the ammonia by bacteria and moulds.

Substances with a narrow carbon-nitrogen ratio are more rapidly and also more completely nitrified. This is shown in the following table:

Proportion of Applied Nitrogen Recovered.

Material applied.	Ammonification Tests. %.	Nitrification Tests. %.	Vegetation Tests. %.
Corn meal	2·12	—	8·31
Rice flour	1·72	—	6·17
Wheat flour	5·56	23·15	22·02
Rye flour	6·94	13·84	23·04
Cotton-seed meal	41·18	42·87	52·31
Linseed meal	46·06	49·07	44·18
Cow-pea meal	29·31	33·12	23·53
Soy bean meal	39·79	42·41	42·99

The presence of readily assimilable compounds does not seem to increase the ammonification of peat to any extent. The addition of sodium nitrate and ammonium sulphate gave slight gains, whilst with blood decreases of 7—18% of the total nitrogen occurred.

On the whole, the ammonification and vegetation tests show sufficient agreement to indicate that the former will be found useful in determining the availability of organic nitrogenous manures.

H. B. H.

Analytical Chemistry.

Apparatus for Electro-analytical Determinations with a Mercury Cathode. PAUL BAUMANN (*Chem. Zeit.*, 1911, 35, 854—855).—Details are given of an improved form of the mercury cathode vessel described by Böttger (Abstr., 1909, ii, 619), the object of the improvement being to facilitate the running-off of the electrolyte from the mercury at the end of the electrolysis, and also to trap any mercury or amalgam which may be carried over. This object is attained by inserting a stoppered tube, opening just above the level of the mercury, into the side and near the bottom of the vessel, there being a bulb in the tube between the stopcock and the vessel; the bulb acts as a trap for any mercury carried over.

The anode, which may be stationary or rotated, is a two-decker gauze electrode, similar in shape to the Hildebrand electrode (Abstr., 1907, ii, 574), and strengthened by appropriate struts.

The apparatus may be used for separations by graded potential. It cannot be heated directly, for fear of breaking, so that when the heat generated by the current used for electrolysis is insufficient, a special heater must be used. This consists of a platinum wire heated electrically and enclosed in a glass tube filled with paraffin oil; the glass tube is then immersed in the electrolyte when heating is necessary. T. S. P.

Detection of Gas in Sealed-tube Reactions. WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1911, 33, 1417—1418).—The author seals on to the Carius tube a tap of the same glass, and is thus enabled to collect any gas formed during the reaction. E. J. R.

Estimation of Organic Matter in Waters by means of Permanganate. HERMANN NOLL (*Zeitsch. angew. Chem.*, 1911, 24, 1509—1518).—The author's experiments show that in the estimation of organic matter in water by Kubel's method with permanganate, the direct action of sulphuric action on permanganate and on any manganese dioxide formed is of no account so far as loss of oxygen is concerned. The sulphuric acid present hinders the formation of manganese dioxide from manganese sulphate and permanganate.

The interaction between manganese sulphate and permanganate takes place according to the equation given by Roscoe and Schorlemmer, namely, $3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$. Manganese dioxide acts auto-catalytically on this reaction, but in water analysis, by Kubel's method, the catalytic effect is negligible.

In the determination of organic matter, the permanganate must always be in considerable excess, otherwise any manganese dioxide which may be formed will take part in the oxidation and the results will be too low. The addition of manganese sulphate to waters containing much chloride is therefore not to be recommended, since the formation of manganese dioxide is thereby increased. It is better in such cases to use Schulze's method.

The author considers that Kubel's method is satisfactory.

T. S. P.

A New Reaction for the Detection of Hydrogen Peroxide. O. von Sobbe (*Chem. Zeit.*, 1911, **35**, 898).—An ammoniacal silver nitrate solution is recommended for the detection of small quantities of hydrogen peroxide. A characteristic grey opalescence or precipitate is obtained. The test is even more delicate than the reaction with potassium iodide and starch usually employed.

L. de K.

Volhard's Method for the Estimation of Chlorine in Potable Waters. A. T. Stuart (*J. Amer. Chem. Soc.*, 1911, **33**, 1344—1349).—In the determination of chlorine in drinking waters by Volhard's method, the author met with various discrepancies, which led to the following investigation. Two c.c. of silver nitrate solution (1 c.c. = 0·001 gram Cl) were added to 100 c.c. of water, and the solution titrated with potassium thiocyanate of strength equivalent to the original silver nitrate solution. Varying volumes (from 0·1 to 100 c.c.) of a 1% solution of ferric sulphate solution were added as indicator. It was found that various quantities of thiocyanate solution were required, the figures showing that in titrating 2 c.c. of silver nitrate, using 1 c.c. of indicators varying in strength from 1 to 10%, the readings may vary between 1·80 and 2·09 c.c. This represents an error not permissible for work of extreme accuracy, involving in its limits 2·9 parts per million of chlorine.

The error is caused by equilibria set up, which may be represented by a combination of the two equations:

$$\left.\begin{array}{r}AgNO_3+KCNS\\ Fe_2(SO_4)_3+6KCNS\end{array}\right\} \begin{array}{c}\longrightarrow\\ \longleftarrow\end{array} \left\{\begin{array}{l}AgCNS+KNO_3\\ 2Fe(CNS)_3+3K_2SO_4\end{array}\right. .$$

The end point is also influenced by the dissociation of the ferric thiocyanate.

The conclusion is drawn that the method is only applicable in water analysis when very small amounts of silver nitrate, not greater than 0·2 c.c., in excess of that required are added.

Similar, but less, variations occur with *N*/10-solutions when large volumes of indicator solution are added.

T. S. P.

Estimation of Iodine in Thyroid. Atherton Seidell (*J. Biol. Chem.*, 1911, **10**, 95—108).—A large number of estimations of iodine in the thyroids of different animals are given; a good deal of irregularity is noted, but the theory that this is due to seasonal influences is regarded as inconclusive. Although the Hunter method of analysis is admitted to be the best, the conclusions drawn from results obtained by the Baumann process are not invalidated.

W. D. H.

Estimation of Small Quantities of Iodine in Animal Fluids. R. Bernier and G. Péron (*J. Pharm. Chim.*, 1911, [vii], **4**, 151—157).—The application of the method already described for the estimation of iodides (this vol., ii, 435) to organic liquids is rendered difficult in many cases by the presence of nitrites, formed by the action of permanganate on carbamide and other similar substances originally present in such products. The nitrites may be eliminated by the use of carbamide or ammonium salts in presence of acids. The following modification of the original process is given: Ten to twenty c.c. of urine, to which 0·5 gram of potassium hydroxide has been added, is evaporated to dryness in a nickel basin at 100°, and the residue calcined over a spirit lamp. The cold calcined residue is dissolved as far as possible in a little distilled water, the exhaustion of the soluble matter being completed with a 10% solution of sodium chloride. To the filtered extract potassium permanganate is added in excess, and the excess destroyed by alcohol. The cold solution is then made up to 110 c.c. and 100 c.c. of filtrate collected. To this 1 gram of ammonium chloride and 10 c.c. of acetic acid are added, and the whole boiled during five to ten minutes. The rest of the process is carried out as described previously (*loc. cit.*). The experimental difficulties met with in certain cases are described, with methods of overcoming them. The process is applicable to normal and pathological urines, blood, blood serum, and various liquids of the organism whether physiological or pathological in origin. A number of typical results with such fluids are quoted. T. A. H.

Estimation of Halogens in Organic Compounds. THEODOR ST. WARUNIS (*Chem. Zeit.*, 1911, **35**, 906—907).—The process may be applied in the case of solid substances or even liquids if they are not readily volatile. 0·2—0·3 Gram of the powdered substance is mixed in a spacious nickel crucible by means of a platinum wire with an intimate mixture of 10 grams of powdered potassium hydroxide and 5 grams of sodium peroxide. After putting on the lid, the crucible is heated in an air-bath at 75°, or at most 85°. When the mass begins to agglomerate, a gradually increased heat is applied by means of a very small flame until the mass has turned liquid, and it is kept in that condition for some time.

The fusion is dissolved in water, and gradually acidified with dilute nitric acid; if any iodine should be liberated, the solution should be decolorised by cautiously adding sulphurous acid. The halogen is then determined by means of silver nitrate, gravimetrically or volumetrically as usual. L. DE K.

Estimation of Halogens in Lipoids. H. CAPPENBERG (*Pharm. Zeit.*, 1911, **56**, 677).—One gram of the substance is placed in a porcelain crucible, a piece of cotton-wool is placed over it, and 10 c.c. of a 10% solution of potassium hydroxide in methyl alcohol are added. The contents of the crucible are evaporated to dryness at a temperature below the boiling point of the alcohol, then ignited over a low Bunsen flame for one hour, and the carbonised residue is dissolved in 100 c.c. of hot water. The solution is filtered, rendered acid with nitric acid, and the halogen is precipitated by the addition of silver nitrate. W. P. S.

Estimation of Dissolved Oxygen Absorbed by Sewage Effluents containing Nitrites and of Nitrites in Sewage Effluents and Water. ROBERT W. CLARKE (*Analyst*, 1911, **36**, 393—396).—*Estimation of Dissolved Oxygen Absorbed.*—The effluent is diluted, say, ten times with pure tap water, and five bottles of known capacity (300 c.c.) are completely filled therewith. The amount of oxygen present at the start and after one, two, and five days respectively is then determined by Winkler's manganese method (introduction of manganous chloride and sodium hydroxide containing potassium iodide; after acidifying with hydrochloric acid, the iodine liberated, which represents free oxygen, is estimated as usual). The author, however, recommends neutralising the free acid before titration with magnesium carbonate; nitrites will then not interfere. The difference in amount of free oxygen at the commencement and after a given interval gives the amount of oxygen absorbed.

Estimation of Nitrites.—A tall bottle holding 500 c.c. is filled with the nitrite-containing water or effluent to within 20 c.c. of the whole content. To this are added 4 c.c. of 33% manganese chloride, and 12 c.c. of the usual sodium hydroxide and potassium iodide solution with an extra gram of the latter are added. After shaking the stoppered bottle and allowing it to stand overnight, all free oxygen will have disappeared from the liquid, which, however, retains the nitrite. The clear liquid is now siphoned off into a 300 c.c. bottle, 3 c.c. of hydrochloric acid are added, and, after neutralising the excess of this with magnesium carbonate, the iodine liberated, representing the nitrite, is titrated with very dilute standard thiosulphate.

L. DE K.

New Method of Estimating the Various Elements of an Organic Substance. (1) Substance Containing C,H,O,N. (2) Substance Containing C,H,O,N,S. (3) Substance Containing C,H,O,N,S,Cl,Br,I. J. A. A. AUZIES (*Bull. Soc. chim.*, 1911, [iv], **9**, 814, 815, 815—819).—For a substance containing carbon, hydrogen, oxygen, and nitrogen, the combustion tube, otherwise arranged in the ordinary manner, is filled with specially prepared thoria in place of cupric oxide. The water and carbon dioxide are collected in the usual way, and the nitrogen peroxide formed in the combustion is collected in a solution of cuprous chloride in hydrochloric acid, placed between the usual calcium chloride tube and the potash bulbs. The nitric peroxide formed is estimated by titrating the absorbent solution with standard stannous chloride.

When the substance to be burnt contains sulphur, a portion of the tube is filled with lead peroxide, or, better, the thoria and the lead peroxide are each enclosed in boats of special form. The sulphur is oxidised to sulphur dioxide by the thoria, and this is absorbed by the peroxide to form lead sulphate, which is determined gravimetrically.

When halogens are present, a third boat containing silver chromate is introduced. After the combustion is complete, the partly transformed chromate is treated with ammonia solution, which dissolves the chromate and chloride, the latter being recovered quantitatively by adding acetic acid to the solution and treating the precipitate with potassium cyanide solution. The residue, insoluble in ammonia solution, is treated with potassium cyanide solution, which dissolves the silver iodide, but leaves the bromide unaffected. Results of simultaneous determinations of the eight elements by this process are quoted. The special boat recommended is figured in the original.

T. A. H.

The Hyperbolæ of Furnace Gas Constituents. ERNST LÁSZLÓ (*Chem. Zeit.*, 1911, 35, 994—996).—The author develops equations by means of which, having determined the percentage of carbon dioxide in furnace gases, the percentage of oxygen and nitrogen in the same can also be calculated, and also the ratio of the air passed into the furnace to that which is theoretically necessary for complete combustion. It is assumed that the ratio of nitrogen to oxygen in the air is known, and also the value of l, when the hydrocarbon burned has the formula C_mH_{lm}.

T. S. P.

Estimation of Silicon in Iron containing much Graphite. C. REICHARD (*Pharm. Zentr.-h.*, 1911, **52**, 939—940).—One gram of the finely-divided iron is heated in a platinum crucible for fifteen minutes over a blast-flame, or for one hour over a Bunsen flame, and then dissolved in 25% hydrochloric acid. The solution is decanted from the small quantity of insoluble matter, and the latter is treated with fuming nitric acid. After the two acid solutions have been mixed together, the insoluble graphite is collected on a filter, washed, and ignited in an atmosphere of oxygen. The portion of the silica which remains in the acid filtrate is estimated in the usual way.

W. P. S.

The Oxidation of Hydrazine. V. Reaction between Potassium Iodate and Hydrazine Sulphate. C. F. HALE and H. W. REDFIELD (*J. Amer. Chem. Soc.*, 1911, **33**, 1353—1362. Compare Brown and Shetterly, Abstr., 1910, ii, 233, 568).—The authors show that the oxidation of hydrazine sulphate by potassium iodate proceeds quantitatively in accordance with the equation given by Rimini (Abstr., 1906, ii, 897), namely, $5N_2H_4,H_2SO_4 + 4KIO_3 = 5N_2 + 12H_2O + 2K_2SO_4 + 3H_2SO_4 + 2I_2$. In each experiment carried out the excess of iodate was determined, and also the volume of nitrogen evolved. The reaction is the same, whether the hydrazine is added to the potassium iodate in the cold (in an atmosphere of carbon dioxide) or at the boiling temperature (in an atmosphere of steam).

The method of procedure recommended is as follows: About 0·3 gram of the hydrazine salt is dissolved in 50 c.c. of water in a 300 c.c. narrow-mouthed conical flask. A measured volume of potassium iodate solution (7·1045 grams per litre) is then added, so that there are 5—10 c.c. in excess. The solution is diluted to 200 c.c., and boiled for thirty minutes over a free flame to expel the iodine. After cooling, potassium iodide and dilute (1 : 4) sulphuric acid are added, and the liberated iodine is titrated with $N/10$-thiosulphate.

The chief disadvantage of the method lies in the length of time required for the expulsion of the liberated iodine. T. S. P.

Estimation of Nitric Nitrogen in Gun Cotton, Nitroglycerol, and Similar Products. HENRI PELLET (*Ann. Chim. anal.*, 1911, **16**, 294—296).—Schloesing's apparatus is preferred. In the case of gun-cotton or saltpetre (used for a check experiment) the substance is placed in the flask containing distilled water, which is then boiled until all the air has been expelled. A solution of ferrous ammonium sulphate strongly acidified with hydrochloric acid is introduced from the funnel tube, and the nitric oxide expelled on boiling is collected and measured.

In the case of substances which suffer volatilisation on boiling, such as nitroglycerol or nitric ethers, the iron solution is placed in the flask, and, after expelling the air by boiling, the nitrate is gradually added in dilute solution from the funnel tube. L. DE K.

Estimation of Nitrites in Waters. GUSTAVE BLANC (*J. Pharm. Chim.*, 1911, [vii], **4**, 205—212).—It is shown that Trommsdorff's method is bad in principle, since the nitric oxide formed by the interaction of zinc iodide with nitrous acid is oxidised in contact with the air, forming more nitrous acid, which reacts with more of the iodide, so that the amount of iodine liberated and titrated may be far in excess of that corresponding with the amount of nitrite originally present. Test analyses confirmed this. Griess' method, on the contrary, was found experimentally not to be subject to any error of this kind.
T. A. H.

Some Sources of Error in the Gasometric Estimation of Nitrates and Nitrites by Schloesing's or Piccini's Methods. OTTO RUFF and EWALD GERSTEN (*Zeitsch. anorg. Chem.*, 1911, **71**, 419—426).—The presence of arsenites or sulphides in a solution of nitrates or nitrites gives rise to errors in the gasometric estimation. In the estimation of nitrates, in which an acid solution of ferrous chloride is required, the presence of arsenites causes a loss of nitric oxide, owing to the formation of nitrous acid, which passes over into the nitrometer. Arsenites only reduce nitrates in acid solution. Nitrites may be estimated satisfactorily, even in presence of arsenites, if the solution is kept neutral. Sulphides, however, prevent the estimation of nitrates or nitrites, the nitrous acid being partly reduced to ammonia. C. H. D.

The Quantity of Nitric Acid Present in Wines. J. TILLMANS (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 201—207).—The author finds that nitric acid is a natural constituent of practically all German wines, the quantity present varying from a mere trace to 18·75 mg. (N_2O_5) per litre. The detection of nitric acid in wine does not, therefore, indicate the presence of added water in the wine. The diphenylamine-sulphuric acid method was employed for the estimation of the nitric acid; this method has been described previously (this vol., ii, 767), but in the case of wine it is necessary to evaporate the diluted sample after the addition of animal charcoal in order to remove substances which interfere with the reaction, the estimation being then made on the evaporated solution diluted with water to its original volume.

W. P. S.

Estimation of Phosphorus in Wine. JEAN DORMANE (*Bull. Assoc. chim. Sucr. Dist.*, 1911, **29**, 63—67).—The total phosphorus in wine is estimated by treating the dry residue from 200 c.c. with calcium hydroxide and heating on a sand-bath. It is then powdered, placed in a platinum boat, and heated in a porcelain tube in a current of air. The portion of the porcelain tube behind the platinum boat is filled with potassium carbonate. The whole tube is heated for two to three hours. The ash and the alkali are dissolved in dilute hydrochloric acid, and the phosphates estimated by means of ammonium-magnesium solution.

In estimating the phosphorus as phosphates, the residue from 100 c.c. of wine is extracted with cold dilute hydrochloric acid, and the phosphates in the filtrate precipitated in the usual manner.

The same process is employed for estimating the organic phosphates, except that the residue is boiled for an hour and a-half with stronger hydrochloric acid. The amount of phosphorus present as inorganic phosphates is deducted from the results. N. H. J. M.

Titration of Phosphoric Acid. M. WAGENAAR (*Pharm. Weekblad*, 1911, **48**, 845—850).—For determining the three hydrogen ions of phosphoric acid, the author recommends the following procedure: For the first ion the solution is tinted red with methyl-orange, and titrated with alkali until yellow; for the second, the titration is repeated after addition of phenolphthalein to the yellow reaction-mixture; for the the third, excess of lead nitrate is added, and the rose-red solution titrated with sodium hydroxide. The action of the lead nitrate corresponds with the scheme:

$$3Pb(NO_3)_2 + 2Na_2HPO_4 \rightleftarrows 4NaNO_3 + Pb_3(PO_4)_2 + 2HNO_3.$$

A. J. W.

The Alkalimetry of Magnesium Ammonium Phosphate and Acidimetry of Ammonium Phosphomolybdate. FRANZ HUNDESHAGEN (*Zeitsch. öffentl. Chem.*, 1911, **17**, 283—294, 302—309, 322—324).—The author again recommends his titration process (Abstr., 1895, ii, 84), which, however, had been previously worked out by Stolbe, and consists in washing the ammonium magnesium phosphate obtained in the usual way with alcohol until free from ammonia; the precipitate is then dissolved in a slight excess of standard acid, and the solution titrated with standard sodium carbonate, using methyl-orange as indicator. Twenty-five test analyses are given, showing the accuracy of the method. If arsenic acid is suspected, a previous separation of this substance should be effected by means of hydrogen sulphide, or else its amount present in the precipitate must be determined and allowed for. One c.c. of *N*/10-acid = 0·003552 gram of phosphoric anhydride, or 0·002016 gram of magnesium oxide. When the process is applied in the so-called "citrate method," the triple phosphate should be purified by re-dissolving it in hydrochloric acid, and reprecipitating it with ammonia, after adding a little of the usual citrate solution and a little magnesium mixture; it will then be free from calcium and fit for titration.

Good results are also obtained by the author's well-known molybdate method, in which the yellow precipitate is dissolved in standard alkali, the excess of which is then titrated with standard acid, using phenolphthalein or litmus as indicator. One c.c. of N-alkali = 0·003078 gram of phosphoric anhydride. Operators are again reminded of the precautions to be taken to ensure the formation of a pure yellow precipitate. A microscopical test will prove the presence or absence of free molybdic acid. L. DE K.

Estimation of Arsenic in Toxicological Analysis. W. NEY (*Pharm. Zeit.*, 1911, 615—616).—A weighed quantity of the substance, such as a portion of an animal organ, is distilled with 100 c.c. of hydrochloric acid, D 1·19, 2 grams of potassium bromide, and 5 grams of hydrazine sulphate until the mixture has been reduced to a syrupy consistence. The distillate is received in 200 c.c of water, and the arsenic trichloride is then titrated with iodine solution in the presence of sodium hydrogen carbonate. W. P. S.

Treatment of Insoluble Residues. ERICH EBLER (*Zeitsch. anal. Chem.*, 1911, **50**, 610—614).—Lead chloride, together with any lead sulphate, is best removed by heating the insoluble matter with ammonium nitrate (40 c.c. of ammonia, D 0·925, and 67 c c. of nitric acid, D 1·3325). Complex cyanides and insoluble (ignited) oxides may, generally, be rendered soluble by fusion at not too high a temperature with potassium hydrogen sulphate; the mass is then extracted with water containing a few drops of hydrochloric acid. The filtrate is tested as usual for metals, and the undissolved matter is examined for silver by treating with dilute sulphuric acid and a little zinc. When reduction is complete, the precipitate is washed with hot water and the excess of zinc and the silver are dissolved in dilute nitric acid; the silver is then tested for as usual.

The residue, which may contain antimonic oxide, stannic oxide, stannic phosphate, and perhaps silica, is collected, ignited, and weighed. It is then fused in a covered crucible at a gentle heat with two or three times its weight of the usual sulphur-potassium carbonate mixture. The mass is extracted with hot water, and the solution is treated according to one of the usual methods for the separation of tin, antimony, etc.

It is advisable to examine the undissolved portion of the fusion for alkaline earths and silica. This is done by fusing with anhydrous sodium carbonate over the blow-pipe. The mass is extracted with water, and both solution and residue are then examined by the usual methods for silica and alkaline earths respectively. L. DE K.

Separation Scheme without the Use of Hydrogen Sulphide. ERICH EBLER (*Zeitsch. anal. Chem.*, 1911, **50**, 603—609).—A slight modification of the process described some time ago (Abstr., 1906, ii, 126). It is recommended first to remove the arsenic by distilling the mixture with fuming hydrochloric acid with addition of hydrazine bromide; the arsenic is then tested for in the distillate. In the presence of complex cyanides these are destroyed by boiling for half an hour in a reflux condenser with a mixture of equal volumes of fuming nitric and hydrochloric acids. Before applying the course without the use of hydrogen sulphide, the hydrochloric acid is expelled by repeated evaporation with nitric acid.

Uranium remains with the alkaline earths as a complex hydroxylamine compound of uranic acid, but is readily separated by a process communicated previously (Abstr., 1908, ii, 987); the alkaline earths are separated by the author's hydrochloric acid process (Abstr., 1909, ii, 347), but instead of a hardened filter an asbestos filter is now recommended.

The alkalis should be tested for in a separate portion of the mixture. The method used for silicates (heating with ammonium chloride and calcium carbonate) will be found very suitable. L. DE K.

Method for the Reduction of Potassium Platinichloride in the Estimation of Potassium by the Platinum Process. A. FIECHTER (*Zeitsch. anal. Chem.*, 1911, 50, 629—632).—The author recommends the process based on the reduction of the potassium platinichloride by means of magnesium ribbon and dilute hydrochloric acid at the boiling point, using only a few drops of acid at first. If 1 gram of the substance guaranteed to contain 5% of K_2O is taken for analysis, 0·2 gram of magnesium ribbon is required; for 20%, 0·5, and for 50% K_2O, 0 8—1 gram of magnesium will be sufficient.
L. DE K.

Estimation of Calcium Nitrate and Calcium Nitrite. ALBERT STUTZER and GOY (*Chem. Zeit.*, 1911, 35, 891).—In the estimation of calcium nitrite and nitrate in the technical products made by the combustion of atmospheric nitrogen, Busch's method (Abstr., 1906, ii, 392) gives unsatisfactory results, and the authors prefer to estimate the nitrite by titration with permanganate and then to estimate the total nitrogen in the oxidised liquid with "nitron."

Since "nitron" is very expensive, the authors recommend that the total nitrogen be determined by reduction to ammonia with Devarda metal (50% Cu, 45% Al, 5% Sn) and distillation of the ammonia into excess of standard sulphuric acid. T. S. P.

Analysis of "Nitrolime." HUBERT KAPPEN (*Chem. Zeit.*, 1911, 35, 950—952).—A series of experiments from which it appears that the total nitrogen in "nitrolime" is best estimated by treating 0·5 gram of the sample with 10 c.c of water before boiling with 30 c.c. of sulphuric acid (Kjeldahl process). Addition of sodium thiosulphate, salicylic acid, and zinc dust does not seem to produce the effect expected by Monnier. Full particulars are found in the tables of the original paper.

For the estimation of cyanamide nitrogen, Perotti's silver process is recommended. In recently prepared samples the results agree very well with the total nitrogen according to Kjeldahl. Old and badly stored samples often contain dicyanodiamide. In the absence of dicyanodiamidine it is best estimated by Caro's process (this vol., i, 119). L. DE K.

Extraction of Gases from Copper by a Chemical Method and the Estimation of Oxygen.

MARCEL GUICHARD (*Compt. rend.*, 1911, **153**, 272—275).—Commercial copper is shown to contain sufficient dissolved oxygen to vitiate estimations of this gas carried out by its means. Fine copper wire previously heated at 600° in a vacuum for a long time should be used for the purpose. A specimen of copper liberated about twice its volume of gas when heated with iodine in a vacuum. W. O. W

Detection of Mercury in Urine. II.

ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1911, **73**, 401—406. Compare this vol., ii, 771).—The "end" solution is prepared in the manner previously described (this vol., ii, 771), and the mercury removed from it by leaving in the warmed solution for an hour or more two or three strips of copper foil about 0·1 mm. thick. These become grey when much mercury is present; they are removed, washed, and dried, care being taken to handle them only with forceps. They are next placed in a clean dry test-tube, which is moderately heated and allowed to cool; the foil is shaken out, a trace of iodine introduced, and the tube warmed until the iodine vapours fill two-thirds of it. The formation of the red mercuric iodide takes place slowly, but is very characteristic.

E. F. A.

The Use of Sulphur Monochloride in the Determination and Analysis of the Rare Earth Minerals.

WILLIAM BROOKS HICKS (*J. Amer. Chem. Soc.*, 1911, **33**, 1492—1496).—Fergusonite was completely decomposed by the action of the vapours of sulphur monochloride, not a trace of metallic acids remaining in the residue, and no rare earths being detected in the volatile portion. Eschynite and euxenite were also readily decomposed, whilst a picked sample of samarskite was decomposed to the extent of 98·78%.

In carrying out the decomposition, the minerals were placed in a porcelain boat in a combustion tube, which was heated while the vapours of sulphur monochloride were passed through it. The volatile chlorides of the metallic acids passed into the receiver, whilst the non-volatile chlorides or oxychlorides of the earth metals remained in the boat.

The principal advantages of this method of decomposition are the ease with which it takes place, the cheapness of the apparatus, and the separation of columbium, tantalum, titanium, and tungsten from the rare earths during the decomposition. The chief disadvantage is that the excess of sulphur monochloride is mixed with the volatile chlorides, but it may easily be overcome by allowing the mixture to pass into dilute nitric acid, and then removing the precipitated sulphur by adding excess of ammonium hydroxide and hydrogen sulphide.

In the non-volatile portions of the above minerals, search was made for scandium, but none was found. Fergusonite contained, however, 2—3% of thorium, whilst yttrium and thorium were found in eschynite. T. S. P.

A New Method for the Separation of Cerium. Charles James and L. A. Pratt (*J. Amer. Chem. Soc.*, 1911, **33**, 1326—1330).—The authors have found that potassium bromate is capable of oxidising cerous nitrate in faintly acid or neutral solution, so that this element may be entirely separated from the other rare earths. The solution of the rare earth nitrates is boiled with potassium bromate in the presence of a lump of marble, the cerium being entirely precipitated as the basic ceric nitrate, with varying amounts of basic ceric bromate. When the operation is carefully conducted, the cerium thus obtained is free from the other rare earths. In working on a large scale with concentrated solutions, it is advisable to use a slight excess of the bromate, and to stop the action while about 1% of the cerium remains in the liquid. Under these conditions, a cerium product is obtained, which, after washing with a 5% ammonium nitrate solution, gives a pale straw-coloured oxide. A saturated solution of the nitrate of this material shows no trace of absorption spectrum when tested with a layer 20 cm. thick.

The above method may be employed for the gravimetric estimation of cerium. The cerium salt is precipitated twice, in each case until the mother liquor gives no test for cerium with hydrogen peroxide; the precipitate is washed with a 5% solution of ammonium nitrate. After the second precipitation the precipitate is dissolved in hydrochloric acid, the cerium precipitated as oxalate, and weighed as oxide.

Details are given of the application of the method to the purification of cerium on a large scale from the monazite earths which have been freed from thorium. T. S. P.

Analysis of Monazite Sands. Gabriel Chesneau (*Compt. rend.*, 1911, **153**, 429—431).—The best methods hitherto published having proved unsatisfactory, the following process, which avoids difficulties caused by the sparing solubility of thorium phosphate in acid, was devised and found to give good results.

2·5 Grams of the sand are fused with 15 grams of fusion mixture until all glistening particles disappear. The mass is extracted with boiling 1% sodium hydroxide (solution *A*). The residue is treated with hot 5% hydrochloric acid (solution *B*), and the process repeated on the insoluble portion. The final residue (TiO_2, ZrO_2, SiO_2) and solution *A* (Al_2O_3, SiO_2, P_2O_5) are analysed in the usual way. Solution *B*, freed from lead and copper, is diluted until it contains exactly 4% of hydrogen chloride, then treated with 4 grams of crystallised oxalic acid for every 100 c.c., and allowed to remain for two days. The filtrate is examined in the usual way for TiO_2, ZrO_2, Fe, etc., and the oxalates of the rare earths calcined below 500°; the oxides are dissolved in nitric acid, with addition of hydrogen peroxide if necessary. After evaporating to dryness and dissolving the residue in 150 c.c. of water, thorium is separated by double precipitation with hydrogen peroxide, according to Wyrouboff's method. The reagent should be free from phosphates, and is advantageously treated with a little ammonium nitrate to avoid formation of colloids. The filtrate is made up to 500 c.c., and the rare earths precipitated in 100 c.c. Cerium is estimated in another 100 c.c. by Job's method, for which details are given.

A monazite sand from Madagascar gave on analysis: ThO_2, 5·5; CeO_2, 22·6; La_2O_3,Di_2O_3, 25·0; Y_2O_3, etc., 0·8; ZrO_2, 1·6; Fe_2O_3, 3·7; Al_2O_3, 0·8; Mn, trace; MgO, 0·4; CaO, 0·5; P_2O_5, 23·5; SiO_2, 8·8; TiO_2, 6·7; loss on ignition, 0·4. Total 100·3. W. O. W.

Precipitation of Aluminium, Chromium, and Iron by Ammonium Nitrite. ERIK SCHIRM (*Chem. Zeit.*, 1911, **35**, 979—980).—Although sodium nitrite may be used in place of ammonium nitrite in the process described previously by the author (Abstr., 1909, ii, 834), it has the disadvantage that alkalis cannot be estimated subsequently in the same portion of the sample. Manganese may be separated from iron by means of sodium nitrite, provided that a small quantity of ammonium sulphate be added to prevent precipitation of the manganese. A double precipitation is, however, recommended in this case. The manganese is then precipitated from the filtrate by means of ammonium persulphate. W. P. S.

Estimation of Manganese as Manganous Oxide, Mangano-manganic Oxide, and Manganese Sesquioxide. PAUL N. RAIKOW and P. TISCHKOFF (*Chem. Zeit.*, 1911, **35**, 1013—1015).—Manganese may be converted quantitatively into manganous oxide by heating the higher oxides in a rapid current of hydrogen, using a Rose's crucible. The higher oxides may be converted quantitatively into mangano-manganic oxide by ignition in a slow current of carbon dioxide. Manganese may also be converted quantitatively into manganese sesquioxide by ignition of the oxides or the carbonate in a current of oxygen.

Manganous sulphate may be converted into the sesquioxide by heating alternately in a current of hydrogen and in air, and finally igniting in a current of oxygen. L. DE K.

Ferric Sulphate as a Standard for Titrating Potassium Permanganate. JAROSLAV MILBAUER and OTTO QUADRAT (*Zeitsch. anal. Chem.*, 1911, **50**, 601—603).—One gram of pure ferric sulphate is dissolved in an Erlenmeyer flask in 25 c.c. of water and 10 c.c. of sulphuric acid, and, after adding a few granules of iron-free zinc, the whole is heated gently until everything has dissolved. An equal volume of water is added, and the solution titrated with permanganate.

Ferric sulphate is best prepared by boiling 10 grams of ferrous sulphate for about an hour with 100 c.c. of sulphuric acid. When cold, the bulk of the acid is poured off through a Gooch crucible, and the remainder removed by washing with alcohol, and then with anhydrous ether. Finally, the salt is dried in a water-oven to constant weight. L. DE K.

Volumetric Estimation of Ferric Salts with Permanganate after Reduction with Zinc. ERICH MULLER and GUSTAV WEGELIN (*Zeitsch. anal. Chem.*, 1911, **50**, 615—623).—When using pure zinc, or zinc in contact with platinum, for the reduction of ferric salts, it is necessary to wait until the zinc has completely dissolved, otherwise there will be a small quantity of iron deposited on the undissolved zinc. This inconvenience may be avoided by working as follows: 100 c.c. of the ferric iron solution (or a smaller volume diluted to 100 c.c.) are mixed with 5 c.c. of sulphuric acid and five to ten drops of *N*-copper sulphate. After adding three or four amalgamated zinc rods (5 cm. in length and 0·6 cm. in diameter), the solution is heated for about two hours at 100° in a current of carbon dioxide. The copper solution need only be added in the first experiment.

L. DE K.

Precipitation of Iron with Hydrazine Hydrate. ERIK SCHIRM (*Chem. Zeit.*, 1911, **35**, 897).—The iron solution containing about 0·1 gram of iron is diluted to 250—300 c c. If necessary, a few drops of hydrochloric acid and a little bromine are added, and the excess of the latter is boiled off. A large excess of ammonia is added, and then a few drops of hydrazine hydrate, which causes the precipitate to turn into a fine, granular black powder, which subsides rapidly and is free from sulphate. After washing and drying, it is ignited, finally over the blast, to constant weight. The filtrate may be used for estimating the sulphate.

Experiments to estimate iron in the presence of zinc by means of hydrazine hydrate are, as yet, unsuccessful. L. DE K.

Simplified Apparatus for Estimating Carbon in Iron G. BUTZBACH and G. FENNER (*Chem. Zeit.*, 1911, **35**, 917).—Two apparatus of the usual type are described and figured. In the first one the condenser is fixed to the flask containing the oxidising liquid by means of a rubber cork, which cannot be affected by spirting acid, and is rendered more effective by a water seal.

In the second one the flask is connected with the condensing tube by means of a ground joint. In both there is an absence of the usual side-tubes, thus rendering them less liable to breakage.

L. DE K.

Employment of Combustion under Pressure in the Estimation of Carbon in Steels. P. MAHLER and E. GOUTAL (*Compt. rend.*, 1911, **153**, 549—551).—The sample of steel contained in a refractory crucible free from calcium carbonate is burnt in oxygen in a calorimetric bomb similar to those employed in determining the calorific power of coal, but having a capacity of about 1 litre. The carbon dioxide is absorbed by barium hydroxide, and estimated by titration. Results given by this method agree closely with those obtained by the copper chloride and combustion process. W. O. W.

Rapid Estimation of Total Carbon [in Iron and Steel]. H. DE NOLLY (*Rev. de Métallurgie*, 1911, **8**, 391—395).—The iron or steel, in the form of fine drillings, is introduced into an asbestos capsule, supported in a litre flask of Jena glass, which is closed with a rubber stopper and supplied with oxygen under a pressure of 30 to 40 cm. of water. The flask contains a measured volume of a 0·4% solution of sodium hydroxide. The metal is ignited by passing a current of 10—15 amperes between a pair of electrodes. When combustion is complete, the flask is shaken to absorb carbon dioxide, and the solution is titrated with sulphuric acid (1 c.c. = 1 mg. of carbon) and phenolphthalein. White cast iron, ferro-silicon, and other brittle alloys are mixed with lead peroxide before ignition. Grey cast iron gives low results, owing to incomplete combustion of the graphite. C. H. D.

Apparatus for the Estimation of Sulphur in Iron and Steel. D. A. WENNMANN (*Chem. Zeit.*, 1911, **35**, 863).—Diagrams are given of two apparatus made entirely of glass, so that all rubber connexions are avoided. T. S. P.

Rapid Estimation of Ferric Oxide in Cement. A. GOLUBINZEFF (*Chem. Zeit.*, 1911, **35**, 961—962).—Two grams of the sample are placed in an Erlenmeyer flask, moistened with 10 c.c. of water, and allowed to remain for ten minutes, when another 75 c.c. of water and then, while shaking, 100 c.c. of *N*-hydrochloric acid are slowly added. The shaking is continued until the greater part of the cement has dissolved, when the solution of the remainder is effected by heating the liquid to boiling; the boiling is then continued for three to five minutes to expel any hydrogen sulphide. The solution is reduced by sulphur dioxide, the excess of which is then boiled off in a current of carbon dioxide. After some fifteen minutes, the exit tube is closed with a piece of rubber and clamp without interrupting the current of carbon dioxide, and the flask is cooled in cold water. The iron is titrated, as usual, with *N*/10-permanganate after adding 8—10 c.c. of a solution of manganese sulphate. L. DE K.

Estimation of Ferrocyanides and Thiocyanates. LÉON RONNET (*Ann. Chim. anal.*, 1911, **16**, 336—337).—The solution is strongly acidified with hydrochloric acid, and a slight excess of a hot solution of ferric chloride is added. After heating for half an hour on the water-bath, the Prussian-blue is collected and washed with hot water. The filter and contents are then transferred to a graduated flask and treated with a sufficiency of 10% solution of potassium hydroxide, and, after being kept for twelve hours with frequent shaking, the whole is made up to a definite volume with water, and a known volume of the filtrate is then acidified with dilute sulphuric acid and titrated for ferrocyanide with *N*/10-permanganate as usual. One c.c. permanganate = 0·0422 gram of crystallised potassium ferrocyanide.

The filtrate from the Prussian-blue is made up to a definite volume, and an aliquot portion is heated on the water-bath with addition of a slight excess of sodium hydrogen sulphite. Solution of copper sulphate is then added in slight excess, and after half an hour the cuprous thiocyanate is collected and washed. The filter and contents are then placed in a flask, and the precipitate is dissolved in dilute ammonia (1 : 2). The solution is acidified with dilute sulphuric acid, and, while still warm, titrated with *N*/10-permanganate; 1 c.c. = 0·001616 gram of potassium thiocyanate. L. DE K.

Quantitative Separation with "Cupferron." OSKAR BAUDISCH (*Chem. Zeit.*, 1911, **35**, 913).—"Cupferron," so useful in the separation of iron from copper, not being readily procurable, the author recommends analysts to prepare it themselves. It is not explosive.

Sixty grams of nitrobenzene, 1000 c.c. of water, and 30 grams of ammonium chloride are well stirred, and to the white emulsion is added 80 grams of zinc dust in very small quantities, so that the temperature keeps between 16° and 18°. When the odour of nitrobenzene has completely disappeared, the solution is drawn off from the zinc hydroxide, and, after cooling to 0° by means of ice, the liquid is saturated with salt, which causes an abundant crystalline precipitate of phenylhydroxylamine. It may be observed that great care must be taken not to let this substance come in contact with the skin, as it is very poisonous. After draining and removing the mother liquor by means of filter paper, the compound is dissolved in 300—500 c.c. of ordinary ether, and after cooling the filtrate to 0°, a current of gaseous ammonia is passed for ten minutes and an excess of amyl nitrite is added. An abundant separation of nitrosylphenylhydroxylamine ammonium ("cupferron") takes place, which is drained, washed with ether, and then pressed between filter paper. It is advisable to place in the stock bottle a lump of ammonium carbonate.

L. DE K.

The Separation of Iron and Vanadium by the Ether Method. EUGEN DEISS and HANS LEYSAHT (*Chem. Zeit.*, 1911, **35**, 869—871, 878—879).—Rothe's ether method (compare Blair, Abstr., 1908, ii, 900) for the separation of iron from other elements cannot be used in its original form for the separation of iron and vanadium, since ether extracts appreciable quantities of vanadium from hydrochloric acid solutions, especially when the vanadium is in the quinquevalent condition. Solutions of quadrivalent vanadium do not give up any vanadium to ether so long as care is taken that reducing agents are present to prevent the oxidation of any vanadium by peroxide usually contained in ordinary ether. In ordinary practice it is not convenient to have such reducing agents present, since they would also reduce the ferric salts. Advantage is therefore taken of the fact that pervanadates are insoluble in ether. After the chief extraction has been carried out by Rothe's method, the ethereal extract, containing the ferric salt and some vanadium, is further shaken several times with ether-hydrochloric acid (hydrochloric acid, D = 1·10, saturated with ether), to which a little hydrogen peroxide has been added. The hydrogen peroxide oxidises the vanadium to pervanadates, which then pass into the aqueous layer.

The many details necessary in carrying out the method are fully described. T. S. P

Estimation of Iron, Ammonia, and Nitrous Acid in Waters by means of the Autenrieth-Koenigsberger Colorimeter. KARL SÜPFLE (*Arch. Hygiene*, 1911, 74, 176—184).—The above colorimeter is strongly recommended in water analysis.

Iron is estimated by the thiocyanate-ether process, ammonia by Nessler's reagent after removing alkaline earths, and nitrites are estimated by *m*-phenylenediamine and sulphuric acid; if necessary, the alkali earths and colouring matters are removed by adding a mixture of sodium carbonate and hydroxide. L. DE K.

Rapid Detection of Elements Furnishing Sulphides Insoluble in Dilute Acids. M. EMMANUEL POZZI-ESCOT (*Bull. Soc. chim.*, 1911, [iv], 9, 812—814).—The mixed sulphides, precipitated by hydrogen sulphide from dilute acid solution, are treated with 25% hydrochloric acid, furnishing (1) a solution which may contain lead, antimony, tin, cadmium, and zinc, and (2) a residue, which may contain copper, molybdenum, arsenic, bismuth, mercury, gold, and platinum.

The solution is treated with ammonia, which precipitates the first three metals, and leaves cadmium and zinc in solution, where they can be detected by the usual tests. The precipitate, which may contain lead, antimony, and tin, is dissolved in hydrochloric acid, and these elements sought for by the usual tests.

The residue, insoluble in hydrochloric acid, is treated with nitric acid, which dissolves copper, molybdenum, arsenic, and bismuth, and leaves undissolved mercury, gold, and platinum, which are then obtained in solution with *aqua regia*. The elements are then sought for in these two solutions by the usual tests. The process is stated to give trustworthy qualitative results more rapidly than that in general use. T. A. H.

Assay of Wolfram Concentrate. H. W. HUTCHIN (*Analyst*, 1911, 36, 398—403).—A recapitulation of the four chief methods for the assay of commercial wolfram. In the aqua regia methods, the tungstic acid is finally obtained by ignition of ammonium tungstate or mercurous tungstate. In the soda digestion and fusion processes, the tungstic acid is finally obtained by ignition of mercurous tungstate.

All four methods seem to be very satisfactory; the old aqua regia ammonium tungstate method has, perhaps, most to commend it, as it allows of operating on 1 to 2 grams, whereas the other methods are limited to quantities of about 0·5 gram of the sample.

L. DE K.

The Action of Salicylic Acid on the Metallic Acids. JOHN HUGHES MULLER (*J. Amer. Chem. Soc.*, 1911, 33, 1506—1510).—Solutions of sodium or potassium columbate, tantalate, thorate, and zirconate are precipitated quantitatively by salicylic acid, whereas titanium is not so precipitated; this difference is used as the basis of a method for the quantitative separation of titanium from the other elements.

Alkali titanates give an intense yellow colour on the addition of salicylic acid; the reaction is extremely delicate, and may be used for the colorimetric determination of this metal. The colour is destroyed by traces of hydrofluoric acid or of fluorides, and is affected by traces of iron. Zirconium gives a brownish tinge to the solution, which is also affected by large quantities of columbium. The effects of the rare earths, etc., are also described, and the colorimetric method is applied to the estimation of titanium in the presence of columbium, tantalum, or thorium.

Five % solutions of sodium tungstate or molybdate are not precipitated by salicylic acid, and the resulting solution gives no precipitate with ammonium hydroxide. Titanium is precipitated under such conditions, but the reaction cannot be used to separate titanium from tungsten and molybdenum. T. S. P.

The Detection of Small Quantities of Alcohol in Fermenting Liquids. ALB. KLÖCKER (*Centr. Bakt. Par.*, 1911, ii, **31**, 108—111). —In the systematic study of yeasts, one of the most important characteristics is the capacity of the organism to ferment different sugars. Where vigorous fermentation occurs, the usual qualitative tests may be employed, but even in cases where no apparent fermentation takes place, the author considers it necessary that actual tests should be made, and describes a modification of Pasteur's drop method, by means of which traces of alcohol may be detected.

Five c.c. of the liquid to be tested are poured into a test-tube 180 mm. long and 24 mm. wide. This is closed with a cork bearing a glass tube 180 cm. long and 3 mm. wide, which is allowed to protrude slightly on the lower side of the cork. The whole is then placed vertically over a flame with wire gauze, and is heated gently, care being taken that bumping does not occur. If alcohol is present, characteristic oily drops appear in the tube; the lower the amount of alcohol, the higher being the point at which these drops occur.

It is claimed that by the use of this method, 0·002—0·001% of alcohol can be detected. H. B. H.

Estimation of both Phenol and *p*-Cresol in Urine. MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1911, **34**, 462—472. Compare this vol., ii, 72).—The urine, after being made alkaline with sodium hydroxide, is evaporated to 1/5th of its bulk, acidified with sulphuric acid, and then distilled in steam. To separate volatile acids from phenols, the distillate is made alkaline with sodium hydrogen carbonate, and distilled in steam in a current of carbon dioxide. The reducing substances are separated then by Neuberg's method by means of lead acetate and sodium hydroxide, and then, after distillation of these substances, the phenols are distilled off after acidification with sulphuric acid. The phenol and cresol are then estimated by the method already given by the authors, which they find preferable to that of Kossel and Penny. The analyses of mixed urines from several individuals showed that 1·5 litres contained 0·0260 gram of *p*-cresol and 0·0186 gram of phenol; 58·1% of the total phenols consisted therefore of *p*-cresol. The details are given of the experiments on which the analytical method is founded. S. B. S.

Estimation of Phenols in the Urine of Oxen. PAUL LIECHTI and W. MOOSER (*Zeitsch. physiol. Chem.*, 1911, **73**, 365—370. Compare Neuberg and Hildesheimer, Abstr., 1910, ii, 1116).—Polemical. The supposed formation of furfuraldehyde on distillation of herbivorous urine with phosphoric acid, derived from dextrose, pentose, or paired glycuronic acid, is shown not to take place. The Kossler-Penny process advocated by Neuberg and Hildesheimer (*loc. cit.*) leads to far larger errors than any neglect of the furfuraldehyde formed. The substitution of phosphoric acid for sulphuric acid in the distillation prevents the formation of urogon, which otherwise fixes iodine; further aldehydes present are not hydrolysed in such a way as to affect the estimation of the phenols. E. F. A.

Estimation of Volatile Acids in Wine. KARL WINDISCH and THEODOR ROETTGEN (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 155—170).—It is recommended that 50 c.c. of the wine should be distilled in a current of steam until 200 c.c. of distillate have been collected; if the distillation is continued beyond this, considerable quantities of lactic acid are found in the distillate. When the wine contains more than 0·2 gram of volatile acids per 100 c.c., it should be diluted with an equal volume of water, and 50 c.c. of the mixture taken for the estimation. The volume of the steam must be so regulated that the wine is first evaporated to 25 c.c. and maintained at this volume until the end of the distillation. The time taken for the distillation is about thirty minutes; the steam should be under as low a pressure as possible, and it is advisable to employ a still-head filled with glass beads in order to reduce the distillation of the lactic acid to a minimum. W. P. S.

Employment of the Electrometric Method for the Estimation of the Acidity of Tan Liquors. II. JOSEPH T. WOOD, HENRY J. S. SAND, and DOUGLAS J. LAW (*J. Soc. Chem. Ind.*, 1911, **30**, 872—876). —A hydrogen electrode is described for use in the electrometric method of estimating the acidity of tan liquors (this vol., ii, 233); slight improvements in the general form of the apparatus are proposed, and experimental details and results are recorded.
W. P. S.

Analysis of Liquids containing a Large Quantity of Tartaric Acid and Small Amounts of Glycerol and Tannin. G. HINARD (*Ann. Falsif.*, 1911, **4**, 391—397).—Having experienced certain difficulties in the analysis of solutions containing about 100 grams of tartaric acid, 10 grams of glycerol, and 3 grams of glycerol per litre, the author gives the following methods for the estimation of these constituents and of the total solids of the solution. The total solids may be estimated by drying 5 c.c. of the solution on pumice-stone over sulphuric acid and under as low a pressure as possible; at the end of twenty-four hours, the temperature of the desiccator is raised to 50°, and the drying is continued over phosphoric oxide to constant weight. For the estimation of the glycerol, 100 c.c. of the solution are treated with sufficient potassium hydroxide to convert the tartaric acid into potassium hydrogen tartrate; the latter is removed by filtration, and the filtrate is evaporated at a low temperature after the addition of freshly prepared lead hydroxide. The residue is extracted with hot alcohol, the solution filtered, excess of lead is precipitated as carbonate, and an equal volume of ether is added, together with a few grams of potassium carbonate. The solution is then filtered, evaporated, and the residue dried under reduced pressure. The tartaric acid may be estimated by the methods used in wine analysis, and the tannin is estimated iodometrically.

W. P. S.

Estimation of Milk Fat by Count of the Fat Globules. H. P. T. OERUM (*Biochem. Zeitsch.*, 1911, **35**, 18—28).—The relationship between the number of fat globules in a given measure, the transparency of the milk (the experimental method for determining which is described), and the fat content is mathematically worked out. The conclusion is drawn that each observer must obtain his own formula for each kind of milk, and the method has, therefore, no immediate practical value.

S. B. S.

Assay of Chloral. L. BOURDET (*J. Pharm. Chim.*, 1911, [vii], **4**, 18).—The author suggests that in assaying chloral by the method prescribed in the French Codex, (1) distilled water, freed from carbonic acid, should be used; (2) a control experiment with water and alkali alone should be made; (3) $N/2$-alkali should be substituted for N-alkali, and (4) the time of contact of the alkali with the chloral should be reduced to fifteen minutes.

T. A. H.

Ulex's Process for the Estimation of Nicotine in Tobacco Extracts and Nicotine Salts. JULES ESSNER (*Ann. Chim. anal.*, 1911, **16**, 339—341).—A recapitulation of Ulex's process (treatment of the extract with a mixture composed of aqueous sodium hydroxide, calcium oxide, and plaster of Paris, removal of ammonia fumes in a desiccator over sulphuric acid, distillation with water, and titration of the nicotine with standard acid), which the author strongly recommends for technical purposes. The author carries out the distillation and titration as follows: The mass is placed in a 3-litre distillation flask containing 2½ litres of boiled water, 10 grams of sodium hydroxide and 10 grams of paraffin (to prevent frothing) are added, and the whole is submitted to distillation. Six portions of 1000, 500, 200, 100, 100, and 100 c.c. respectively are collected and titrated separately with $N/2$-hydrochloric acid, using delicate litmus solution as indicator; 1 c.c. of acid = 0·081 gram of nicotine.

L. DE K.

Comparative Studies on the Nicotine Estimations in Tobacco Extracts. JULIUS TÓTH (*Chem. Zeit.*, 1911, **35**, 926—927). —At the author's suggestion, J. KRAMPERA analysed a sample of tobacco extract by the methods of Kissling, Ulex, Degrazia, and Tóth, and the results are given in a table; in a second table are given the results of analyses made by the methods of Kissling, Koenig, Tóth, and the modified process of the latter. This consists in substituting xylene for toluene in the extraction of the nicotine; the results obtained by titration and polarisation are very concordant.

On the whole, the author has reason to prefer his own modified process. L. DE K.

Estimation of Quinine as Acid Citrate in Certain Organic Liquids.

THOMAS COCKBURN and J. W. BLACK (*Analyst*, 1911, **36**, 396—398).—A slight modification of Nishi's process for the estimation of quinine in urine (Abstr., 1909, ii, 710). Two hundred and fifty c.c. of urine are rendered alkaline with concentrated aqueous sodium hydroxide and extracted three times with ether. The ethereal extracts are washed with small quantities of water, evaporated, the residue dried and dissolved in 20 c.c. of anhydrous ether, and the solution is filtered into a weighed flask with which has also been weighed a small asbestos filter tube, and the undissolved matter is washed with small quantities of ether. The quinine is now precipitated by adding 10 c.c. of a saturated ethereal solution of citric acid, and the closed flask is left for twenty-four hours. The ether is then poured off through the filter-tube, and the deposit is washed thrice in succession with 10 c.c. of ether, D 0·720. The tube is then placed in the flask, and the whole is dried, first gently, finally at 100°, and re-weighed; 100 parts of the acid citrate = 62·79 parts of quinine.

The process may be used in the presence of caffeine, but not of other cinchona alkaloids. L. DE K.

Separation of Urobilin by means of Talc and its Detection.

C. CARREZ (*Ann. Chim. anal.*, 1911, **16**, 337—339).—The urine is defecated by mixing 45 c.c. with 30 c.c. of Denigès' mercury reagent, and to 30 c.c. of the clear filtrate is added 1 gram of talc, which on shaking removes all the urobilin; the talc is then at once collected on a filter and washed with water. In order to prove the presence of the urobilin, the talc is treated on the filter with 5 or 10 c.c. of Oliveri's reagent (zinc chloride 10 grams, ammonia 30 grams, strong alcohol 80 grams, ethyl acetate 20 grams), when at once a filtrate is obtained presenting a beautiful green fluorescence and exhibiting in the spectroscope very neatly the band γ.

Or the talc may be treated with 10 c.c. of alcohol containing 5% of hydrochloric acid. To the filtrate is then added 5—6 c.c. of chloroform and 100—150 c.c. of water, and the whole is well shaken. The chloroform layer separates readily, and is then removed and filtered through a small filter moistened with chloroform. On adding an alcoholic solution of zinc acetate (1 : 1000), a green fluorescence is gradually formed, and the band γ is more distinct than before.

L. DE K.

Estimation of Amino-groups in Amino compounds and in Urine and a Method for the Analysis of Proteins.

DONALD D. VAN SLYKE (*Ber*, 1911, **44**, 1684—1692; *J. Biol. Chem.*, 1911, **10**, 15—55. Compare this vol., ii, 164, 779, 780).—Glycine, cystine, and guanosine give high values when treated by the method already described.

Carbamide reacts slowly with the nitrous acid solution, and this reaction must be allowed for in estimating the amino-acid nitrogen in urine. After removal of ammonia from the urine made alkaline with sodium hydroxide solution, two estimations are made of the amino-acid nitrogen, one after six minutes and the other after the mixture has been left for twelve minutes. The difference between the two gives the error due to the reaction of the carbamide, and can be subtracted from the result given by the six minute determination.

Full details are given of a somewhat revised scheme for the analysis of proteins by the method of hydrolysis and nitrogen determinations. The following substances have been treated in this way: gliadin, edestin, hair, gelatin, fibrin, hæmocyanin, hæmoglobin, and the results are expressed in percentages of ammonia nitrogen, melanin nitrogen, cystine-, arginine-, histidine-, lysine-nitrogen, amino-nitrogen of filtrate, and non-amino-nitrogen of filtrate. Gelatin and hæmoglobin did not give any cystine nitrogen. J. J. S.

An Inner Anhydride Reaction of Albumin. BRUNO BARDECK *Chem. Zeit.*, 1911, **35**, 634).—The author's iodoform process (this vol., ii, 826) when applied to albumins shows that these give very intense anhydride reactions. L. DE K.

Rapid Gravimetric Estimation of Urinary Albumin. E. SIMONOT (*Bull. Soc. chim.*, 1911, [iv], **9**, 839—842).—This method, which depends on the coagulation of the albumin by metaphosphoric acid, is stated to afford complete precipitation of the albumin in a form in which it can be easily and rapidly filtered, and washed (compare Denigès, Abstr., 1893, ii, 248).

Five grams of sodium metaphosphate are dissolved in cold water, and made up to 100 c.c., or 5·70% grams of the metaphosphate may be dissolved by boiling in water during five minutes and made up to 100 c.c. as suggested by Denigès (*Chim. Anal.*, 3rd Edit., 1907, p. 1011). A preliminary trial having shown that the urine contains more than 0·5 gram albumin per litre, enough to yield about 10 grams is taken, filtered, made up to 100 c.c. if necessary, heated on the water-bath during ten minutes (during fifteen minutes if the quantity is 200 c.c.), and then for every 100 c.c. of liquid, 5 c.c. of the metaphphate solution and 1 c.c. of hydrochloric acid are added and the heating continued during five to ten minutes. The coagulum is filtered on a dry tared filter and washed with boiling water until free from hydrochloric acid, and then twice with alcohol and once with ether. As much liquid as possible is removed by gentle pressure, and the coagulum dried at 110—120°. The weight, re-calculated for 1 litre of urine and multiplied by 0 88, gives the amount of albumin per litre in the urine examined.

T. A. H.

Estimation of Lecithin. C. VIRCHOW (*Chem. Zeit.*, 1911, **35**, 913—914).—The author has slightly modified his process. One gram of the substance is boiled three times in succession with 10 c.c. of absolute alcohol, and the filtrate and washings, measuring about 50 or 60 c.c., are distilled off. After removing the last traces of alcohol by blowing, the weighed residue is dissolved in 10 c.c. of absolute ether, which is then poured through an asbestos filter tube; the residue is then washed three times with ether.

The ether is distilled off, and the weighed residue treated with 3—4 c.c. of fuming nitric acid; the solution is transferred to a platinum dish, and the flask rinsed three times in succession with 2 c.c. of fuming nitric acid. After evaporating the acid on the water-bath, the residue is mixed with 1 gram of dry sodium carbonate, using a platinum spatula. Five grams of the usual potassium nitrate–sodium carbonate mixture are now added, and the whole is heated to fusion for four to five minutes. The fusion contains the phosphorus of the lecithin as phosphoric acid, which is then estimated by the usual magnesia process. L. DE K.

A Method for Ash Analysis. KARL STOLTE (*Biochem. Zeitsch.*, 1911, **35**, 104—107).—The essential feature of the method consists in ashing the dried organic substance in a platinum basin placed inside a larger porcelain basin but kept from direct contact with it by pieces of porous plate, or an inverted crucible lid. S. B. S.

A New Colour Reagent for Callose. M. TSVETT (*Compt. rend.*, 1911, **153**, 503—505).—The reagents hitherto in use for callose are slow in action; the following one is very rapid. A 1% aqueous solution of resorcinol, containing 0·1% of concentrated ammonia, is allowed to remain for several days exposed to the air. It gradually undergoes oxidation, and gives rise to a blue substance apparently identical with Würster's resorcinol-blue, which the author calls *resoblue*.

Resoblue does not stain cellulose, but in thirty to sixty seconds it imparts a deep blue colour to callose. It can also be mixed with other stains to give double reactions; thus the mixture with Congo-red is stable, and colours callose blue and cellulose red. Other mixtures are also suggested. E. J. R.

Use of Nickel Hydroxide in Tannin Estimation. PURAN SINGH (*J. Soc. Chem. Ind.*, 1911, **30**, 936—937).—Results of experiments carried out by the author indicate that nickel hydroxide may be employed as a substitute for hide-powder in the analysis of tanning materials. The figures obtained were in fair agreement with those found when hide-powder was used. W. P. S.

Application of the Bromo-derivative Methods for the Assay of Vulcanised Rubber Wares. WERNER ESCH (*Chem. Zeit.*, 1911, **35**, 971—972).—The process in use is based on the following assumptions: (1) 136 parts of rubber hydrocarbons absorb 319·7 parts of bromine or 64 parts of sulphur; (2) if 136 parts of hydrocarbons have already absorbed 32 parts of sulphur (in consequence of vulcanisation), only 159·85 parts of bromine can be taken up; (3) the sulphur absorbed is not acted on by bromine solutions; (4) if from the total weight is deducted the combined sulphur and the bromine absorbed, the value of the rubber substance present is obtained; (5) from 64 parts of combined sulphur or from 319·7 parts of bromine absorbed, the presence of 136 parts of rubber hydrocarbons may be deduced.

According to the author's experiments, these assumptions cannot be entertained, and the process is therefore quite untrustworthy.

L. DE K.

Estimation of the Specific Gravity of very small Quantities of Milk. ALOIS KREIDL and EMIL LENK (*Biochem. Zeitsch.*, 1911, **35**, 166—168).—As fat is not extracted from milk by simple mixture with a lipoid solvent, the specific gravity can be determined by dropping the milk into mixtures, such as benzene-chloroform, benzene-carbon tetrachloride, etc., and finding the specific gravity of the mixture in which the milk neither sinks nor floats. S. B. S.

A New Modification of the Forensic Chemical Test for Blood. OTTO VON FURTH (*Zeitsch. angew. Chem.*, 1911, **24**, 1625—1628).—In testing for blood, the author recommends a combination of Leer's pyridine test with the leucomalachite-green test (Adler, Abstr., 1904, ii, 459). The object to be tested is boiled for some minutes with a few drops of 50% potassium hydroxide to which a few drops of alcohol have been added. After cooling, the liquid is extracted with pyridine. The pyridine layer is separated, and again shaken with concentrated potassium hydroxide, after which about 1 c.c. of the solution is run on to a filter paper laid on a glass plate. This is then tested with the leucomalachite-green solution, to which has previously been added 1% of hydrogen peroxide.

A full discussion of the sensitiveness of the test and of any errors which may occur is given. T. S. P.

Meyer's Reagent for the Detection of Blood. A. SARTORY (*Compt. rend.*, 1911, **152**, 131—133).—The red coloration produced by blood in presence of hydrogen peroxide with phenolphthalein previously reduced by zinc, is also given by alkali hydrogen carbonates. The test cannot therefore be taken as specific for blood, and should only be used as a confirmatory test. W. J. Y.

Estimation of Gelatin. W. GREIFENHAGEN, J. KÖNIG, and A. SCHOLL (*Biochem. Zeitsch.*, 1911, **35**, 217—227).—Beckmann's formaldehyde method is of little practical value. Precipitation by Nessler's reagent by Vamvaka's method brings down all the gelatin, but it also precipitates proteoses. Although trichloroacetic acid (Obermayer's method) only produces a turbidity with dilute solutions of gelatin, it does not completely precipitate proteoses, and this reagent therefore cannot be employed for separating these substances from gelatin. Mercuric chloride solution does not produce a quantitative separation, but if it precipitates the same amount of nitrogenous matter as zinc sulphate, the conclusion may be drawn that gelatin is not present.

Mercuric iodide can also be employed as a precipitant. If the solution is first precipitated by zinc sulphate, the precipitate redissolved, and mercuric iodide in acetone or alcohol added (with precautions described in detail by the authors) and a precipitate is then produced which contains a large proportion of the nitrogenous matter which was precipitated by the zinc sulphate, then it may be deduced that gelatin is present. A satisfactory method for separating gelatin from proteoses does not exist. S. B. S.

Analyses of Liquorice Juices. L. Gadois and J. Gadois (*Bull. Soc. chim.*, 1911, [iv], **9**, 741—743).—The analyses of liquorice juices by different methods having furnished discrepant results, the following analytical method was adopted: The moisture was estimated by drying at 100°, insoluble matter by two extractions with cold water for twenty-four hours, and the ash by ignition. The glycyrrhizin was determined by precipitating the resinous matter from aqueous solution with alcohol, concentrating the filtrate, and precipitating with hydrochloric acid in a weighed beaker, the precipitate being washed with water, treated with ammonia, and the ammonium derivative dried at 100°. W. G.

A New Method for the Detection of Salvarsan (Diaminodihydroxyarsenobenzene). J. Abelin (*Münch. Med. Woch.*, 1911, **19**. A Reprint).—A very little of the salvarsan is dissolved in 2—3 c.c. of water, and the yellow solution is decolorised by addition of 3—4 drops of dilute hydrochloric acid. After cooling the solution, 3—4 drops of a 0·5% solution of sodium nitrite are added, when a diazo-compound is formed, showing a vivid yellowish-green fluorescence. The liquid is now added, drop by drop, to a 10% solution of resorcinol, to which an excess of sodium carbonate has been added, when a beautiful red colouring matter will be formed; care must be taken that the liquid remains alkaline.

When applying the process to urines, 7—8 c.c. of the sample are acidified with 5—8 drops of dilute hydrochloric acid, and when cold, 3—4 drops of the above sodium nitrite solution are added. A few drops of the liquid are then added to 5 c.c. of the alkaline resorcinol solution, or the ring test may be applied successfully.

Atoxyl, treated as above, yields an orange colouring matter.

L. de K.

Pyro-Analyses of Drugs. Leopold Rosenthaler (*Ber. Deut. pharm. Ges.*, 1911, **31**, 338—346).—A microscopical and chemical investigation of crystalline sublimates obtained in vacuum from a number of drugs. Probably it would be better still to subject their extracts to the sublimation process. For the micro-illustrations and properties of the various sublimates, the original paper should be consulted.

The following drugs were examined: *Cortex chinae, Folia uvae ursi, Cortex frangulae, Cortex cascarae sagradae, Rhizoma rhei, Gallae, Rhizoma hydrastis, Opium, Cubebae, Semen calabar, Piper nigrum,* and *Fructus anisi.* L. de K.

General and Physical Chemistry.

The Density and Refraction of the System Furfuraldehyde + Water. F. Schwers (*Bull. Acad. roy. Belg.*, 1911, 641—652).—The densities and refractive indices of binary mixtures containing 4·6, 5·7, 6·5, and 96·3% of furfuraldehyde have been measured at different temperatures.

Curves are plotted to show the volume contraction which occurs in the formation of the various solutions in its dependence on the temperature. These curves exhibit certain irregularities, which in the case of the dilute furfuraldehyde solutions are similar to those which have been observed previously in the case of mixtures of water with diacetyl glycol and ethyl acetoacetate.

In regard to the refractive index, the observed values differ from those calculated by an amount which is more or less independent of the composition and the temperature of the binary mixture. Observations with the hydrogen lines H_α and H_β and the yellow helium line show that the difference depends on the wave-length of the light used. H. M. D.

Refractive Indices of Liquid Crystals. Paul Gaubert (*Compt. rend.*, 1911, **153**, 573—576. Compare Abstr., 1909, ii, 529; Wallerant, *ibid*).—The author records observations on the refractive indices of the isotropic forms of cholesterol, cholesteryl benzoate, acetate, decoate, and propionate; also of mixtures of the latter with the decoate and with *p*-azoxyphenetole. Measurements could not be made in the case of some of the mixtures, owing to solidification of the superfused liquid taking place without production of the optically positive anisotropic phase.

The difference between the refractive index of the isotropic liquid and the liquid crystal is small. Crystals of the doubly refractive liquid phase, produced before solidification, are optically positive, whilst those belonging to the anisotropic liquid phase existing at a higher temperature are negative. The experiments on mixtures showed that their optical properties do not follow the laws relating to the mixture of isomorphous solid crystals, apparently owing to the occurrence of one substance in a polymorphous, crystalline liquid form, unknown in the pure substance. W. O. W.

The Secondary Spectrum of Hydrogen. C. Porlezza (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 176—183).—The measurements of the secondary spectrum of hydrogen have now been extended to the yellow and red regions, as far as λ 6963, and to the ultra-violet as far as λ 3295. New lines are found in both regions, as well as in the region λ 4807—4253. The wave-lengths are tabulated. Certain lines observed by Croze (this vol., ii, 558) are not found, and the differences are possibly due to the difference in diameter of the capillaries used by the two observers, otherwise the lines found only by Croze must be due to the presence of an impurity (compare Watson, Abstr., 1909, ii, 453). C. H. D.

The Ratio of the Intensities of the Series Lines of Hydrogen in the Canal Ray Spectrum. FRITZ LUNKENHEIMER (*Ann. Physik*, 1911, [iv], **36**, 134—152).—The relative intensities of the lines H_α and H_β in the hydrogen canal ray spectrum have been measured for different velocities of the luminous particles. For this purpose the intensities of the two lines were compared with that of light of the same wave-length emitted by a Nernst lamp, and also by a Geissler discharge tube, which were operated under constant conditions. In some experiments, the comparison was effected subjectively, and in others by means of photographic records. Within the limits of the errors of experiment, the results obtained show that the ratio of the intensities of the two hydrogen lines is independent of the velocities of the canal ray particles. This is opposed to the result obtained by Stark and Steubing (Abstr., 1908, ii, 546), who found that an increase in the velocity of the particles is accompanied by an increase in the relative intensity of the lines of smaller wave-length. It is probable that the relative intensities are dependent on the gas pressure in the discharge tube, and this may account for the divergent results obtained by Stark and Steubing. H. M. D.

The Resonance Spectra of Iodine Vapour and their Destruction by Gases of the Helium Group. ROBERT W. WOOD (*Phil. Mag.*, 1911, [vi], **22**, 469—481. Compare this vol., ii, 169, 170).—A method is described by which the resonance spectra of iodine can be exhibited to an audience by means of a Cooper-Hewitt lamp and a small pocket spectroscope. With the improved illumination of the vapour which can be obtained by means of suitably arranged quartz-mercury arc lamps and a cylindrical vapour tube, new photographs of the resonance spectra excited by the green and the two yellow mercury lines have been obtained. The spectrum excited by the green line consists of a series of equidistant lines, eighteen members of which are shown in the photographic records. The two yellow lines give rise to a series of fifteen equidistant doublets, two of which are situated below and twelve above the exciting lines. The series excited by $\lambda = 5790 \cdot 5$ is much more intense than the series due to $\lambda = 5769 \cdot 5$; this is probably due to a closer coincidence between the wave-length of the less refrangible yellow line of mercury and one of the absorption lines of the iodine vapour. The wave-lengths of the various lines are considered to be correct to about one Ångstrom unit. From a comparison of the wave-length differences in each series, it is found that these increase as the red end of the spectrum is approached.

As the result of a comparison of the effects produced by the various inert gases in transforming the resonance spectrum into the banded spectrum, which is excited by white light, it is found that helium is the most active. In presence of krypton at 1·7 mm. pressure, the band spectrum could only just be distinguished, and with xenon at 1·5 mm. pressure, no trace of the band spectrum was found, although the intensity of the resonance emission was reduced to about one-fourth of its original value.

Further observations in which the vapour was excited by polarised light show that the resonance lines are themselves polarised, and from this it may be inferred that the directed motion passed over by the light waves to the resonant electron is passed on as directed motion to the other electrons. When in presence of helium the resonance spectrum is completely replaced by the band spectrum; the emitted light is still found to be partially polarised. H. M. D.

The Colorimetric Dilution Law. ARTHUR HANTZSCH (*Annalen*, 1911, **384**, 135—142. Compare Piccard, this vol., ii, 561).—Piccard's views are at variance with the results of the author's experiments on chromoisomerides, which show that Beer's law is untenable even for isomerides. The law holds for the structurally unchangeable ethyl diethylacetoacetate and ethyl ethoxycrotonate in all solvents, but in the case of ethyl acetoacetate in hexane the equilibrium is shifted with increasing dilution in the direction of the more strongly absorptive enol form, a result which is confirmed in a purely chemical way by titration with bromine (Meyer, this vol., i, 350, 832, 833).

The author also shows that Beer's law is inapplicable to solutions of the colourless and the yellow modifications of ethyl dichlorodihydroxyterephthalate and of the colourless and the yellow forms of *o*-nitroaceto-*p*-toluidide (all of which are unimolecular in solution), and also to the chromoisomeric pyridine, quinoline, and acridine salts (this vol., i, 673).

Contrary, therefore, to Piccard's views, the author is of opinion that the untenability of Beer's law denotes the existence of chromoisomerides in equilibrium in the solution, provided that polymerides have previously been shown to be absent. C. S.

The Colour of Iodine Solutions. HEINRICH LEY and K. VON ENGELHARDT (*Zeitsch. anorg. Chem.*, 1911, **72**, 55—62).—A re-examination of the absorption spectrum of freshly prepared solutions of iodine in ethyl alcohol confirms the results formerly obtained (Abstr., 1910, ii, 813) with a single band at 1/λ 2150. The different results obtained by Waentig (Abstr., 1910, ii, 117) and Crymble, Stewart, and Wright (*ibid.*, 470), showing two absorption bands, are due to the use of old solutions. The gradual decomposition may be followed spectroscopically.

The violet solutions of iodine in hexane or chloroform have identical spectra, with a band at 1/λ 2000 and another in the ultra-violet. Beer's law is not followed, especially in the ultra-violet region. The ethereal solution is intermediate in character, and the differences between the spectra are less than those found by Waentig. The absorption coefficients of a solution of iodine in benzene show that in this case, also, the head of the band lies at 1/λ 2000. It is held that the brown solutions contain additive compounds, I_2L_m, but the constitution of the violet solutions is still uncertain. C. H. D.

Absorption Spectra of Triphenylmethyl and of Salts of Triphenylcarbinol. KURT H. MEYER and HEINRICH WIELAND (*Ber.*, 1911, **44**, 2557—2559).—Non-conducting solutions of triphenylmethyl (and also of other triarylmethyls) in organic solvents are sharply distinguished from the triphenylmethyl ion, assumed to be present in solutions of salts of triphenylcarbinol, by means of the spectroscope. Whilst the latter exhibit continuous absorption in the more refrangible region of the (visible) spectrum, solutions of triphenylmethyl are characterised by a banded spectrum consisting of one strong, sharply defined band and a second, which is weaker.

The conducting solution of triphenylmethyl in liquid sulphur dioxide exhibits the continuous absorption of the triphenylmethyl ion (probably, therefore, a salt-like additive compound of solute and solvent is formed), but after removing the sulphur dioxide by a current of carbon dioxide and dissolving the residue in benzene, the yellow solution shows the banded spectrum of triphenylmethyl. These results are claimed to be in harmony with Baeyer's theory (Abstr., 1905, i, 281). C. S.

Crystalline Liquids. H. VON WARTENBERG (*Physikal. Zeitsch.*, 1911, **12**, 837—839. Compare Bose, 1909, ii, 383; this vol., ii, 184). —The optical behaviour of the crystalline liquid forms of *p*-azoxyanisole and *p*-azoxyphenetole has been examined when the turbid liquids are subjected to the influence of a magnetic field. Observations were made with parallel and convergent polarised rays of light and in directions parallel and at right angles to the lines of force. Both substances were found to behave like uniaxial crystals, and thus the crucial test suggested by Nernst (*Zeitsch. Elektrochem.*, 1910, **16**, 702) is in favour of Bose's theory of the liquid crystalline state of aggregation. The magnetic field has no influence on the clearing temperature in either of the substances investigated.

H. M. D.

Development of Colours on Fibres by Light Energy. OSKAR BAUDISCH (*Chem. Zeit.*, 1911, **35**, 1141—1142).—Silk and wool may be dyed a brilliant cherry-red, which is quite fast, by treating the fabric with an aqueous ammoniacal solution of the ammonium salt of α-nitrosonaphthylhydroxylamine, steaming, drying, and finally exposing to the action of light.

During the steaming process, the α-nitrosonaphthylhydroxylamine, which is fixed on the fibres, decomposes with the formation of α-nitrosonaphthalene; the latter substance, probably aided by the reducing action of the animal fibre, then changes into α-azoxynaphthalene, which under the influence of light becomes red, in all probability owing to its transformation into the corresponding hydroxyazonaphthalene.

It is not improbable that other nitrosoarylhydroxylamines will be found to behave in a similar manner.

α-Nitrosonaphthylhydroxylamine is a white, crystalline substance, which is very sensitive to the action of light; the *ammonium* salt crystallises in white leaflets, and is most readily obtained by the action of amyl nitrite on a cold solution of α-nitronaphthylhydroxylamine containing an excess of ammonia; the *copper* salt,

$$(C_{10}H_7O_2N_2)_2Cu,$$

crystallises from chloroform in glistening, greyish-blue needles; the *iron* salt is very soluble in ether, forming an intense red solution.

W. H. G.

The Ranges of α-Particles from Various Radioactive Substances and a Relation between the Range and Period of Transformation. HANS GEIGER and J. M. NUTTALL (*Phil. Mag.*, 1911, [vi], **22**, 613—621).—A film of the active substance was placed centrally in a silvered globe of 8 cm. radius, and the ionisation current in air determined at various pressures. This is independent of the pressure until the range of the α-particle becomes equal to the radius of the globe. At this point the ionisation current begins to diminish as the pressure is further reduced. From the point of inflexion on the curve the range is found, and from this the initial velocity of the α-particle can be calculated. The results obtained are given in the table:

Substance.	Range at 15°.	Range at 0°.	Initial velocity.
Uranium	2·72 cm.	2·58	1·51 × 10^9 cm./sec.
Ionium	3·00 ,,	2·84	1·56 ,,
Radium	3·30 ,,	3·13	1·61 ,,
Polonium	3·77 ,,	3·58	1·68 ,,
Thorium	2·72 ,,	2·58	1·51 ,,
Radio-thorium	3·87 ,,	3·67	1·70 ,,

If the logarithm of the range is plotted against the logarithm of the period of transformation, the points for the uranium–radium series fall approximately on a straight line, whilst those for the actinium series fall on another straight line of similar slope, parallel to the first. The thorium series is still being investigated. The results in the other two series include in each case five α-ray-giving products. The period of ionium calculated from the range of its α-particles is nearly one million years. That of radium-*C* similarly calculated should be about a millionth of a second. The range is proportional to the cube of the velocity, so that similar straight lines would result on plotting the logarithm of the periods and of the velocity of the α-particles. On this rule, which at present is empirical, an explanation suggests itself why no α-rays of low range are known, for the period of transformation would be so great that the activity would be beyond the limit of detection.

F. S.

Production of Helium by Radium. BERTRAM B. BOLTWOOD and ERNEST RUTHERFORD (*Phil. Mag.*, 1911, [vi], **22**, 586—604).—A quantity of radium chloride, freed from radio-lead and polonium by treatment with hydrogen sulphide after addition of bismuth, lead, and antimony, was sealed up in a Jena glass combustion tube and the air exhausted. By γ-ray measurements the quantity of radium was found to be 0·191 gram. Re-measured at the close of the experiments the quantity found was 0·193 gram. In the first experiment the time of accumulation was eighty-three days, and the volume of helium evolved on heating the tube was 6·58 cu. mm. at *N.T.P.* In the second experiment the time of accumulation was 132 days, and, after the withdrawal of the gases, the radium chloride was dissolved in dilute hydrochloric acid and the helium collected. The total helium was 10·38 cu. mm. The two results agree in giving the rate of production of helium per gram of radium, in equilibrium with its first three α-ray-giving products, as 156 cu. mm. per year. The theoretical rate, calculated from the number of α-particles expelled, is 158 cu. mm. The radium standard employed was 97·22% pure in terms of that used in the atomic weight determinations by Thorpe. The production of helium from a known amount of radium emanation was found to be in fair agreement with that calculated. The production of helium was also observed from preparations containing polonium.

F. S.

The Relative Number of Ions Produced by the β-Particles from the Various Radioactive Substances. HANS GEIGER and ALOIS F. KOVARIK (*Phil. Mag.*, 1911, [vi], 22, 604—613).—By assuming that the ionisation produced by a β-particle does not depend appreciably on the velocity, and examining cases where the β-ray-giving product is in equilibrium with an α-ray-giving product, the relative number of ions produced per atom disintegrating by the β-rays can be determined; for the number of α-particles can be counted, and this is identical with the number of atoms breaking up giving β-rays. The ionisation due to β-rays divided by this number gives the β-ray ionisation per atom disintegrating. The number of α-particles was determined by an ionisation method at low pressure from data previously accumulated (Abstr., 1909, ii, 473), and checked by scintillation experiments. The number of ions produced per cm. of path per atom disintegrating was found to be similar in the case of the β-ray products thorium-*D* and the corresponding actinium product, and about twice as great as in the cases of radium-*E* and uranium-*X*, whilst radium-*C* was intermediate. In the first case the number found was 136, in the second 69 and 78, and in the third 108. The most probable explanation is that different numbers of β-particles are expelled per atom disintegrating in the different cases. If it is assumed that two β-particles are given per atom of thorium-*D*, the number of ions produced per cm. in air by a high velocity β-particle is 67. This is higher than Durack's value, in which, however, the reflexion of the β-particles by the walls of the ionisation chamber was not corrected for.

F. S.

The Emission of Electrons in Chemical Reactions. FRITZ HABER and GERHARD JUST (*Ann. Physik*, 1911, [iv], 308—340. Compare Abstr., 1909, ii, 853; this vol., ii, 572).—An improved method is described for the investigation of the electron emission which takes place when electro-positive metals react with certain gases. With this apparatus experiments have been made in which a potassium–sodium alloy was allowed to react with the vapour of carbonyl chloride at very low pressure, the surface of the reacting alloy being continuously renewed by the formation of a rapid succession of drops at the extremity of a silver capillary terminating in the neighbourhood of a silver plate connected with the electric discharge measuring apparatus.

The results of these experiments confirm previous conclusions, and show that the reaction at the ordinary temperature and in the absence of light is accompanied by the emission of electrons, resulting in the charging of the alloy to a potential of about one volt. That the carriers of the electric discharge are free electrons is proved by the behaviour towards a magnetic field.

When the carbonyl chloride is replaced by bromine, free electrons are also emitted, but if the sodium–potassium alloy is replaced by cæsium-, potassium-, or lithium-amalgam, negative ions are produced. In all cases the effect is of unipolar character, and is observed in the entire absence of light. H. M. D.

Transformation and Nomenclature of the Radioactive Emanations. ERNEST RUTHERFORD and HANS GEIGER (*Phil. Mag.*, 1911, [vi], **22**, 621—629).—The new short-lived products of transformation of the thorium and actinium emanations give α-rays, and have half-value periods respectively of 0·14 sec. and 0·002 sec. (compare next abstract). In each case they carry positive charges when produced, and are carried in an electric field to the negative electrode, constituting, therefore, the first members of the active deposits analogous to radium-*A* (compare Geiger, this vol., ii, 683). They may be put into evidence in the dark by immersing a rod coated with zinc sulphide into the emanations. On charging it negatively, the end instantly lights up, and as suddenly dies out when the rod is discharged. The actinium product of period 0·002 sec. was observed by Giesel eight years ago (Abstr., 1903, ii, 193) in this phenomenon, which he termed the "*E*-rays." The thorium product can be put into evidence by driving an endless wire, by a motor, through small holes in ebonite corks closing a cylinder containing a source of thorium emanation, and charging the wire negatively. The wire, as it leaves the cylinder, is active when the motor is working, and its activity and the decay along the wire can be examined by a zinc sulphide screen. It is proposed to call the new products thorium-*A* and actinium-*A*, in accordance with the nomenclature in the radium series, where radium-*A*, the first short-lived α-ray-giving product of the emanation, has been known from the start. Hence the next rayless products, previously termed thorium-*A* and actinium-*A*, will now be designated thorium-*B* and actinium-*B*, and are thus made analogous to the rayless product radium-*B*. The next two α-ray-giving products of thorium are termed thorium-C_1 and -C_2, analogously to radium-C_1 and -C_2, the β-ray succeeding product is termed thorium-*D* as at present, the corresponding actinium products being also termed actinium-*C* and actinium-*D*. The group radium-C_1 and -C_2 corresponds with the *C* and *D* members of their series, in that radium-C_2, and possibly radium-C_1, also gives β- and γ-rays. On the new nomenclature, the *A* substances are short-lived, and give α-rays; the *B* substances are the longest lived of the active deposit products, and give only feeble non-penetrating β-rays. The *C* substances all give α-rays, and in the case of radium, β- and γ-rays also, the *D* substances of thorium and actinium giving the β- and γ-rays. F. S.

Radioactive Products of Short Life. H. G. J. Moseley and Kasimir Fajans (*Phil. Mag.*, 1911, [vi], 22, 629—638).—A source of actinium or thorium emanation was contained in an ebonite box, open at one end, the edges of which, covered with velvet pressed against a disk capable of rotation at a high speed. Inside the box was a metal gauze which could be positively charged with respect to the disk, so causing the short-lived products actinium-*A* and thorium-*A* (compare preceding abstract) to be deposited on the rotating disk. Two sector-shaped ionisation chambers, the faces of which opposite the disk were covered with gold-beater's skin and aluminium leaf, were arranged in definite positions on the periphery of the disk, and the ionisation in them compared with the disk revolving at known speed. From the decay of activity over the period required for the disk to turn from opposite the first to opposite the second ionisation chamber, the periods of the products were determined. The half-period of actinium-*A* was found to be 0·002 second, λ being 347 ($sec.^{-1}$), and that of thorium-*A* 0·145 second. With similar apparatus an examination was made of the active deposit of actinium to test the question whether the α-ray-producing member actinium-*C* was complex (compare Abstr., 1910, ii, 768). No evidence of any short-lived product was found, the formation of the β- and γ-ray producing actinium-*D* appearing to follow the disintegration of actinium-*C* directly. F. S.

The Number of Ions Produced by the β- and γ-Rays from Radium-*C*. A. S. Eve (*Phil. Mag.*, 1911, [vi], 22, 551—562).—By the use of very lightly built electroscopes of known capacity, constructed out of light metal rods covered with thin aluminium foil, the number of ions produced by the β- and γ-rays respectively of known quantities of radium at known distances from the electroscope has been determined. For the γ-rays, the radium preparation was surrounded with thin cylinders of zinc or lead, and placed between the poles of an electromagnet to deflect the β-rays. The β-rays were used from various sources, the most satisfactory being from a thin leaf of aluminium coated with the active deposit. The total number of ions produced per second by the γ-rays from a curie of radium-*C* (the radium-*C* in equilibrium with 1 gram of radium) is $1·1 \times 10^{15}$, the number produced per c.c. per second at a distance of 1 cm. from the radium-*C*, in air at atmospheric pressure, is $3·74 \times 10^{9}$. Corresponding values for the β-rays are 4×10^{14} and $1·3 \times 10^{11}$, but these could only be approximately evaluated. The average number of ions made by the flight of one β-particle of radium-*C* is $1·2 \times 10^{4}$, or about 48 ions per cm. of path, assuming that one curie produces $3·4 \times 10^{10}$ β-particles per second. It is estimated that only one out of every 180 molecules traversed by the β-particle is ionised. If the γ-ray is considered as an entity, one being expelled per atom of radium-*C* disintegrating, it produces 3×10^{4} ions on the average, or 1·2 ions per cm. of path. Calculating from the ionisations as a measure of the

energy, the heating effects of radium, 110 calories per gram per hour, are due, 103·5 calories to α-rays, 2·0 to β-rays, and 4·5 to γ-rays.
F. S.

The Concentration and Isolation of Radioactive Substances by "Fractional Adsorption." ERICH EBLER and M. FELLNER (*Ber.*, 1911, **44**, 2332—2338 *).—The method employed is to shake the solution for some hours with metasilicic acid gel, (prepared by the hydrolysis of dilute vapour of silicon tetrachloride and subsequent dialysis ; this vol., ii, 723), and then to volatilise the silicic acid by means of hydrofluoric acid. With dilute solutions of radium barium chloride, from 90 to 100% of the radium was so adsorbed and concentrated in a preparation from one-fourth to one-fiftieth of the initial weight in different experiments. With radio-lead 86 to 95% was adsorbed, and the concentration of weight was from one-third to one-hundredth, but the separate activities of the constituents, radium-*D*, -*E* and -*F*, are not stated. The radium-*F* was adsorbed more than the radium-*D*. With uranium-*X*, the greater part of the active matter was adsorbed. Many advantages are claimed for the method. The small quantities of the materials adsorbed are of no disadvantage. Greater concentration of the material by a single operation is possible than by any other process, and no intermediate products result as in ordinary fractional crystallisation. F. S.

Valency in Gaseous Ionisation. J. FRANCK and W. WESTPHAL (*Phil. Mag.*, 1911, [vi], **22**, 547—551).—The conclusion of Millikan and Fletcher (this vol., ii, 573) that ionisation of gases by radium or Röntgen rays is never accompanied by the liberation of more than one electron from a gas molecule, is considered to be irreconcilable with certain observations. Although the conditions necessary for the production of multivalent ions have not yet been established, there can be little doubt that such ions are formed in certain circumstances.
H. M. D.

The Carriers of Electricity in Gases. A. BECKER (*Ann. Physik*, 1911, [iv], **36**, 209—280).—The author has investigated the nature of the carriers of the electric charge in gases ionised by Röntgen rays, ultra-violet light, and cathode rays.

Under the influence of Röntgen rays, dust-free gases give rise solely to rapidly moving carriers, and the presence of water or other vapours appears to have no influence on the mobility of the carriers. This behaviour differs from that found in the ionisation of gases by ultra-violet light, the much larger, slowly moving carriers which are formed in this case being probably due to chemical changes brought about by the ultra-violet rays. The condensation nuclei which give rise to the large carriers do not appear to be the immediate consequence of this action, for evidence has been obtained in favour of the view that these nuclei result from the action of the product of the chemical change on traces of foreign vapours present in the gas.

In the case of gases which contain oxygen, the primary product is probably ozone, and this, by interaction with substances like sulphur dioxide, ammonia, and hydrogen sulphide, gives rise to solid or liquid particles. The activity of ozone in the formation of slowly moving carriers has been examined in detail, and found to depend on the concentration both of the ozone and of the vapour with which the ozone reacts.

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* and *Zeitsch. anorg. Chem.*, 1911, **73**, 1—30.

Cathode rays give rise to a much smaller number of the slowly moving carriers, and it is supposed that these are not really due to the cathode rays, but to the action of the ultra-violet light which accompanies the cathode ray radiation.

In reference to the rapidly moving carriers, experiments are described which show that these are of larger dimensions than the gas molecules. Whatever the nature of the condensation process which is involved in the production of these carriers, it appears that the process takes place very rapidly, and may be considered complete after the lapse of a few tenths of a second. In this respect the condensation process differs from that resulting in the formation of the slowly moving carriers. H. M. D.

Ionisation of Gases by Canal Rays. R. SEELIGER (*Physikal. Zeitsch.*, 1911, **12**, 839—842).—Canal rays from a discharge tube were made to pass between the plates of a condenser arranged so as to measure the ionisation produced, and the rays were then collected by means of a cylindrical receiver which enabled the number of positively charged particles to be determined.

In hydrogen, at a pressure of 0·01 mm., the relationship between the saturation ionisation current and the positive charge acquired by the receiver indicates that n particles give rise to $n/3$ ions per cm. In oxygen the number of ions produced is about four times as large. For small variations of pressure the number of ions generated is proportional to the gas pressure, but is independent of the velocity of the canal rays as measured by the magnitude of the discharge potential. H. M. D.

Radioactive Ions. J. FRANCK and LISE MEITNER (*Ber. Deut. physikal. Ges.*, 1911, **13**, 671—675).—To test Wellisch's hypothesis, that ions in a mixture of gases retain their charge for only a short time and can pass it on from one kind of molecule to another, the mobility found experimentally being a mean of the mobilities of different charged molecules, experiments have been made with the positively charged recoil atoms of thorium-*D* expelled from the active deposit of thorium. Two brass tubes connected to the poles of a battery were fitted concentrically into a glass tube. The opposed ends of the brass tubes were covered with wire gauze; the one of which connected to the negative pole was made active in the thorium emanation before the experiment. A current of air or hydrogen was maintained through the tubes from the positive inactive to the negative active gauze, the recoiled atoms of thorium-*D* thus having to travel with the field against this gas stream. The mobility of the recoiled atoms could thus be deduced from the velocity of gas stream necessary to prevent the atoms reaching the negative gauze. The mobility in air was between 0·7 and 1·6 cm./sec. for unit *P.G.*, and in hydrogen greater than 5 cm./sec. These values are, within the error of experiment, the same as apply for other ions in these gases. This result is opposed to Wellisch's hypothesis, for the method would remove from the gas the recoiled atoms when they lost their charge, with the result that much smaller mobilities would be shown by these ions than has been found. F. S.

The Spontaneous Charging of Polonium. NORMAN CAMPBELL (*Physikal. Zeitsch.*, 1911, **12**, 870—871).—Hauser's views (this vol., ii, 685) relating to the part played by δ-rays in the spontaneous charging of a polonium plate are criticised. The assumption that the number of rays which leave the active plate when at a potential of $+E$ is equal to the number which have a kinetic energy greater than eE is unjustifiable. The data obtained in the investigation of the penetrating power of the rays permit also of an alternative explanation. According to this the primary δ-rays are completely absorbed by extremely thin layers, and the changes which are observed on increasing the thickness of these layers are due to the absorption of α-rays and the production of secondary δ-rays. H. M. D.

Application of the Content of Uranium and Lead of Some Minerals to the Determination of the Ages of the Rocks containing Them. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 131—138).—The author criticises the work of Strutt (Abstr., 1910, ii, 1023) and of Holmes (this vol., ii, 570) on the determination of the age of rocks by means of the ratio between the amounts of lead and uranium contained in them. The mean values deduced by Holmes for rocks of the Christiania district of Norway can have little significance, because the differences between the values calculated for different rocks (admittedly of the same formation) are very great; in fact, the calculated age of that deposit varies from 336 to 558 million years. The author has collected analytical data, due to Blomstrand and others, for a number of other minerals of the same formation, and from them deduces ages varying from 41 million years to 17,302 million years. Notably discordant results (935 to 1533 million years) are also obtained when different specimens of the same mineral (uraninite) from the formation in question are considered. The Norwegian formation is not exceptional, for similar irregularities are observed in the results from the deposits of gadolinite in Texas (mentioned by Boltwood) and for thorianite from Ceylon. Among the reasons for the inapplicability of this method for estimating geological time, the following are adduced: (1) Strutt's formula, if it is to lead to exact results, demands more precise determination of the ratio Pb/U than is possible at present; (2) most of the minerals hitherto examined have suffered far-reaching change since they first came into existence; (3) the method requires that the lead contained in the mineral shall have originated solely from the uranium; in that case the ratio Pb/U for minerals of the same formation should be constant, whereas Holmes found (in the case of the Christiania formation) that the ratio usually increases as the percentage of uranium diminishes. R. V. S.

The Intensity of the Earth's Penetrating Radiation at Different Altitudes and a Secondary Radiation Excited by It. J. C. McLennan and E. N. Macallum (*Phil. Mag.*, 1911, [vi], **22**, 639—646).—The intensity of the earth's penetrating radiation was compared, in a hermetically sealed zinc vessel of 30 litres capacity of 0·5 mm. wall-thickness, at different heights. On the ground at Toronto, 5·8 more ions per c.c. per second were produced than on the ice on Toronto Bay, and this was assumed to be the measure of the penetrating radiation. On a clock tower of the City Hall, 64 metres high, the difference was 2·8 ions per c.c. per second, so that at this height the rays are diminished to 48 per cent. This is in agreement with Eve's calculation (this vol., ii, 89). A secondary radiation due to the earth's penetrating radiation was observed from a high brick wall encircling the university lawn. It extended a distance of 14 or 15 metres, and thus corresponds with β-rays. This produces about 1·5 ions per c.c. per second. F. S.

Radioactivity of Certain Russian Mineral Springs. P. G. Mezernitzky (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, *Phys. Part*, 244—255).—The author has examined electrometrically a number of mineral waters from various parts of Russia, all of which exhibit radioactivity, some of them to a greater degree than the waters of Carlsbad, Marienbad, Nauheim, Gastein, etc. T. H. P.

Conductivities, Temperature-coefficients of Conductivity, and Dissociation of Certain Electrolytes. H. H. Hosford and Harry C. Jones (*Amer. Chem. J.*, 1911, **46**, 240—278. Compare Abstr., 1910, ii, 256).—The electrical conductivity of aqueous solutions of some fifteen inorganic salts has been measured at temperatures between 0° and 65° and at dilutions ranging from 2 to 4096 litres per mol. The salts examined include a number of alums and other double salts.

In agreement with previous results, it is found that the temperature-coefficients are generally much greater for the salts which form hydrated salts at the ordinary temperature than for those which separate out in the anhydrous form. In addition to the dehydration of hydrates, decrease in polymerisation is a probable cause of abnormally rapid increase in conductivity with rise of temperature, and there is evidence that sulphates are polymerised in concentrated solutions.

The data for solutions of the violet and green varieties of potassium and ammonium chromium sulphates show that the change from the violet to the green modification is accompanied by an increase in conductivity, the magnitude of which becomes smaller as the solutions become more dilute, and may become negative. This is attributed to the greater resistance of the green modification to the hydrolytic action of the solvent. Previous measurements at 25° have shown that the conductivities of double salts are less than the sum of the conductivities of the constituent salts. The same relationship holds at all temperatures from 0° to 65°, and the conductivity data show further that the dissociation of such double salts is but slightly affected by change of temperature. H. M. D.

Conductivity, Temperature-coefficients of Conductivity, and Dissociation of Certain Electrolytes in Aqueous Solution from 0° to 35°. Probable Inductive Action in Solution and Evidence for the Complexity of the Ion. L. G. WINSTON and HARRY C. JONES (*Amer. Chem. J.*, 1911, **46**, 368—413).—In continuation of earlier work (Jones and Hosford, preceding and earlier abstracts), determinations have been made, at temperatures from 0° to 35° and at various dilutions, of the electrical conductivity and dissociation of the following thirty salts: ammonium nitrate and sulphate, ammonium hydrogen sulphate, sodium sulphate, borax, potassium acetate and permanganate, dipotassium hydrogen phosphate, strontium acetate, magnesium bromide, nitrate, formate and acetate, cadmium chloride, bromide and iodide, lead chloride, aluminium chloride, nitrate and sulphate, chromium chloride and sulphate, manganous sulphate, silver nitrate, cobalt bromide, copper sulphate, uranyl chloride, nitrate, sulphate and acetate.

In general, the results obtained confirm those of the earlier experiments. It has been found that, in all cases, the conductivity increases with rise of temperature and with dilution. The temperature-coefficients, expressed in conductivity units, increase with rise of temperature, except in the case of ammonium hydrogen sulphate and uranyl sulphate, whilst when expressed as percentages they decrease in all cases. The more highly hydrated salts have large temperature-coefficients, and, from a consideration of these constants, the amount of hydration seems to be closely related to the water of crystallisation. At certain dilutions, cadmium iodide, chromium chloride, uranyl acetate, and silver nitrate show an increase in percentage dissociation as the temperature rises. Cadmium iodide and lead chloride, which have no water of crystallisation, have temperature-coefficients as large as those of highly hydrated salts, such as copper sulphate. These instances appear to be exceptions to the results obtained previously, and indicate that there must be some other factor operating which produces the same effect as hydration. It is considered probable that, in such cases, inductive action takes place through the solvent between charged ions and neutral molecules, and that this gives rise to the formation of complex molecules and ions in solution. E. G.

The Dielectric Constant of Certain Liquids at High Pressures. RUDOLF ORTVAY (*Ann. Physik*, 1911, [iv], **36**, 1—24).—The influence of pressure on the dielectric constant of ethyl ether, benzene, toluene, xylene, carbon disulphide, chloroform, paraffin, light petroleum, and castor oil has been measured for pressures up to 500 atmospheres. Nernst's method, in the differential form described by Philip, was employed in the measurements. In all cases, the dielectric constant increases with the pressure in such a way that it can be accurately represented by an equation of the form $Dp = D_1(1 + \alpha p + \beta p^2)$, in which α is positive and β negative. $\alpha \cdot 10^4$ varies from 2·187 for ethyl ether to 0·538 for paraffin, and $\beta \cdot 10^7$ from 0·714 for ethyl ether to 0·324 for paraffin.

In the case of benzene, toluene, and xylene, the variation of the dielectric constant with the pressure is nearly the same.

The value of $(D-1)v/(D+2)$, in which v represents the specific volume of the liquid, was found to diminish to the extent of 1·3% for ethyl ether and of 1·17% for benzene, when the pressure is raised from 1 to 500 atmospheres. H. M. D.

Chemico-physical Investigations on Animal Liquids. IV. Technique of the Electrometric Method for the Study of the Reaction of the Liquids of the Organism. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 107—111. Compare Abstr., 1908, ii, 869).—In the practical application of the electrometric method to the study of the reaction of organic liquids, an important difficulty is due to the diffusion potential which is set up between the liquid under examination and the standard liquid. The author has compared the results obtained by the two methods of overcoming this difficulty in use, namely, (1) the addition of an excess of a neutral electrolyte to both solutions; (2) the insertion of a concentrated solution of potassium chloride between the two liquids (compare Bjerrum, Abstr., 1905, ii, 793). His concentration cells were as follows respectively: H | serum | KCl(1·75 or 3·5N) | HCl (0·01N) | H, and H | serum | NaCl (0·125N) | HCl (0·01N) + NaCl (0·125N) | H. The results show a small difference of electromotive force amounting to about 0·0025 volt, that of the former cell being the greater. Reasons are adduced in favour of the second method being the more correct. R. V. S.

Normal Elements. P. J. H. VAN GINNEKEN and HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1911, **77**, 744—760).—A theoretical paper. In the first section the requirements of a satisfactory normal element are considered. The second section is mainly an extension of the views of Reinders (compare Abstr., 1902, ii, 639) on the application of the phase rule to a normal element, regarded as a system not in equilibrium. The general condition for a normal element is that it must be composed of two parts, both of which are in themselves invariant systems (as regards temperature and pressure) of the same components. G. S.

Transport Numbers and Molecular Complexity. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 124—129).—The author has worked out equations, based on Einstein's formula (compare Lorenz, Abstr., 1910, ii, 577), connecting transport numbers and molecular complexity, and proposes to employ them to determine the degree of polymerisation of certain electrolytes. R. V. S.

A Case of Electrolytic Saturation Current. GEORGE JAFFÉ (*Ann. Physik*, 1911, [iv], **36**, 25—48).—Measurements of the electric conductivity of solutions of lead oleate in hexane and light petroleum indicate that saturation currents can be obtained similar to those observed in the ionisation of gases. The conductivity apparatus consisted of a condenser with guard-ring and parallel electrodes, the distance between which could be varied. The applied potential differences were varied from 500 to 3000 volts per cm., and the current measured by means of a Curie piezo-quartz apparatus with a Dolezalek electrometer as null instrument. For potentials (e) greater than about 500 volts per cm. the current (i) can be represented by the equation $i = a + ce$, in which a and c are constants. Since a is relatively very large, it follows that the current is mainly carried by ions which are formed at such a slow rate that a condition of saturation is attained. The residual current (ce) is probably due to impurities which it is impossible to avoid entirely.

It is shown that the rates of formation and of re-combination of the ions of the lead oleate can be deduced from the experimental observations. Both processes are of the second order, and the degree of ionisation is therefore independent of the concentration of the salt. From experiments on the influence of temperature on the conductivity, it is found that the temperature-coefficient of the rate of formation of the ions is negative between 0° and room temperature, and then becomes positive as the temperature rises further.

Some observations relating to the conductivity of solutions of ethyl alcohol in light petroleum are also recorded. Under ordinary conditions, such solutions exhibit unipolarity, a negative temperature-coefficient, and an abnormally rapid increase of the current with increasing potential. This is found to be due to traces of impurities, for when carefully purified materials are employed, the anomalous phenomena disappear. H. M. D.

Magneto-optical Effects Exhibited by Chlorine and Iodine. A. HEURUNG (*Ann. Physik*, 1911, [iv], **36**, 153—176).—Two forms of apparatus are described by means of which the author has investigated the influence of a magnetic field on the optical behaviour of chlorine and iodine, both of which give a banded absorption spectrum. In the case of chlorine the rotation of the plane of polarisation was measured for wave-lengths varying from $\lambda = 518\mu\mu$ to $\lambda = 640\mu\mu$, but the data show no appreciable increase in rotation in the region of absorption. The behaviour of an absorption band towards a magnetic field appears therefore to be quite different from that of individual absorption lines.

From observations with iodine vapour between crossed nicols, it has been found that the application of a magnetic field gives rise to considerable illumination in the green part of the spectrum, and several new lines make their appearance. This magneto-optical effect could not be eliminated by rotation of the analysor or by the insertion of a quarter-wave plate, from which it appears that only a small portion of the light is polarised. The effect of the magnetic field on the individual absorption lines obtained by using a grating was also examined, but no change could be detected. Between crossed nicols, some of these lines become brighter when the field is applied, but the resulting light emission is not polarised to more than a small extent. H. M. D.

Adjustable Electric Signal Thermometer. FRANZ MICHEL (*Chem. Zeit.*, 1911, **35**, 1111).—An apparatus on the principle of Beckmann's thermometer, so arranged that electrical contact will be made at any pre-arranged temperature and an audible or visible signal thereon given. L. DE K.

Specific Heat of Water. ANDRÉ COTTY (*Ann. Chim. Phys.*, 1911, [viii], **24**, 282—288).—Determinations of the specific heat of water in a Bunsen calorimeter, provided with a special device for measuring the temperature of the water added, show that the specific heat is 1·0067 at 0°, diminishes to 0·9994 at 20°, and then rises to 1·005 at 35°. The specific heat at 15° is taken as unity. These figures agree closely with those of Bartoli and Stracciati (Abstr., 1893, ii, 443; 1895, ii, 5, 6). T. A. H.

Measurements of Specific Heat at Low Temperatures with the Copper Calorimeter. F. KOREF (*Ann. Physik*, 1911, [iv], **36**, 49—73).—The copper calorimeter described by Nernst and Lindemann (Abstr., 1910, ii, 263) has been employed for the measurement of the mean specific heats of a large number of substances over the temperature intervals −190° to −80° and −80° to 0°. It is shown that accurate results can be obtained by the author's method of operating, which is described in detail.

Data are recorded for aluminium, copper, zinc, lithium, sodium, potassium, boron, graphite, diamond, bromine, the halogen salts of sodium and potassium, calcium fluoride, oxide, hydroxide and carbonate, silver iodide, lead iodide, quartz and carbon disulphide. In addition, the latent heat of vaporisation of carbon disulphide was measured, the mean value obtained being 86·87 cals. The experimental data are finally discussed from the point of view of Nernst's heat theorem, and also in relation to the Planck-Einstein theory of energy quanta. H. M. D.

The Energy Content of Solid Substances. WALTHER NERNST (*Ann. Physik*, 1911, [iv], **36**, 395—439).—The chief results of the work described in this paper have been published previously (compare Abstr., 1910, ii, 263; this vol., ii, 368, 464, 466). The substances for which the energy content can be calculated with the aid of a single frequency number include both elements and compounds, the latter being such that the vibration frequencies of the component atoms are nearly equal. For other elements, such as sulphur and carbon (as graphite), and compounds like silica (quartz), lead chloride, silver chloride, mercurous chloride, silver iodide, and benzene, the use of two or more frequency numbers is necessary. These frequencies have been calculated in a number of cases, and from these the values of the energy content are derived and compared with the experimental values.

From the observed convergence of the atomic heats of solid crystalline and amorphous substances towards zero at very low temperatures, it follows that the conception of temperature ceases to have any meaning in respect of all those properties which are dependent on the average behaviour of the atoms. Such properties are, for example, energy content, volume, compressibility, and chemical potential, and since chemical potential is a measure of free energy, it appears that the author's heat theorem must be regarded as a special case of a more general principle.

On the basis of the knowledge furnished by this investigation of the variation of the energy content with the temperature, the way has been paved for the development of a theory of the solid state of aggregation which should allow of the deduction of the most important properties of solids in a simple manner. H. M. D.

Prevention of Bumping. H. Spurrier (*J. Amer. Chem. Soc.*, 1911, **33**, 1632—1633).—It is sometimes necessary, especially in soap and oil analyses, to remove alcohol from an aqueous solution which is covered with a layer of oil. In boiling such a liquid great inconvenience is caused by bumping. This difficulty can be overcome by introducing a piece of glass tube, open at both ends, into the vessel, one end of the tube being below, and the other above, the surface of the liquid. If a beaker is used, it should be covered whilst ebullition is proceeding, in order to prevent loss by the spurting of small quantities of the liquid up the tube. E. G.

A Simple Direct Electrical Method of Determining Heats of Vaporisation. Nicolai N. Nagornoff and L. Rotinjanz (*Zeitsch. physikal. Chem.*, 1911, **77**, 700—706).—The comparison method with electrical heating described by Marshall and Ramsay (compare Abstr., 1896, ii, 349) is employed. The arrangement used is described and figured, and the mode of working described in detail. The external glass mantle, a cylindrical vessel 6 cm. wide and 17 cm. long, is sealed on to a Liebig's condenser and is well insulated. The boiling vessel, a glass beaker 4 cm. wide and 11 cm. high, is filled with the liquid to be vaporised, and rests on narrow supports on the base of the outer vessel, which is closed by a well-ground stopper through which the wires conveying the current pass. For further details the original paper must be consulted.

It is shown that the results are in good agreement with those obtained by previous observers by the electrical method, but are rather higher than those obtained by the calorimetric method. The cause of this discrepancy has not been elucidated.

The heats of vaporisation of certain compounds, in calories per gram, are as follows: *cyclo*Hexane, 85·4; methyl*cyclo*hexane, 76·4; chloro*cyclo*hexane, 74·9; *cyclo*hexanol, 108·1; ethyl *n*-propyl ether, 82·7, and ethyl *iso*butyl ether, 74·9. The value of Trouton's constant for all the compounds examined is close to 21·0, except for *cyclo*hexanol, which, like other hydroxyl compounds, gives a much higher value (24·9). G. S.

Relation of Heat of Vaporisation to other Constants at the Boiling Temperature of Some Liquids at Atmospheric Pressure. Jack P. Montgomery (*Amer. Chem. J.*, 1911, **46**, 298—307).—For a number of non-associated liquids which yield normal vapours, certain relationships are shown to exist at the ordinary boiling point. For such normal liquids the heat of vaporisation is proportional to the volume of unit weight of the saturated vapour; it is also proportional to the square of the velocity of the molecules. The quantity of heat required to vaporise unit volume of such a liquid is proportional to the number of molecules in this volume and to the absolute temperature. In the case of isomeric substances the absolute boiling temperature is in many cases proportional to the density of the liquid at the boiling point. Finally, the absolute boiling temperature is directly proportional to the molecular weight and to the square-root of the number of atoms in the molecule, and inversely proportional to the relative size of the molecules as measured by the quantity b in van der Waals' equation.

From a consideration of these relationships, the conclusion is drawn that none of the heat of vaporisation is required for intra-molecular work, but that all the heat is used up in overcoming cohesion and in giving the molecules sufficient kinetic energy to balance the pressure of the surrounding atmosphere. H. M. D.

Molecular Attraction and the Properties of Liquids. RICHARD D. KLEEMAN (*Phil. Mag.*, 1911, [vi], **22**, 566—586. Compare this vol., ii, 257).—A theoretical paper in which various forms of the equations connecting the internal heat of vaporisation and the surface tension of liquids with the temperature, density, and the density of the saturated vapour are further discussed. H. M. D.

[Variation of Vapour Pressure with Temperature.] IVAR W. CEDERBERG (*Zeitsch. physikal. Chem.*, 1911, **77**, 707—718).—On the basis of considerations partly theoretical and partly experimental, the vapour-pressure formula: $A \log^2 p + B \log p + C = \theta_0/T - 1$ is deduced, where θ_0 is the critical temperature on the absolute scale, and A, B, and C are constants to be determined from the experimental data. In the form $\log p = [A' - (B'\theta_0)/T]^{\frac{1}{2}} - C'$, where A', B', and C' are new constants, this formula has been tested through a wide range of temperature from −10° upwards, and is found to represent the experimental results more satisfactorily than any other formula hitherto proposed. At very low temperatures, Nernst's well-known formula gives slightly better results. G. S.

Apparatus for Continuous Working in Fractional Distillations in a Vacuum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 30—35).—The apparatus carries two flasks as receivers, and is so constructed that either of them can be removed and replaced without altering the pressure inside the apparatus even momentarily, so that the distillation may be really continuous. R. V. S.

Heat of Combination of Acidic Oxides with Sodium Oxide. VII. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1911, [iv], **32**, 202—206. Compare Abstr., 1910, ii, 585, 828).—The heat changes involved in the action of sodium peroxide on copper, silver and gold, and the corresponding oxides have been determined. The results show that the higher oxides of these metals combine with sodium oxide with considerable development of heat to form compounds which are stable at high temperatures. The following data are recorded: $CuO + O + Na_2O = Na_2O,CuO_2 + 29500$ cal.; $2Ag + 2Na_2O_2 =$

$Na_2O,Ag_2O_2 + Na_2O + 6000$ cal.; $2Ag + O_2 + Na_2O = Na_2O,Ag_2O_2 + 44800$ cal.; $Ag_2O + O + Na_2O = Na_2O,Ag_2O_2 + 39400$ cal.; $2Ag + O = Ag_2O + 5400$ cal.; $2Au + 3Na_2O_2 = 3Na_2O,Au_2O_3 + 30400$ cal.; $Au_2O_3 + 3Na_2O = 3Na_2O,Au_2O_3 + 100900$ cal.; $2Au + 3O = Au_2O_3 - 12300$ cal. H. M. D.

Thermochemical Studies. IV. Diazo- and Azo-compounds. WOJCIECH SVENTOSLAVSKY (*Ber.*, 1911, **44**, 2429—2437.* Compare Abstr., 1910, ii, 588, 691).—The measurements already described (*loc. cit.*) have been repeated with improved methods, care being taken, in particular, to maintain the experimental room below 3°. The results are substantially as before, with the exception that the heat of neutralisation of benzenediazonium hydroxide is 11·68 cal. instead of 13·7 cal. The heats of neutralisation of *o*- and *p*-tolyldiazonium hydroxides are 12·06 cal. and 13 cal. respectively. The heat of formation of the normal diazo-salts when hydrolysis is almost completely absent is 6·85 cal. for diazobenzene and 5·34 cal. for *p*-diazotoluene. E. F. A.

Thermochemical Studies. V. Diazo- and Azo-compounds. Monoamines. WOJCIECH SVENTOSLAVSKY (*Ber.*, 1911, **44**, 2437—2445.† Compare Abstr., 1910, ii, 588, 691).—The heats of diazotisation of a number of mono- and di-amines have been determined by the methods already described (*loc. cit.*). The heat of diazotisation of the NH_2 group varies slightly with the constitution of the amine; it depends on three factors, the heat of neutralisation of the diazonium compound, the true heat of diazotisation, and the heat of salt formation of the amine. The introduction of a methyl group in the ortho-position increases the magnitude of the first two factors. The heats of diazotisation of benzidine and dianisidine are less than those of aniline and *o*-toluidine; this is probably due to the influence of the adjoining phenyl radicles on the basic nature of the diazonium base. The heat of formation of the diazo-salt is greater for derivatives of benzidine and dianisidine than for diazobenzene and its homologues. The heat of combination of the diazo-compounds with *β*-naphthol is more nearly a constant, but a correction must be applied for the difference between the heat of neutralisation of the diazonium hydroxide and of sodium hydroxide. E. F. A.

Pyknometer for Density Determinations. LUDWIG VON KREYBIG (*Chem. Zeit.*, 1911, **35**, 1120).—The determination of the density of viscous liquids is often accompanied by difficulties caused by the liquid adhering to the parts of the pyknometer above the mark, etc. The pyknometer devised by the author consists of a small flask fitted with a stop-cock in the lower part of the neck. The bore of the stop-cock is very wide, and there are two holes of the same width in the neck of the flask where the stopper fits. In making a density determination, the flask is filled with the viscous liquid, the stop-cock connecting with the body of the flask and the neck. When the temperature is constant, the stopper is turned through 90°, and any liquid in the neck and bore of the stopper is removed by means of a volatile solvent, after which the weighing can be made. The results are trustworthy to the fourth decimal place. T. S. P.

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* and *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1060—1075.

† and *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1076—1083.

Volume Changes in the Formation of Solutions. HERMANN WOLFF (*Ann. Physik*, 1911, [iv], **36**, 177—182).—From a consideration of the free energy changes, the author deduces a relationship between the differential volume effects which accompany the absorption of small quantities of water or alcohol by a given mixture of these two substances. Available data are insufficient to test the validity of the differential equation. H. M. D.

Viscosity and Fluidity of Suspensions of Finely-divided Solids in Liquids. EUGENE C. BINGHAM and T. C. DURHAM (*Amer. Chem. J.*, 1911, **46**, 278—279. Compare this vol., ii, 372).—The viscosity of suspensions of infusorial earth, china clay, and graphite ("Aquadag") in water and ethyl alcohol has been measured at different temperatures by means of an Ostwald viscometer having a capillary of relatively large diameter and about 40 cm. long. The fluidity decreases rapidly as the proportion of the suspended solid increases, the decrease being directly proportional to the volume concentration of the solid. By extrapolation of the fluidity concentration curves it is found that the fluidity becomes zero at a definite concentration which is independent of the temperature and of the dimensions of the particular apparatus used in the viscosity determinations. The volume concentration corresponding with zero fluidity varies with the nature of the solid suspension, and when the same solid is suspended in different liquids the zero fluidity concentrations are not necessarily the same.

The fluidity of solid suspensions in water is altered considerably when small quantities of electrolytes are added, hydrogen and hydroxyl ions having a specially large influence.

Incidentally, attention is drawn to the considerable errors which frequently occur in the use of Ostwald viscometers as a consequence of the neglect to take into account the kinetic energy imparted to the liquid in its motion through the capillary. H. M. D.

The Viscosity of Binary Liquid Mixtures in the Neighbourhood of the Critical Dissolution Temperature. PAUL DRAPIER (*Bull. Acad. roy. Belg.*, 1911, 621—640).—Measurements of the viscosity of *cyclo*hexane, nitrobenzene, aniline and *n*-hexane, and of various mixtures of the first pair and the last pair of liquids have been made at a series of temperatures in the neighbourhood of the respective critical dissolution temperature.

In the case of the pure liquids, the fluidity diminishes with rise of temperature according to the equation $\phi = a + b(t - 20^\circ)$. Mixtures exhibit a similar relationship at temperatures much higher than the critical dissolution temperature, but as this temperature is approached, the fluidity temperature curves show marked deviations and become concave to the temperature axis.

The fluidity of the two series of binary mixtures can be additively represented in terms of the fluidities of the components if the temperature is sufficiently removed from the critical, but in the neighbourhood of this dissolution temperature the isothermal fluidity concentration curves deviate considerably from the requirements of the additive law. The observed variations in viscosity are supposed to be connected with certain changes in the liquid which give rise to the phenomenon of opalescence, and in this connexion reference is made to the possibility of explaining the viscosity relationships on the basis of the views of Donnan and of Smoluchowski. H. M. D.

Adsorption of Solutions. II. Gerhard C. Schmidt (*Zeitsch. physikal. Chem.*, 1911, **77**, 641—660).—In a previous paper (Abstr., 1910, ii, 1041) a formula was proposed which represents satisfactorily the adsorption by charcoal of acetic acid from aqueous solution through a considerable range of concentration. For still greater variations of concentration, however, the formula is not valid, nor does it express the fact that adsorption is an equilibrium phenomenon. Regarding the amount of adsorption as determined by equilibrium between the adsorbing force and the solution pressure, the formula $[(a-x)S]/v=Kxe^{A(S-x)S}$ is deduced, in which x represents the amount adsorbed, a the amount of solute originally present, v the volume, S the maximum amount adsorbed, and A and K are constants. The formula represents the results satisfactorily when the concentration of the charcoal is varied in the ratio 1 : 8, and that of the acetic acid in the ratio 1 : 3000.

The objections raised by Marc (compare this vol., ii, 258) to the author's theory are not valid. In particular, there is no evidence of discontinuity in the adsorption curve of acetic acid by charcoal, as suggested by Marc. G. S.

Anomalous Adsorption. Alfred Lottermoser (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 135—136).—The occurrence of maximum adsorption at a particular concentration, which was observed by Biltz (Abstr., 1910, ii, 830) in the adsorption of certain colouring matters, has also been found by the author in the adsorption of potassium iodide from aqueous solution by silver iodide. This anomalous behaviour is found to be due to an increase in the size of the silver iodide particles under the influence of the potassium iodide solution. The solvent action of the more dilute solutions and the precipitation which accompanies increase in concentration lead to the formation of a more dense and apparently crystalline modification from the originally amorphous silver iodide. H. M. D.

Diffusion of Electrolytes in Colloids. Luigi Rolla (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 47—51).—The author has worked out a method for determining the coefficient of diffusion, k^2, in Fourier's equation: $\partial c/\partial t=k^2.\partial^2 c/\partial t^2$ by measurement of the time elapsing before the maximum electromotive force is attained between two electrodes immersed in gelatin into which an electrolyte is allowed to diffuse. The arrangement employed consists of a glass tube containing two parallel, plane, circular, silver disks, which are perforated with many small holes. The tube is filled with pure gelatin in such a manner that the surface of the gel at the bottom of the tube is plane and parallel to the electrodes. A solution of the electrolyte (potassium chloride, sodium chloride) is circulated past this gelatin surface for a short time; pure water is then substituted for the electrolyte (so that the concentration on the external surface of the gelatin is zero), and the time required for the electromotive force to reach a maximum is observed. The results agree well with those obtained by other methods. R. V. S.

Aggregation and Crystallisation of Water in Connexion with the Physical Condition of Substances. I. SKWORZOFF (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 107—112).—Observations relating to the formation and liquefaction of ice crystals are described which lead the author to the conclusion that liquid water must be regarded as having a definite molecular structure ("latent crystalloid structure") and not as a chaotic aggregation of molecules, as is usually assumed. In reference to this view, the physical properties of water in the different states of aggregation are examined in some detail. H. M. D.

Isomerism and Polymorphism. HANS STOBBE (*Ber.*, 1911, 44, 2732—2735).—The author's views (Abstr., 1910, i, 623) having been misunderstood by Biilmann (this vol., i, 367), the former discusses them again.

Where in two substances having the same empirical composition the atoms are differently arranged in dissimilar molecules, the substances are isomeric chemical compounds, but where identical molecules are differently grouped in dissimilar crystals, the substances are two forms of presentation (Erscheinungsformen), two species (Gattungen) or modifications of a single polymorphous chemical compound. Where the two substances are isomerides, their differences are present, not only in the crystalline form, but also in the dissolved and fused states. With the two modifications of a single chemical compound, however, the two solutions are identical, as also are the two fused masses. On these assumptions, the limits between isomerism and polymorphism are sharply drawn, and there is no limiting region, such as Biilmann imagines from the author's previous considerations.

To determine which of these two cases exists in a particular instance often presents considerable practical difficulties, especially when the two individuals either have closely approximating physical constants or show a high velocity of transformation. The author regards calcspar and aragonite as two modifications of dimorphous calcium carbonate; rutile, anatase, and brookite as three modifications of trimorphous titanium oxide, and the four crystallographically different monochloroacetic acids as modifications of a single tetramorphous acid, and so on; and, in general, he regards such chemical compounds as polymorphous so long as there is no certain proof of the existence of two chemically different calcium carbonates, etc. He regards it as beyond doubt, however, that improved methods will in some cases result in compounds at present looked on as modifications of "one" dimorphous chemical substance being considered later as "two" truly isomeric compounds (compare Schaum, Abstr., 1910, i, 391). T. H. P.

Colloidal Chemistry of Histological Silver Staining. RAPHAEL E. LIESEGANG (*Koll. Chem. Beihefte*, 1911, 3, 1—46).—Cajal's method of staining nerve tissue by means of a silver solution has been examined from the colloido-chemical point of view, and the conditions are formulated which must be observed in order to ensure satisfactory preparations. A comparison is made between the various phases of the staining process and those involved in the development, toning, and fixing of a photographic plate. H. M. D.

The Significance of the Degree of Dispersity in the Investigation of the General Properties of Sulphur Hydrosols. SVEN ODÉN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 100—106).—Methods of preparing sulphur hydrosols are described which yield particles of approximately uniform size. With these hydrosol preparations, experiments have been made to test the validity of Svedberg's equation: $S = e^{k(t-t_0)}$, in which S represents the percentage concentration of the colloidal sulphur, t the temperature of the solution, k and t_0 constants which depend on the degree of dispersity of the hydrosol and the concentration of electrolyte in the solution (compare Abstr., 1909, ii, 309). For a given degree of dispersity, k is nearly independent of the concentration of the electrolyte (sodium chloride), whilst t_0 increases with the quantity of the coagulant. For a given salt concentration, k and t_0 diminish as the degree of dispersity of the hydrosol increases, the rate of diminution of t_0 being much greater than that of k. The addition of acids in small quantities reduces the value of t_0, whilst k remains unchanged. The validity of the exponential equation may be employed as a means of testing the uniformity of size of the particles of hydrosol. When particles of different sizes are present, this equation is incapable of representing the dependence of the equilibrium between the coagulum and the solution on the temperature.

The influence of temperature on the equilibrium which results when unequally granulated hydrosols are coagulated and of the degree of dispersity on the salt-fixing capacity of the coagulum are also discussed.
H. M. D.

Coagulation of Copper Ferrocyanide. NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 136—138).—A chemically pure colloidal solution of copper ferrocyanide can be obtained by prolonged dialysis of the solution obtained in the interaction of copper chloride or sulphate and sodium ferrocyanide in equivalent proportions. The influence of various electrolytes on the coagulation of the negatively-charged colloidal particles has been examined in some detail. These experiments show that coagulation is determined by the cations, the nature of the anion having little influence on the coagulating power of the electrolytes. For cations of different valency this coagulating power increases with the magnitude of the electric charge. In the case of the alkali metals, it increases with increasing atomic weight and with increasing velocity of diffusion of the cation. H. M. D.

Plasticity, Especially of Barium Sulphate. PAUL EHRENBERG (*Zeitsch. angew. Chem.*, 1911, **24**, 1957—1958).—Polemical against Atterberg (this vol., ii, 605), the author especially combating his views on the cause of plasticity. T. S. P.

Formation of Layers in Heterogeneous Systems. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 97—100).—If a system consisting of two different kinds of particles is acted on by an external force, which causes the two sets of particles to move with uniform speed, but with different velocities, a simple graphical consideration indicates that this motion must result in the setting up of a series of alternating strata. The stratification which is found when insoluble substances are formed as the result of the action of an aqueous solution of one substance on a solid jelly containing the second reacting component, can be explained satisfactorily by reference to the velocities of the reacting molecules or ions. The view that this stratification is due to the formation of supersaturated solutions is considered to be very improbable. H. M. D.

General Integrals of Chemical Kinetics. FERENCZ JÜTTNER (*Zeitsch. physikal. Chem.*, 1911, **77**, 735—743).—The integrals for the differential equation expressing the rate of reversible reactions are obtained, and certain deductions regarding the integrals of irreversible reactions and regarding chemical equilibria are given. G. S.

Equilibria in the Precipitation of Lead Carbonate. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1911, **72**, 106—108).—Sodium carbonate solution has been shaken with several sparingly soluble lead salts at 25°, and the equilibrium determined by analysis. Equilibrium constants are obtained for the bromide, chloride, and sulphate. C. H. D.

Reduction of Mercuric Chloride by Phosphorous Acid and the Law of Mass Action. JAMES B. GARNER, JOHN E. FOGLESONG, and ROGER WILSON (*Amer. Chem. J.*, 1911, **46**, 361—368).—It has been observed that the action of phosphorous acid on mercuric chloride proceeds very slowly in dilute aqueous solutions at the ordinary temperature. It was, therefore, considered of interest to determine the extent of the reaction, the effect of different temperatures and concentrations, and the order of the reaction.

The results have shown that at 25° and 30°, and at various concentrations, the reaction takes place in accordance with the equation: $2HgCl_2 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2HgCl + 2HCl$. There is no equilibrium point, but the reaction proceeds to completion. It is demonstrated that the reaction is of the fourth order, and its velocity constant is therefore expressed by the equation:

$$K = 1/3t[1/(a-x)^3 - 1/a^3].$$

E. G.

The Composition of Solid Phases in Four Component Systems. James M. Bell (*J. Physical Chem.*, 1911, **15**, 580—586. Compare Schreinemakers, Abstr., 1909, ii, 559).—Four component systems are qualitatively represented by a tetrahedral diagram in perspective. For quantitative purposes the space diagram must be projected on to two of the faces of the tetrahedron. For this purpose orthogonal projection and projection by lines parallel to one edge of the tetrahedron have been employed. The author discusses a method of "perspective" projection in which the lines radiate from the apex of the tetrahedron to project the curve on the base. The method, which is illustrated by reference to the system

H_2O–NaCl–$BaCl_2$–$CuCl_2$,

is more complicated than parallel projections. R. J. C.

The Thermal Analysis of Quaternary Systems. Nicola Parravano and G. Sirovich (*Atti. R. Accad. Lincei*, 1911, [v], **20**, ii, 206—211).—The tetrahedral method of representation may be used for quaternary systems, each face representing one of the component ternary systems. The course of the eutectic lines and planes is traced in the simple case in which neither compounds nor solid solutions are formed. In the thermal analysis of such systems, mixtures may be so chosen as to lie on a plane passing through one edge of the tetrahedron and a given point, and the isothermals are then drawn on the isosceles triangle thus obtained. It is shown how these curves are utilised for the construction of the isothermal surfaces in the space-model. C. H. D.

Rates of Solution of Certain Metals in Dissolved Iodine and their Relation to the Diffusion Theory. Ralph G. Van Name and Rowland S. Bosworth (*Amer. J. Sci.*, 1911, [iv], **32**, 207—224. Compare Abstr., 1910, ii, 280).—Further measurements of the rates of dissolution of metals in aqueous solution of iodine containing dissolved iodides have been made, and these show that iron, cobalt, and nickel dissolve at the same rate as was previously found for cadmium, zinc, mercury, copper, and silver. From experiments with disks of cadmium, it is found that the rate of dissolution remains practically constant on the addition of sulphuric acid to the solution provided the acidity does not exceed $0{\cdot}1N$; when the acidity is further increased, the rate of dissolution diminishes. The rate at which cadmium dissolves is also dependent to a small extent on the nature of the dissolved iodide, and from the data for solutions containing potassium, cadmium, sodium, hydrogen, barium, lithium, magnesium, and calcium iodides, it appears that the velocity constants roughly correspond with what would be expected from the probable rates of diffusion of the corresponding tri-iodides.

Tin and magnesium dissolve more quickly than the other metals investigated. In the case of tin, this is supposed to be due to the primary formation of a stannous salt and the removal of iodine by the subsequent oxidation which occurs. The high velocity in the case of magnesium is probably due to the disturbing action of hydrogen bubbles which are evolved at the surface of the metal.

The results obtained are considered to support the view of Nernst that such dissolution processes are primarily determined by rates of diffusion. H. M. D.

The Velocity of Hydration of Metaphosphoric Acid. I. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1911, **72**, 85—88. Compare Abstr., 1910, ii, 607, 951; this vol., ii, 107).—The velocity of hydration of metaphosphoric acid increases with the concentration of the aqueous solution in a linear manner, indicating that the hydration is accelerated by the metaphosphoric acid itself, and not by the hydrogen ions. C. H. D.

Course of the Intramolecular Transformations between *iso*Butyl and *tert.*-Butyl Bromides, and the Catalytic Actions Thereby Coming into Play. ROGER F. BRUNEL (*Annalen*, 1911, **384**, 245—271. Compare this vol., i, 413).—In furtherance of his object of ascertaining the change of free energy in reactions between organic compounds of comparatively simple structure, the author has determined the amounts of *iso*- and of *tert.*-butyl bromides existing in equilibrium at a high temperature (*loc. cit.*). The change of free energy, however, cannot be calculated from this equilibrium ratio without a knowledge of the course of the dissociation of the bromides into olefine and hydrogen bromide. Michael and Leupold (this vol., i, 250), amongst others, have examined this dissociation, and, stating it to be independent of the presence of catalysts, have introduced the conception of "static equilibrium" to explain their results. According to the author, this conception is unnecessary, since the dissociation of the bromides is not independent of the presence of catalysts. The apparatus used is described and figured. It is found that the velocity of dissociation of both bromides in the gaseous state, particularly that of *iso*butyl bromide, is largely influenced by the degree of cleanliness of the walls of the vessel, and also by the presence of the liquid phase. The presence of the liquid phase also influences, although to a smaller extent, the velocity of the intramolecular transformation of the one bromide into the other. In no case has the intramolecular transformation been observed without accompanying dissociation, and the author is of opinion that the dissociation is an essential intermediate stage of the transformation. C. S.

Velocity of Racemisation. WALTER HERZ (*Chem. Zentr.*, 1911, ii, 67; from *Jahresber. Schles. Ges. vaterland. Kult.*, 1911, reprint).—The rate of change of the optical rotation of hyoscyamine and scopolamine in the presence of bases was measured by Gadamer (compare Abstr., 1901, i, 605). The present author now shows that the rate at which racemisation occurs in these reactions is represented by the equation $kt = \log_e[a/(a-2x)]$, where a represents the initial concentration, and x the amount changed. The racemisation constant of hyoscyamine at 5° is for sodium hydroxide, $6{\cdot}5 \times 10^{-3}$, for tropine, $1{\cdot}9 \times 10^{-2}$; the constant of scopolamine at 2—4° is for sodium hydroxide, 0·77, for tropine, $1{\cdot}9 \times 10^{-2}$. This method may be used for the measurement of hydroxyl ion concentrations. G. S.

New Distillation Flask. ALFRED DAHLE (*Chem. Zeit.*, 1911, **35**, 1027).—A flask which is suitable for use in the distillation of fatty acids under reduced pressure is described. The neck of the flask is closed by a rubber stopper through which passes a glass tube, the lower end of which is widened out so as to nearly touch the neck of the flask. A capillary tube is fitted down the centre of this glass tube, whilst a side-tube on the neck of the flask carries a thermometer, and is provided with a second side-tube which is connected with the condenser. W. P. S.

Gas Generation Apparatus. GEORG PREUSS (*Chem. Zeit.*, 1911, **35**, 1131).—A modified Kipp's apparatus provided with extra large tubulures into which are ground wash-flasks. By the usual groove and hole arrangement these also serve as taps. L. DE K.

Tap for Hydrogen Sulphide Apparatus. JAMES H. WALTON, jun. (*J. Amer. Chem. Soc.*, 1911, **33**, 1586—1587).—A special form of tap is described, which cannot be left open by the student. It consists essentially of a strong spring pinch-clip which is fastened on to a board and closes the thick-walled rubber tube through which the gas is delivered. The clip is opened by pressing an iron lever, and on releasing the lever the supply is instantly cut off. The rate of flow is regulated by a screw pinch-cock situated at a higher point on the rubber tube. It is advisable to enclose the tap in a box, so that the student has access only to the end of the lever and about two inches of the end of the rubber tube. E. G.

An Extraction Apparatus. WALTER L. HALLE (*Biochem. Zeitsch.*, 1911, **36**, 245—247).—The apparatus, which is figured, is constructed of metal, and is capable of containing 2 kg. of material. It is of the ordinary Soxhlet pattern, but with two special features. About half way up the ascending limb of the syphon there is an additional tube with a tap. If the latter is opened, the liquid in the extractor will syphon off when it is only half full. On the descending limb of the syphon, near the bottom, there is another tube and tap; by opening the latter and fixing a tube to a condensor, the organic solvent can be distilled off. S. B. S.

Extraction Apparatus which Prevents the Formation of Emulsions. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1911, **16**, 382—383).—When a liquid is extracted with an immiscible solvent, the emulsion which is liable to form may be prevented by the use of a separating funnel, from which the air may be exhausted before the liquid and solvent are shaken together. The stopper of the tube is pierced with a hole, which, by rotating the stopper, may be placed in connexion with a small side-tube on the neck of the funnel; the air is exhausted from the funnel through this side-tube, the stopper is turned so as to close the funnel, the contents of the latter are shaken, and should any trace of emulsion result, this may be broken down by allowing air to enter the funnel suddenly. W. P. S.

Rapid Filtering Funnel. H. Spurrier (*J. Amer. Chem. Soc.*, 1911, 33, 1584—1585).—The rate of filtration from an ordinary funnel can be increased to about two and a-half times the normal rate by etching deep lines extending from the apex of the funnel to points about two-thirds of the way up the sides. The grooves are not large enough to allow a filter paper to be broken by the stream from a wash-bottle, but are sufficiently wide for the filtrate to flow down. Such funnels are particularly useful for filtering gelatinous precipitates.

E. G.

Automatic Filter. Marston L. Hamlin (*J. Amer. Chem. Soc.*, 1911, 33, 1584).—The apparatus described is designed for the filtration of large quantities of liquid containing a precipitate of such a character as to be capable of passing readily through the stem of a separating funnel. It has been used in filtering barium carbonate from large amounts of solution in the preparation of inositol.

A large separating funnel is placed on a ring-stand over an ordinary funnel containing a folded filter-paper, the lower end of the stem of the separating funnel being slightly above the apex of the paper. A tube passes through a rubber stopper in the neck of the separating funnel, and is led down so that its lower end is at the level at which it is desired to maintain the liquid in the lower funnel. The liquid is placed in the separating funnel, the stopper inserted, and the stop-cock opened. The solution then runs into the lower funnel until it reaches the tube, and thus prevents the admission of air to the upper vessel. When the level in the lower funnel has fallen sufficiently, a small amount of liquid is siphoned over into the separating funnel and the lower one fills up again. E. G.

Method of Filling Reagent Bottles. James H. Walton, jun. (*J. Amer. Chem. Soc.*, 1911, 33, 1585—1586).—In order to enable students to fill their own reagent bottles with concentrated acids or other reagents without having to handle heavy bottles, a method has been devised by which the reagents are forced from the bottles by means of air-pressure. The bottles are placed on a table, two feet above which runs a pipe connected with the source of air-pressure. From this pipe valves are suspended by means of rubber tubing which fit into funnels which with delivery tubes are inserted through the stoppers of the bottles. The construction of these valves is described with the aid of a diagram. In the case of carboys, it has been found that the pressure required to force out the liquid is sufficient to drive out the stopper from the neck of the carboy, and a special arrangement has therefore been devised to prevent this. E. G.

Lecture Experiment: The Fermentation of Pyruvic and Oxalacetic Acids. Carl Neuberg and Laszló Karczag (*Ber.*, 1911, 44, 2477—2479).—An application of the method already given (this vol., ii, 320, 520). W. J. Y.

Inorganic Chemistry.

Isomeric Inorganic Compounds. Adolph Law Voge (*J. Amer. Chem. Soc.*, 1911, **33**, 1563—1566).—During the compilation of an index of inorganic compounds according to their condensed formulæ, several new instances of isomerism and polymerism were observed. A list of these is now given, together with references to the papers in which the compounds are described. E. G.

Atomic Weight of Hydrogen. Gustave D. Hinrichs (*Rev. gen. Chim. pure Appl.*, 1910, **13**, 351—354).—A review of the various determinations of the atomic weight of hydrogen which have been carried out since the time of Berzelius; the author considers that from the most trustworthy results the atomic weight of hydrogen must be 1·0078 ($O=16$). F. M. G. M.

The Sand-Filtration and Precipitation of Chalk Waters. A. T. Nankivell (*J. Hygiene*, 1911, **11**, 235—258).—The ordinary submerged sand-filter bed is unsuitable for the purification of chalk waters. It removes micro-organisms, but favours the growth of algæ and other organisms. It can be made effective by the deposition of aluminium hydroxide on the surface of the sand, and it is best to exclude the light. The Porter Clark process is not only efficient for softening chalk waters, and also is an efficient steriliser; it is more effective than filtration through sand and aluminium hydroxide. W. D. H.

Amorphous Sulphur. VII. Freezing-point Curves of Liquid Sulphur on Separation of "Nacreous Sulphur" and Rhombic Sulphur Respectively. Alexander Smith and Charles M. Carson (*Zeitsch. physikal. Chem.*, 1911, **77**, 661—676. Compare Abstr., 1903, ii, 139, 284; 1905, ii, 382, 580; 1906, ii, 157).—As there is no general agreement regarding the nomenclature of the different modifications of sulphur, the authors suggest the adoption of the symbols used by Muthmann. According to this, rhombic sulphur is represented by the symbol S_{I}, prismatic sulphur by S_{II}, the nacreous modification discovered by Gernez as S_{III}, and a fourth very labile monosymmetric modification (not further referred to in the paper) as S_{IV}. For mobile and viscous liquid sulphur the symbols S_λ and S_μ, which have met with general acceptance, are retained.

S_{III} can readily be obtained in lustrous, needle-shaped crystals by heating sulphur to a temperature exceeding 150°, then keeping at 98°, crystallisation being initiated by rubbing the inside of the tube with a glass rod.

For each of these modifications there is a freezing-point curve, depending on the relative proportions of S_λ and S_μ in the liquid with which the respective solids are in equilibrium. The respective freezing points when no S_μ is present are known as "ideal" freezing points, and are obtained by extrapolation. The ideal freezing point of S_I is

119·25°, of S_{II} 112·8°, and of S_{III} 106·8°. The "natural" freezing point of S_I is 114·5° (3·6% of S_μ), of S_{II} 110·2° (3·4% of S_μ), and of S_{III} 103·4° (3·1% of S_μ).

From the heat of fusion of monoclinic sulphur, as determined by Lewis and Randall (this vol., ii, 371), and the depression of the freezing point of S_λ due to S_μ, the conclusion is drawn that the formula of S_μ is S_6, which agrees with the vapour density determinations of Preuner and Schupp (compare Abstr., 1910, ii, 118).

With regard to some criticisms of Wigand (this vol., ii, 878) on the exact temperature of the equilibrium $S_\lambda \longrightarrow S_{II}$, the authors maintain the accuracy of their previous results. G. S.

Metallographic and Photochemical Studies of the System Sulphur–Tellurium. MASUMI CHIKASHIGÉ (*Zeitsch. anorg. Chem.*, 1911, **72**, 109—118 *).—Thermal analysis shows that sulphur and tellurium do not form a compound. Two series of solid solutions are formed, of very limited concentration, and the eutectic point lies at 109° and 7% Te (compare also Pellini, Abstr., 1909, ii, 726; Jaeger, *ibid.*, 1910, ii, 497). The transformation temperatures of sulphur at 400° and at 96·5° are lowered by tellurium. Whilst β-S holds 2% Te in solid solution, α-S retains only 0·5%, but the separation of the excess only takes place under the influence of light. Molten β-S dissolves 10% Te, and molten γ-S 20% Te. The precipitate obtained from solutions of tellurous acid and hydrogen sulphide, formerly supposed to be a compound TeS_2, is a mixture.

The solid solutions containing less than 0·5% Te are not sensitive to light. They include the Japanese red sulphur. The supersaturated crystals, containing from 0·5 to 2% Te, change from red to yellow or brown when exposed to light, the most active rays being $\lambda = 4500$. The decomposed portions are more readily dissolved by carbon disulphide than the original crystals. C. H. D.

Oxidation of Hydrazoic Acid [Azoimide]. HAROLD EATON RIEGGER (*J. Amer. Chem. Soc.*, 1911, **33**, 1569—1576).—It has been shown by Browne and Shetterly (Abstr., 1909, ii, 658) that azoimide is produced in varying amounts by the oxidation of hydrazine in acid solution with different oxidising agents. Thiele (Abstr., 1908, ii, 940) has suggested that the lowness of the yields of azoimide obtained in this way by the action of certain oxidising agents is due to the ease with which azoimide itself undergoes oxidation. In order to test this hypothesis, experiments have now been made to ascertain the extent to which azoimide is oxidised in aqueous solution under conditions similar to those prevailing in the work on the oxidation of hydrazine.

The oxidising agents employed were (1) hydrogen peroxide, potassium chlorate, and potassium persulphate, which were found by Browne and Shetterly to oxidise hydrazine with formation of considerable amounts of azoimide; (2) potassium permanganate, manganese dioxide, and ferric oxide, which give but small quantities of azoimide under the same conditions; and (3) potassium iodate, which yields little or no azoimide.

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* and *Mem. Coll. Sci. Eng. Kyoto*, 1911, **3**, 197—210.

It has been found that of the reagents of the first class, hydrogen peroxide does not oxidise azoimide to an appreciable extent, potassium chlorate exerts a slight oxidising action, and potassium persulphate effects considerable oxidation. Of the oxidising agents belonging to the second class, potassium permanganate oxidises azoimide vigorously, manganese dioxide but slightly, and ferric oxide not appreciably. Potassium iodate does not oxidise the compound at all.

It is evident, therefore, that of the seven oxidising agents studied, only two, hydrogen peroxide and potassium permanganate, behave consistently with Thiele's explanation. A more satisfactory explanation is that proposed by Browne and Shetterly (*loc. cit.*), namely, that intermediate condensation products are formed during the oxidation, and that these decompose in different ways. E. G.

Theory of Silicates. FELIX SINGER (*Sprechsaal*, 1911, **44**, 52—54, 69—72).—A theoretical paper in which the author expresses his views on the constitution of some derivatives of felspar and other complex silicates, demonstrating the same by numerous graphic formulæ. The work of Pukall (Abstr., 1910, ii, 780), Thugutt, and Moroziewiecz is also discussed. F. M. G. M.

Preparation of Colourless Alcoholic Potassium Hydroxide. HANS MALFATTI (*Zeitsch. anal. Chem.*, 1911, **50**, 692).—Potassium hydroxide is rubbed in a mortar with fully an equal amount of calcium oxide, a little alcohol being added to prevent irritating dust. The paste thus obtained is transferred by means of alcohol to a flask, which is then filled with alcohol. After frequent shaking, the liquid is allowed to clear and then siphoned off.

This solution keeps colourless for years, even in presence of air. The author attributes this to the fact that the treatment with calcium oxide removes traces of colloidal metals (copper and iron, for instance), which, as shown experimentally, may be the cause of the darkening of the solution. L. DE K.

Double Salts Formed between Sparingly Soluble Sulphates and Alkali Sulphates. MAURICE BARRE (*Ann. Chim. Phys.*, 1911, [viii], **24**, 145—256. Compare Abstr., 1909, ii, 667, 733; 1910, ii, 710, 718, 781; this vol., ii, 42).—The results now given have been recorded previously in part (*loc. cit.*). The first portion of the paper is devoted to a study of the range of existence of the double salts of calcium, strontium, and lead with those of the alkali metals and ammonium. In the second portion a similar study is made of the double sulphates of (1) thorium and (2) cerium and lanthanum with the alkali metals, and a number of new compounds of this type are described in greater detail than before (*loc. cit.*). The solubilities of silver and mercurous sulphates in alkali sulphate solutions are also discussed.

At atmospheric temperature, and when less than 2·8% of potassium sulphate is in solution, no double salt is produced with calcium sulphate, but with more potassium sulphate, syngenite,

$$K_2SO_4,CaSO_4,H_2O,$$

is formed. This begins to be replaced at temperatures above 31·8° by the compound $K_2SO_4,5CaSO_4,H_2O$ (van't Hoff and others, Abstr., 1904, ii, 561; 1905, ii, 319). With ammonium sulphate the compound $(NH_4)_2SO_4,CaSO_4,H_2O$ is alone stable at the lower temperatures; at 17° this begins to be transformed into $(NH_4)_2SO_4,5CaSO_4,H_2O$, and the latter gives place completely to $(NH_4)_2SO_4,2CaSO_4$ at 110°. The first begins to be transformed into the third directly at 76°. With sodium sulphate, sodium-syngenite, $Na_2SO_4,2CaSO_4,H_2O$, begins to form at 30°, and its range of existence is largely coincident with that of glauberite, $Na_2SO_4,CaSO_4$, and there is no definite point at which one passes into the other, the former being always in a metastable condition and liable to change into glauberite (van't Hoff, Abstr., 1900, ii, 284).

Strontium sulphate and lead sulphate form no double sulphates with sodium sulphate, and barium sulphate does not combine with sodium, potassium, or ammonium sulphate in the conditions observed in these experiments. The heats of formation of the double salts referred to are tabulated in the original, which also contains graphs illustrating the ranges of existence of the various compounds, drawn from data given in this and the previous papers (Abstr., 1909, ii, 667, 733).

The solubility of mercurous sulphate in water at 16·5° is 0·055%, and at 100° 0·092%, the quantities of free sulphuric acid formed at these two temperatures being 0·008% and 0·071% respectively (compare Drucker, Abstr., 1902, ii, 74). The residue obtained by repeatedly washing mercurous sulphate with water has the composition assigned to it by Gouy (Abstr., 1900, ii, 481), but as some metallic mercury is formed, the reaction must be more complex than is sometimes assumed. No double salt with potassium sulphate is formed.

From the data given previously (Abstr., 1910, ii, 718; this vol., ii, 42) it appears that thoria cannot be completely separated from ceria by treatment of the two sulphates with excess of potassium sulphate solution, since a too concentrated solution of the latter would precipitate both salts completely. Sodium sulphate solution would give a better, but still incomplete, separation. A 1% sodium sulphate dilution dissolves 3 to 4 grams of thorium sulphate, but only 0·02 gram lanthanum sulphate or 0·007 gram of cerium sulphate. Ammonium sulphate solution cannot be applied usefully to effect this separation.

T. A. H.

Potassium Barium Orthothioantimonate. EMANUEL GLATZEL (*Zeitsch. anorg. Chem.*, 1911, 72, 100—105).—Antimony pentasulphide and barium hydrogen sulphide yield barium orthothioantimonate. Solid potassium chloride is added to the solution in about four times the quantity required by the equation $2KCl + Ba_3Sb_2S_8 = 2KBaSbS_4 + BaCl_2$. In order to prevent oxidation during evaporation, a solution of potassium hydrogen sulphide is added. The double salt separates slowly, and may be recrystallised from water containing potassium hydrogen sulphide.

Potassium barium orthothioantimonate,

$KBaSbS_4,6H_2O$ $(K_3SbS_4,Ba_3Sb_2S_8,18H_2O)$, forms colourless crystals which darken in air. When heated it melts, losing water, and solidifies on cooling to a crystalline mass.

C. H. D.

Preparation of Borax. II. Mario G. Levi and O. Garavini (*Gazzetta*, 1911, **41**, i, 756—781. Compare Abstr., 1910, ii, 501).—In the present paper the investigation of the reaction between boric acid and sodium chloride is continued, and the reactions between boric anhydride and sodium chloride and between boric acid and sodium sulphate are also dealt with.

From new experiments in which the temperature was raised only 10° at a time, it is shown that, although the reaction between sodium chloride and boric acid has a greater velocity at 140° than at lower temperatures, yet it has begun at 120°, or perhaps even lower, so that it would seem that metaboric acid also is able to displace hydrochloric acid from sodium chloride. At 170° the reaction does not proceed so far in the presence of borax as it does when borax is absent, and the authors consider that this favours their hypothesis that a state of equilibrium is reached in the mixture. The equilibrium which is reached at 150° is not altered below 500°; between 500° and 600° a considerable evolution of free chlorine begins. Above 600° the limit of the reaction increases regularly, until at 1200° 75% of the sodium chloride is decomposed, or, if the heating at that temperature be prolonged, complete decomposition may occur. At the same time a loss of boric acid takes place which may reach 10%. The evolution of chlorine is less when the reaction is conducted in an atmosphere of nitrogen, but it is not abolished. Three possible causes of the evolution of chlorine are suggested: (1) oxidation of the hydrogen chloride (favoured by catalytic action of the solids present, as in Deacon's process); (2) the presence of boric anhydride; (3) dissociation of the hydrogen chloride itself, which is found to begin at 800° under these experimental conditions.

The action of boric anhydride on sodium chloride is accompanied with a considerable evolution of chlorine, which increases with the temperature. The reaction seems to begin at 500° (5% of sodium chloride decomposed after four hours). In this case also the decomposition of sodium chloride is less in an atmosphere of nitrogen. It is suggested that the reaction in the presence of air may follow the equation: $2B_2O_3 + 2NaCl + O = Na_2B_4O_7 + Cl_2$.

The velocity of reaction between boric acid and sodium sulphate is much less than in the case of sodium chloride; after four hours at 1200° only 59% of the sulphate is decomposed. The reaction begins at 500°, that is, above the probable temperature at which pyroboric acid is converted into the anhydride. In agreement with this, it is found that the reaction proceeds at about the same rate when boric anhydride is taken instead of boric acid. The sulphuric acid is almost entirely decomposed at the temperature of the experiments, yielding sulphur dioxide.

R. V. S.

Melting Temperatures of Sodium and Lithium Metasilicates. F. M. Jaeger (*J. Washington Acad. Sci.*, 1911, **1**, 49—52).—Pure lithium metasilicate, prepared by repeatedly fusing and grinding a mixture of lithium carbonate and quartz in the proper proportions, crystallises rapidly as glistening needles with $D^{24\cdot 9}$ 2·5203. Its melting point, determined with the standard thermo-element of Day and Sosman (this vol., ii, 496), is sharply defined at 1201·8°, thus affording a suitable point (between copper, 1200°, and diopside, 1391°) for calibration purposes. Owing to under-cooling (to the extent of 100°) the solidification temperature is variable.

The solidification temperature of sodium metasilicate has been given by previous observers at various points ranging between 1007° and 1056°. A nearly pure sample was found to melt at 1088°, but the temperature of solidification was disturbed by under-cooling.

L. J. S.

Lithium Silicates. II. R. RIEKE and K. ENDELL (*Sprechsaal*, 1911, **44**, 97—99).—A continuation of previous work (this vol., ii, 490) on the physical and chemical properties of fused alkali silicates containing varying proportions of silica. The results are tabulated and exhibited in curves, whilst microphotographs illustrate the structure of the cooled substances. F. M. G. M.

The Binary Systems of Magnesium and Calcium Chlorides with the Chlorides of Potassium, Sodium, Silver, Lead, Copper, Zinc, Tin, and Cadmium. OTTO MENGE (*Zeitsch. anorg. Chem.*, 1911, **72**, 162—218).—In the thermal analysis of mixtures of chlorides, it is necessary to use equal volumes of each mixture, as on account of the low thermal conductivity an alteration of volume does not cause a proportional change in the arrest time. A volume of 2·5 c.c. is used, enclosed in a tube of Jena glass. Mixtures containing magnesium chloride undergo partial decomposition, so that the solidified mass must be dissolved in water and the separated magnesium oxide estimated.

Magnesium and calcium chlorides form a eutectiferous series, with the eutectic point at 621° and 42·8% $CaCl_2$. Solid solutions are probably formed at the calcium end of the series. The freezing-point curve of mixtures of magnesium and potassium chlorides has two maxima at 485° and 437°, corresponding with the compounds $KCl,MgCl_2$ and $2KCl,MgCl_2$. This is confirmed microscopically. The curve for mixtures of magnesium and sodium chlorides has a eutectic point at 55% NaCl and 430°, and two breaks, indicating a compound $NaCl,MgCl_2$, and another of uncertain composition. Magnesium chloride forms simple eutectiferous series with silver, lead, cuprous, zinc, and stannous chlorides, the eutectic points, especially in the last two cases, being very close to the end of the diagram corresponding with the added chloride. Magnesium and cadmium chlorides are isomorphous, and give a continuous freezing-point curve.

Calcium and potassium chlorides give a freezing-point curve with a single conspicuous maximum, corresponding with the compound $KCl,CaCl_2$, m. p. 754°. The calcium-sodium chloride curve has a break at 600°, corresponding with the compound $4NaCl,CaCl_2$. The mixtures of calcium chloride with silver, lead, cuprous, zinc, and stannous chlorides closely resemble in their behaviour the mixtures with magnesium chloride. Calcium and cadmium chlorides form a continuous series of solid solutions, the freezing-point curve showing a minimum, although the two salts are not isomorphous.

A comparison of the binary mixtures of the metals with those of the corresponding chlorides shows that when two metals of the group examined form intermetallic compounds, their chlorides do not combine, whilst metals which do not combine yield chlorides which form double salts. C. H. D.

The System Water–Calcium Chloride–Calcium Hydroxide at 25°. FRANS A. H. SCHREINEMAKERS and TH. FIGEE (*Chem. Weekblad*, 1911, **8**, 683—688).—In this application of Schreinemakers' graphic method, two new oxychlorides of calcium, $CaO,CaCl_2,2H_2O$ and $4CaO,CaCl_2,14H_2O$, have been isolated. A. J. W.

Solubility of Zinc Oxide in Fused Lead Silicate and Borate. A. D. HOLDCROFT (*Trans. Eng. Ceramic Soc.*, 1909—1910, **9**, 37—40).—An account of experiments in which varying quantities of zinc oxide were fused with lead silicate (litharge 78·8 parts, flint 21·2 parts) at 850° and 1000°, and the amount of zinc present in the fusions subsequently estimated; the lead silicate was also replaced by lead borate. The results indicated that at the lower temperature 7—10 parts of zinc oxide dissolved in 100 parts of lead silicate, and 50—60 parts of zinc oxide in 100 parts of lead borate, whilst at 1000° the solubilities were 13—14 and 60—70 respectively.

F. M. G. M.

Potassium Ammonoplumbite. EDWARD C. FRANKLIN (*J. Physical Chem.*, 1911, **15**, 509—520. Compare Abstr., 1905, ii, 581).—Lead imide (PbNH), prepared by the action of potassamide on lead iodide in liquid ammonia, is soluble in excess of potassamide. From the solution, *potassium ammonoplumbite* with ammonia of crystallisation was obtained. The substance, recrystallised from liquid ammonia in absence of air, forms large, colourless crystals, with the composition $PbNK,2\frac{1}{2}NH_3$. On drying at 20°, efflorescence takes place, and the composition becomes $PbNK,2NH_3$. At 100° the ammonia is further reduced, and a chocolate-brown substance of formula $PbNK,NH_3$ remains. Above 100° no further loss of ammonia occurs, but at 140—145° the salt explodes.

The formula of the brown substance may be written $NH_2{\cdot}Pb{\cdot}NHK$ or $PbNH{\cdot}KNH_2$ or $HPb(:NH){\cdot}NHK$. It is reconverted into the colourless variety on addition of ammonia. Potassium ammonoplumbite is discoloured by traces of air, and when exposed to the atmosphere or to water or dilute acids, explodes with violence. It is considered to be the ammonia analogue of potassium plumbite, although it has not been obtained free from the last molecule of ammonia of crystallisation. R. J. C.

Lead Silicates. PAUL WEILLER (*Chem. Zeit.*, 1911, **35**, 1063—1065. Compare Hilpert and Nacken, Abstr., 1910, ii, 955).—The thermal analysis of mixtures of lead oxide and silica shows that the metasilicate, $PbSiO_3$, is stable, but an orthosilicate is not found. All mixtures containing more than 8% of silica yield a mass on cooling which is partly glassy and partly crystalline, whilst those containing from 12 to 32·5% SiO_2 form homogeneous glasses if rapidly cooled. Mixtures still richer in silica again show a tendency to crystallise, the glass being devitrified in parts.

The density curve shows a change of direction at the composition of the metasilicate, this compound being formed with expansion, and the further inclination of the curve points to the existence of a more acid silicate. The refractive index curve of the glassy mixtures shows a change of direction at the composition of the metasilicate.

The temperature at which reduction by hydrogen takes place is determined by observing the change of colour through a window in a vertical electric resistance furnace. This temperature remains constant at 240° in mixtures containing free lead oxide, but rises to 285° at the composition of the metasilicate, and again remains constant. C. H. D.

Crystallographic Observations on Cerium Sulphate Tetrahydrate. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 149—150).—Already quoted in a paper by Cingolani (Abstr., 1908, ii, 385). R. V. S.

Preparation of a Compound Containing Aluminium, Boric Acid, and Active Oxygen. CHEMISCHE FABRIK COSWIG-ANHALT (D.R.-P. 235050).—Compounds of aluminium and boric acid have previously been prepared. The *compound*, $Al_2Na_2B_2O_9,5H_2O$, containing 7—9% of active oxygen, was obtained by slowly treating a cooled solution of sodium aluminate (6·6 parts) with boric acid (5 parts) and 30 parts of a 10% solution of hydrogen peroxide; it forms a colourless powder, sparingly soluble in water, and gradually hydrolysed thereby, whilst it combines the disinfectant properties of both boric acid and hydrogen peroxide. F. M. G. M.

Thermal Analysis of Binary Mixtures of the Chlorides of Bivalent Metals. CARLO SANDONNINI and G. SCARPA (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 61—68. Compare this vol., ii, 800; Ruff and Plato, Abstr., 1903, ii, 588).—The paper deals with the thermal analysis of the systems $SnCl_2$–$PbCl_2$, $MnCl_2$–$CdCl_2$, $SnCl_2$–$CdCl_2$, $MnCl_2$–$SnCl_2$, and $MnCl_2$–$PbCl_2$.

The melting point of cadmium chloride is 568° (Ruff and Plato gave 598°); that of lead chloride is 495°, and that of manganese dichloride is 650°. Anhydrous manganese dichloride was prepared by heating the hydrated chloride in a current of dry hydrogen chloride; when heated in air it evolves chlorine, but in nitrogen it melts unchanged.

Stannous chloride and lead chloride give mixed crystals in all proportions, as also do cadmium chloride and manganous chloride.

The other pairs give simple eutectics; that of the system $SnCl_2$–$CdCl_2$ lies at 233° (90 mols. % of stannous chloride); that of the system $SnCl_2$–$MnCl_2$ is situated also at 233° (95 mols. % of stannous chloride); that of the system $PbCl_2$–$MnCl_2$ lies at 408° (70 mols. % of lead chloride). R. V. S.

Further Ferro-magnetic Compounds of Manganese. EDGAR WEDEKIND and THEO. VEIT [with K. FETZER] (*Ber.*, 1911, **44**, 2663—2670. Compare Abstr., 1909, ii, 541)—*Manganese bismuthide*, MnBi, was obtained by the interaction of manganese thermite and bismuth. It forms octahedral and eight-sided columnar crystals, which are strongly magnetic; it is very sensitive towards acids, with the exception of concentrated hydrochloric acid, which reacts very slowly and may be used for purification. The same compound was also obtained, but with difficulty, by the direct fusion of the components in an atmosphere of hydrogen.

Manganese selenide, MnSe, was formed by heating manganese and selenium in an evacuated bomb-tube. It is crystalline in structure, weakly magnetic, and readily decomposed by water and mineral acids, hydrogen selenide being evolved. The *telluride*, MnTe, was prepared in a similar way, and has similar properties; it is crystalline, and has a silvery lustre.

Manganese silicide, Mn_2Si, was obtained from manganese thermite and silicon as a crystalline, greyish-black powder, which is relatively stable towards acids, and has hardly any magnetic properties. The *sulphide*, MnS, was also prepared by the alumino-thermic method; it is weakly magnetic, the magnetic properties becoming more pronounced on heating. The mineral alabandin behaves similarly. It has D^{17} 3·9.

Manganese arsenide, was obtained by heating manganese and arsenic together. The resulting regulus was freed from manganese with dilute hydrochloric acid, and from excess of arsenic by heating in chlorine or bromine. A black, crystalline powder was left, which, on analysis, gave figures approximating to those calculated for MnAs. It was not pure, however, and on further heating in an electric oven, arsenic was lost and the compound Mn_2As formed (compare Hilpert and Dieckmann, following abstract). It is distinctly magnetic, in contradistinction to the arsenide first formed.

Manganese carbide cannot be prepared by the alumino-thermic method. The compound, Mn_3C, obtained in the electric furnace is magnetic.

The compounds of manganese with tervalent elements are the most strongly magnetic. T. S. P.

Arsenides. I. Iron and Manganese Arsenides. SIEGFRIED HILPERT and THEODOR DIECKMANN (*Ber.*, 1911, **44**, 2378—2385).—The authors find that the best method for preparing pure arsenides of the metals is to heat them at a high temperature with the vapour of arsenic under pressure. The finely-powdered metal and the arsenic are sealed up in an evacuated bomb-tube of Jena glass, and heated for several hours at 700—750°, a temperature much higher than the boiling point of arsenic. After cooling, the almost chemically pure arsenide can be mechanically separated from the arsenic which has condensed on the walls of the tube, and is then readily purified by further treatment.

Iron arsenide, $FeAs_2$, after purification by treatment with dilute hydrochloric acid, was obtained as a silver-grey powder, which is probably microcrystalline. It is stable towards dilute and concentrated hydrochloric acid. The melting point, as determined by heating in a sealed quartz tube, lies between 980° and 1040°; D = 7·38. When heated at 680° in a current of hydrogen, the arsenide FeAs is obtained as a silver-white, crystalline powder. It is similar in its chemical properties to the diarsenide, and has m. p. 1020° and D = 7·83. Both these arsenides are completely non-magnetic.

Manganese arsenide, MnAs, could only be obtained in the pure condition when manganese prepared from the amalgam was used. Alumino-thermic manganese did not give satisfactory results (compare Wedekind, Abstr., 1907, ii, 353). It is a greyish-black powder, showing, apparently, no crystalline structure, D = 6·2; in its chemical properties it is similar to the iron arsenides. When heated in a current of hydrogen, arsenic is gradually volatilised, but no other compound is formed. It is strongly magnetic, but loses its magnetic properties when heated at 40—50°, the effect being a reversible one.

No evidence has been found for the existence of a compound Mn_2As (compare Wedekind, *loc. cit.*).

Phosphides may be prepared in a similar manner to the arsenides, and are to be reported on later. T. S. P.

The Internal Structure of Martensite and Pearlite. M. OKNOFF (*Metallurgie*, 1911, 8, 539—541).—The method of examining serial sections of steel (this vol., ii, 495) has been further applied, the thickness of the layer removed at each grinding being only 0·001 mm. The arrangement of ferrite and martensite in a steel containing 0·7% C, quenched from 750°, closely resembles that of ferrite and pearlite. Martensite, examined in a steel containing 0·5% C, quenched from 1000°, proves to be composed of plane lamellæ, 0·003—0·007 mm. broad, and only 0·001 mm. thick. Pearlite, examined in annealed steel, proves to be composed of curved, parallel lamellæ, about 0·001 mm. thick and of ten or twelve times that breadth. C. H. D.

Formation of Iron Carbonyl. A. STOFFEL (*Chem. Weekblad*, 1911, 8, 722—734).—An investigation of the conditions governing the formation of iron pentacarbonyl. Up to 60°, the influence of temperature on the reaction is slight, but just below 80°, adsorption of the reaction product by the iron at first retards the formation of the carbonyl, and finally inhibits it. Above 80° dissociation stops the action, so that large quantities in the state of vapour cannot be formed.

The presence of ammonia accelerates the combination of carbon monoxide and iron; that of hydrogen sulphide exerts no influence.

A. J. W.

Peroxides. Carl Tubandt and W. Riedel (*Ber.*, 1911, **44**, 2565—2570).—When a fine aqueous suspension of nickel peroxide is treated with dilute sulphuric acid, a solution is obtained which liberates iodine from potassium iodide, and decolorises permanganate to some extent. These reactions are not due to the formation of hydrogen peroxide (compare Tanatar, Abstr., 1909, ii, 484), which is not present even in traces, since its presence cannot be detected either with titanium dioxide or with chromic acid and ether. The authors are of the opinion that the liberation of iodine is due to the formation of persulphuric acid, or of Caro's acid, even in the dilute sulphuric acid used. The decoloration of the permanganate is only apparent, the colour being masked by the green colour of the nickel solution, as may be shown by experiments with nickel sulphate.

The formation of hydrogen peroxide when nickel peroxide acts on a solution of hydrocyanic acid in the presence of potassium cyanide is verified (compare Tanatar, *loc. cit.*). It is not formed from the nickel peroxide, however, but by the auto-oxidising action of the complex nickel cyanides formed. This is supported by the fact that nickel hydroxide, or any nickel salt, may be used in place of the peroxide.

There is thus no reason for placing nickel peroxide in a special class among the peroxides, and, moreover, the above results offer no support for Tanatar's views on the constitution of the peroxides. The work of Pellini and Meneghini (Abstr., 1909, ii, 506, 486) is not affected by the above. T. S. P.

Nickel Peroxide and its Behaviour in Salt Formation. Carl Tubandt and W. Riedel (*Zeitsch. anorg. Chem.*, 1911, **72**, 219—232. Compare preceding abstract).—The oxidation of nickel salts with various oxidising agents yields only precipitates of nickel peroxide. The product of the action of cold acetic acid on nickel peroxide is not, as supposed by Benedict (Abftr., 1906, i, 333), an acetate of tervalent nickel, but a colloidal solution of the peroxide, as is shown by ultramicroscopic investigation. Phosphoric acid forms very stable colloidal solutions of this kind. Concentrated phosphoric acid, on the other hand, forms a green solution, which contains the phosphorus analogue of Caro's acid (Schmidlin and Massini, Abstr., 1910, ii, 498). Benedict's nickelic sulphate is a nickelous solution containing Caro's acid, and the red colour observed by him in portions of the filtrate is due to the presence of manganese, which is oxidised to permanganic acid by the nickel peroxide.

Strongly cooled alcoholic solutions of acids yield with nickel peroxide dark red solutions, which prove, however, to be colloidal. In the electrolysis of nickel cyanide solutions between platinum electrodes, dark red solutions are obtained, which have reducing properties, and contain the suboxide, Ni_3O. The electrolysis of alkali carbonate solutions containing nickel between nickel plates, using a diaphragm, yields a dark solution which contains only the colloidal peroxide. All attempts to obtain nickelic salts have, therefore, been unsuccessful. C. H. D.

Uranium Hexafluoride. OTTO RUFF and ALFRED HEINZELMANN (*Zeitsch. anorg. Chem.*, 1911, **72**, 63—84).—Uranium hexahalides have not been prepared previously. The hexafluoride has now been prepared in three ways. Fluorine reacts with uranium pentachloride at $-40°$ according to the equation: $2UCl_5 + 5F_2 = UF_4 + UF_6 + 5Cl_2$. The two fluorides are separated by distillation. The course of the reaction suggests that uranium pentachloride is really a double compound, UCl_4,UCl_6. The pentachloride also reacts with dry hydrogen fluoride, forming a compound UF_5,xHF, which breaks up on distillation into UF_4 and UF_6. The difficulty of separation of the volatile hexafluoride from hydrogen fluoride makes this method a less useful one. Uranium carbide, UC_2, prepared at 2450° from uranium dioxide and carbon, yields only the tetrafluoride with pure fluorine, but in presence of chlorine at $-70°$ it yields the hexafluoride.

Uranium hexafluoride, UF_6, has the vapour density 11·7 (calc. 12·16) at 448° in a platinum vessel. The vapour pressure determined by Smith and Menzies' method (Abstr., 1910, ii, 1037) has also been determined at various temperatures, using 0·1 gram substance for each determination. The boiling point is 56·2°, and the calculated mean latent heat of evaporation between 42° and 57° is 29·4 cal. per gram, or 10,360 cal. per gram-molecule. The compound forms glistening, colourless or pale yellow, monoclinic crystals, m. p. 69·2° (corr.), at which temperature it has a vapour pressure of two atmospheres. It has $D^{20\cdot7}$ 4·68

Uranium hexafluoride is highly reactive, attacking glass if traces of water are present, and reacting vigorously with water, alcohol, ether or benzene, depositing carbon in the last case. It reacts more slowly with carbon disulphide, paraffin, chloroform, and nitrobenzene. The best solvent is tetrachloroethane. It also reacts with nitric oxide, ammonia, and arsenic trichloride. It is reduced by most non-metals and metals, except gold and platinum. Sulphur forms US_2 and UF_4, together with a gas condensing at $-40°$ and freezing at $-135°$, which appears to be a new sulphur fluoride. C. H. D.

Vanadium Bromides. OTTO RUFF and HERBERT LICKFETT (*Ber.*, 1911, **44**, 2534—2538).—The methods of preparation of the following compounds are based on those worked out for the vanadium chlorides (this vol., ii, 291).

If bromine vapour or, better still, a mixture of bromine and sulphur bromide vapour is passed over a mixture of vanadium pentoxide and sulphur at a red heat, the distillate does not consist of vanadyl tribromide, $VOBr_3$ (compare the corresponding chlorine compounds, *loc. cit.*), but of a product which, on being heated in a vacuum at 240°, leaves a residue of pure vanadyl dibromide, $VOBr_2$, sulphur bromide and bromine distilling away. If the temperature of the residue is raised to 360°, the vanadyl dibromide partly sublimes and partly decomposes with evolution of bromine, leaving a violet residue consisting of the hitherto unknown *vanadyl bromide*, VOBr. If this compound is further heated in a vacuum to 480°, vanadium tribromide distils away, leaving a residue of vanadium trioxide.

Vanadium tribromide is readily obtained by the action of bromine vapours on vanadium carbide, V_4C_3, at a dark red heat.

Full details of the methods of preparation of the above compounds are given.

Vanadyl bromide, VOBr, crystallises in violet octahedra, and has D^{18} 4·0002. It is only very slightly soluble in water, acetic anhydride, ethyl acetate, and acetone. T. S. P.

Vanadium Fluorides. OTTO RUFF and HERBERT LICKFETT (*Ber.*, 1911, **44**, 2539—2549).—By the action of fluorine on vanadium or on the vanadium chlorides, mixtures of vanadium fluorides were obtained which could not be separated readily. Satisfactory methods for the preparation of the various fluorides by the action of anhydrous hydrogen fluoride on the anhydrous chlorides and bromides have, however, been worked out.

When anhydrous hydrogen fluoride is passed over heated vanadium trichloride, a brown intermediate product is formed at 120—130°. At 340° the brown powder change to a green one, which still contains chlorine unless the passage of hydrogen fluoride is continued for six to eight hours and the temperature raised to a dark red heat. *Vanadium trifluoride*, VF_3, is then left as a greenish-yellow powder, which is almost insoluble in water and the usual organic solvents. The melting point lies above 800°, and it sublimes at a bright red heat; D^{19} 3·3628.

Vanadium tetrafluoride, VF_4, is produced by the action of anhydrous hydrogen fluoride on vanadium tetrachloride, the reaction being started at $-28°$ and the temperature allowed to rise to 0° in the course of two hours. It is a brownish-yellow, loose powder, which is very hygroscopic, deliquescing in the air to a blue liquid; readily soluble in water (blue solution) and acetone (green solution); it has D^{23} 2·9749. Above 325°, it decomposes into vanadium pentafluoride and vanadium trifluoride.

Vanadyl difluoride, VOF_2, is prepared by heating vanadyl dibromide in a current of anhydrous hydrogen fluoride, first at 150—200° and then at 600—700° for six hours. It is yellow in colour, slightly soluble in acetone, but insoluble in other solvents; D^{19} 3·3956.

Vanadyl trifluoride, VOF_3, is prepared from vanadyl trichloride in a similar manner to that described for the preparation of vanadium tetrafluoride; it may also be obtained by heating vanadium trifluoride to a red heat in a current of oxygen. It forms yellowish-white crusts, and is very hygroscopic, deliquescing in the air to a brownish-yellow solution. At 132°, when heated in glass tubes, it decomposes, red vanadium pentoxide being deposited; it then melts at about 300° and boils at 480°. In a current of oxygen, it sublimes at 130°. It has $D^{20\cdot5}$ 2·4591.

Vanadium pentafluoride, VF_5, is obtained as a pure white sublimate when the tetrafluoride is heated in a current of nitrogen, the temperature being gradually raised from 300° to 650°, and the latter temperature maintained for two and a-half hours. At the ordinary temperature, it possesses an appreciable vapour pressure, and in moist air becomes yellow, owing to the formation of oxyfluorides. It is readily soluble in water, alcohol, chloroform, acetone, and light petroleum. When heated in sealed glass tubes it does not melt, even above 200°, but it readily attacks the walls of the tube. It has D^{19} 2·1766, and b. p. 111·2°/758 mm. It is the only vanadium compound in which five halogen atoms are bound to one vanadium atom.

Special methods were devised for the estimation of the vanadium and fluorine in the above compounds. T. S. P.

The Action of Calcium Fluoride on Vanadium Pentoxide. Wilhelm Prandtl and Hermann Manz (*Ber.*, 1911, **44**, 2582—2585).—When a mixture of vanadium pentoxide and calcium fluoride is heated to a red heat in an open platinum crucible, some of the vanadium is volatilised, the amount depending on the ratio $CaF_2 : V_2O_5$. When the ratio is 1 : 1, the loss is from 12% to15%, and it increases to 30% with the ratio 5 : 1. If the crucible is covered with a lid, or with another crucible, which is kept cool during the heating, the latter is afterwards found to be coated with shining, needle-shaped crystals of vanadium pentoxide, which are dark brownish-red when hot, and yellow when cold. Their formation is probably due to the volatilisation of a volatile vanadium fluoride or oxyfluoride, which is decomposed by the oxygen and water vapour of the air. This is made probable by the fact that when the reaction mixture is heated in a platinum tube in a current of nitrogen, an almost colourless, deliquescent sublimate is obtained. Analyses of the sublimate did not lead to any satisfactory conclusions; it contained quadrivalent vanadium. When the mixture is heated in a glass tube, the latter is strongly attacked, silicon tetrafluoride being formed.

T. S. P.

Tantalum, Tungsten, and Hydrogen. Adolf Sieverts and E. Bergner (*Ber.*, 1911, **44**, 2394—2402).—Using the method previously described (Abstr., 1910, ii, 410, 851), the solubility of hydrogen in tantalum at varying temperatures up to 1330° has been measured. Under the same hydrogen pressure the solubility decreases with rise in temperature, and at a given temperature (above 450°) it is proportional to the square-root of the pressure. The solubility curve is very similar to that obtained with palladium and hydrogen, and quite different from the curves of copper, nickel, iron, cobalt, and platinum. With palladium and tantalum, the absorption is an exothermic process, whereas with the other metals it is endothermic. The order of solubility is much the same for tantalum and palladium.

When heated in hydrogen, tantalum wire undergoes a structural alteration, becoming brittle and crystalline (compare Pirani, Abstr., 1905, ii, 718), which properties it retains after the hydrogen has been extracted by heating in a vacuum.

Nitrogen reacts slowly with tantalum at temperatures above 900°, forming a nitride.

The solubility of hydrogen in tungsten is very small at temperatures up to 1500°, and the values obtained were not equilibrium values. Nitrogen does not react with tungsten, even at 1500°.

T. S. P.

Mineralogical Chemistry.

The Laws of Mineral Association from the Point of View of the Phase Rule. VICTOR M. GOLDSCHMIDT (*Zeitsch. anorg. Chem.*, 1911, **71**, 313—322).—The phase rule may be applied to mineral associations in the form: The maximum number of solid minerals that can co-exist in a stable condition is equal to the number of independent components contained in them. The number can only be exceeded at certain definite temperatures or pressures, at which transformations occur. The rule is applied to a number of mineral associations, including cases in which the components may unite to form binary or ternary compounds. An application to crystalline hornblendes of the Christiania region, derived from clays and limestone by contact-metamorphosis, shows the usefulness of the rule in determining which associations are possible, the components in this case being CaO, MgO, Al_2O_3, and SiO_2, whilst fifteen distinct minerals are possible, four of which may co-exist. C. H. D.

Bismuth Ores. EDUARD PRIWOZNIK (*Österr. Zeitsch. Berg. Huttenwesen*, 1910, **58**, 713—716).—A bismuth ore for which the name *emplectite* is proposed contains S 19·10%, Bi 62·09%, and Cu 18·8%, with the empirical formula $Cu_2Bi_2S_4$ and D^{22} 6·223; it forms rhombic crystals, isomorphous with copper glance, and is found at Freudenstadt, in the Black Forest, in Norway, and at Dognaczka in Hungary.

Wittichenite has the formula $Bi_2Cu_6S_6$, D 6·006, and is obtained from Wittichen, in the Black Forest. A third copper bismuth ore, $2Cu_2S,3Bi_2S_3$, was described by Maderspach, but is not sufficiently characterised. F. M. G. M.

Hydrothermal Silicates. EMIL BAUR and F. BECKE (*Zeitsch. anorg. Chem.*, 1911, **72**, 119—161).—For the preparation of aqueous solutions of silicates at temperatures approaching a red heat, steel cylinders may be employed without a platinum lining, as the steel is only slightly attacked. The cylinder, with walls 18 mm. thick and a capacity of 11 c.c., is closed by means of a steel screw, rendered tight by a soft copper ring. The cylinder is only one-third filled with liquid, and is heated vertically in an electric resistance furnace. Each charge is exposed for 12 to 16 hours to a constant temperature of 350° or 450°.

The action of superheated alkaline solutions on crystalline quartz, alumina, etc., is very slow, and it is necessary to use amorphous materials. A clear solution is not formed, but the amorphous mass is converted into microscopic crystals without external change of form. The products are identified microscopically. The following minerals have been obtained, starting from silica, alumina, lime, and potassium or sodium hydroxide: Quartz, opal, orthoclase, albite, oligoclase, potassium faujasite, analcite, potassium nepheline hydrate, andalusite, pyrophyllite, muscovite, stilbite, gyrolite, and sodium and potassium pectolite. The results are shown graphically on a diagram obtained from the tetrahedral representation of the quaternary system by drawing two planes through a point within the tetrahedron, each parallel with one face, and uniting the two triangles obtained in a plane.

The potassium faujasite contains much zeolitic water. Calcium aluminium silicates are not obtained under the conditions of the experiment, however the composition of the mixtures used is varied. The mixtures richest in alkali always yield zeolites, not felspars. Mixtures containing lime always yield pectolite. Leucite is not found under these conditions. Tridymite is also absent, and the modification of crystalline silica which occurs is always α-quartz. The andalusite obtained is possibly metastable, but transformation into sillimanite is not observed. It is probable that metastable phases are often present in zones of contact metamorphism. C. H. D.

Composition of Nephelite. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1911, 1, 109—112).—In the triclinic felspars are the well-known isomorphous molecules, $NaAlSi_3O_8$ (albite), $Ca_{\frac{1}{2}}AlSiO_4$ (anorthite), $NaAlSiO_4$ (carnegieite), and $KAlSi_3O_8$ (microcline); and there is a parallel series of monoclinic felspars. These compounds also form an isomorphous series of hexagonal modifications, namely: $NaAlSiO_4$ (essential component of nephelite; prepared artificially) and $KAlSiO_4$ (kaliophilite), to which may be added by analogy, $Ca(AlSiO_4)_2$ and $NaAlSi_3O_8$. The composition of nephelite can be very simply explained by the isomorphous mixing of these molecules; thus the recent analyses of Foote and Bradley (this vol., ii, 122) and of Morozewicz (Abstr., 1908, ii, 201) correspond very closely with:

	Foote and Bradley.	Morozewicz.
$NaAlSiO_4$	70·4%	74·7%
$KAlSiO_4$	19·0%	19·7%
$NaAlSi_3O_8$	10·6%	5·6%

L. J. S.

Minerals and Rocks of the Composition $MgSiO_3$–$CaSiO_3$–$FeSiO_3$. ROBERT B. SOSMAN (*J. Washington Acad. Sci.*, 1911, 1, 54—58).—The published analyses of pyroxenite rocks and pyroxene minerals are calculated to molecular percentages of the metasilicates and plotted on a triangle with $MgSiO_3$, $CaSiO_3$, and $FeSiO_3$ at the three corners, representing a three-component system. It is seen that the rock analyses all lie in a limited "eutectic field," with the rhombic pyroxenes on one side and the monoclinic pyroxenes on the other. The relations are in harmony with the experimental data of Allen and White (Abstr., 1909, ii, 247). L. J. S.

Physiological Chemistry.

Variations in the Response of Healthy Men to Dyspnœic Conditions Produced by Breathing a Confined Volume of Air. THEODORE HOUGH (*Amer. J. Physiol.*, 1911, **28**, 369—390).—By breathing a confined volume (30 litres) of air, dyspnœa sets in, and healthy men attempt to secure increased ventilation of the lungs by increasing the rate or depth (or both) of the respiratory efforts. As a rule, rate and depth vary inversely; increase of rate occurred in five only out of twenty-five men. The employment of muscles of expiration is another variable factor. The facts described harmonise with the theory that the chief stimulus is the tension of carbon dioxide in the blood. W. D. H.

Gaseous Metabolism in Anaphylactic Shock. FRITZ LOENING (*Arch. exp. Path. Pharm.*, 1911, **66**, 84—109).—In anaphylaxis, disturbances and lowering of heat-production and oxidation processes are always found. W. D. H.

Protein Cleavage Products in Expired Air. WOLFGANG WEICHARDT (*Arch. Hygiene*, 1911, **74**, 185—193).—Tubercle bacilli pass into the expired air; it is therefore not improbable that decomposition products of bacilli, mucus, etc., do so also. By breathing into distilled water and evaporation of the water, a ponderable residue is obtained, which contains high molecular products of protein decomposition. Dissolved in normal salt solution, the biological test in mice in producing sensibilisation is obtained. Negative findings in the same direction by Inaba are criticised. W. D. H.

The Oxygen-transport Capacity of Blood Warmed to Different Temperatures. LEO VON LIEBERMANN and FRANZ WIESNER (*Biochem. Zeitsch.*, 1911, **35**, 363—367).—From experiments on the rate of production of the blue colour with guaiacum-turpentine mixture, the conclusion was drawn that blood heated to different temperatures up to 50° is not appreciably altered in respect to its capacity to act as transporter of oxygen. At 50°, however, there may be some difference in respect to the capacity of taking up oxygen from the air, owing to the formation of methæmoglobin. S. B. S.

Chemical Studies in Blood Regeneration. ERNST MASING (*Arch. exp. Path. Pharm.*, 1911, **66**, 71—83).—In anæmic rabbits and geese, characteristic changes occur in the phosphorised constituents of the blood which are believed to be related to regeneration of that fluid. In rabbit's serum, the phosphorus in the alcohol-ether extract is increased, and the red corpuscles are richer in phosphatides than normal. The nucleic acid in the red corpuscles is higher than normal in both anæmic rabbits and geese. Richness in nucleic acid and phosphatides is a mark of young corpuscles. W. D. H.

The Action of Choline on Blood-Pressure. EMIL ABDERHALDEN and FRANZ MÜLLER (*Zeitsch. physiol. Chem.*, 1911, **74**, 253—272).—Most observers agree that the typical action of choline is to lower blood-pressure, except in atropinised animals. Modrakowski and Popielski alone find that it raises arterial pressure, and attribute the results of others to impurities. The present research gives the results of choline injections under various conditions of narcosis, etc., and the outcome is that the typical action of choline is to lower pressure, and that the presence of impurities will not account for the differences observed. Some of the authors' preparation was sent to Popielski to test the matter, and he reported that it produced a rise of blood-pressure. Unfortunately for Popielski, the specimen sent (by mistake) was an impure specimen, which, according to him, should have produced a fall of pressure. It did produce a fall of pressure in Berlin, and so did the pure specimens. W. D. H.

Lactic Acid in Human Blood. H. FRIES (*Biochem. Zeitsch.*, 1911, **35**, 368—385).—A method is described in detail for estimating lactic acid in blood, of which the essential processes consist in precipitating the proteins by mercuric chloride in acid solution, extracting the protein-free solution with ether, converting the lactic acid thus extracted into a zinc salt, oxidising the latter with permanganate, and estimating the aldehyde thus formed by Ripper's bisulphite method. As a result it was found that lactic acid often occurs in human blood, but the average amount is not increased in fevers, and no conclusions can be drawn from the amount as to changes in the general metabolic processes. Lactic acid is increased after strenuous muscular work. Blood from the cadaver contains more lactic acid than that obtained from the living subject; the amount in the latter increases if it be incubated at 40° for two hours. There is no information available as to the origin of lactic acid in blood.

S. B. S.

The Fat of Dog's Blood under Normal and Various Experimental Conditions (Digestion, Hunger, and Phosphorus, Phloridzin and Chloroform Poisoning). LEONE LATTES (*Arch. exp. Path. Pharm.*, 1911, **66**, 132—142).—In normal dogs the light petroleum extract (Kumawaga-Suto's method), which contains higher fatty acids and cholesterol, varies between 0·3% and 0·42% of the blood, and is higher in venous than in arterial blood. This is doubled during absorption of food rich in fat, especially milk. It is also increased by poisoning with phloridzin and with phosphorus, and slightly in the early stages of inanition. Chloroform narcosis has practically no effect.

W. D. H.

The Distribution of Reducing Substances in the Blood of Mammals. H. LYTTKENS and J. SANDGREN (*Biochem. Zeitsch.*, 1911, **36**, 261—265. Compare Abstr., 1910, ii, 785).—The blood-corpuscles of all the mammals investigated contain more or less the same amount of reducing substance, which is equivalent in reducing power to 0·05—0·08% dextrose, and varies slightly in the same species. It is not dextrose, however, as the reducing power remains intact after fermentation. The blood-serum contains, in the same animals, a reducing substance which is not dextrose, in amounts varying between 0·032 and 0·045% of dextrose equivalent. The dextrose itself, however, varies largely in the different animals, being 0·222% for rabbits, 0·248% for guinea pigs, and 0·291% for cats, whereas for man, pig, sheep, ox, and horse, it varies between 0·063 and 0·095%. It is assumed that in the smaller animals the ratio of body surface to body weight is large, and therefore the combustion is more intense; hence the larger amount of dextrose in the blood stream. The authors reply to some criticisms of Michaelis and Rona on their methods, giving certain experimental facts in their support. S. B. S.

Enzymatic Decomposition of Hydrogen Peroxide. George Senter (*Zeitsch. physiol. Chem.*, 1911, **74**, 101—103. Compare Abstr., 1903, ii, 661).—Waentig and Steche (this vol., i, 759) state that the decomposition of hydrogen peroxide by the enzyme of blood is not in general a reaction of the first order, as found by Senter and by Euler. The author points out that the conclusions of Waentig and Steche can only be regarded as valid when it is shown that the enzyme does not undergo oxidation during the reaction. G. S.

Passage of the Internal Secretion of the Pancreas of the Fœtus into the Blood of the Mother. Anton J. Carlson and Fred M. Drennan (*Amer. J. Physiol.*, 1911, **28**, 391—395).—If a dog deprived of its pancreas becomes pregnant, or if a pregnant dog has its pancreas removed, pancreatic diabetes is lessened or prevented. This is due to the fœtal pancreas, the secretion of which passes into the mother's blood; this effect is most noticeable in the second half of gestation, when the fœtal pancreas is better developed and the Islands of Langerhans capable of playing their normal rôle. W. D. H.

The Presence in the Blood of the Pancreatic Internal Secretion. Fred M. Drennan (*Amer. J. Physiol.*, 1911, **28**, 396—402).—Intravenous injections of fresh defibrinated blood from a normal dog into a dog deprived of its pancreas lowers the percentage of urinary sugar for a period of less than twenty-four hours. Control experiments show this must be due to the presence of the pancreatic internal secretion in normal blood. This is an unstable substance, and disappears when the blood is left a few hours. W. D. H.

Changes in Blood and Bone-Marrow Produced by Hæmorrhage and Blood-destruction. Cecil Price Jones (*J. Path. Bact.*, 1911, **16**, 48—70).—After receiving 10 c.c. of a 1% solution of phenylhydrazine, the regeneration of red corpuscles in the rabbit is arrested or masked for at least six days. No such delay occurs after hæmorrhage. The cause of the delay is probably a toxic action on the bone-marrow. The type of regeneration is different in the two cases; the colour index is raised more by phenylhydrazine than by hæmorrhage, and the blood shows a higher grade of megalocytosis. W. D. H.

Hæmolysis by Ammonia. ED. STADLER and H. KLEEMAN (*Biochem. Zeitsch.*, 1911, 36, 301—320).—By means of direct titration it is shown that the amount of ammonia taken up by blood-corpuscles after washing with saline follows the laws of adsorption phenomena, and in this way the conclusions of Gros are confirmed, who arrived at the same result by the measurement of the amount of hæmolysis. The adsorption is much slower if the experiments be carried out in isotonic sucrose instead of sodium chloride solutions. This is not due to the difference in the amount of the ammonia taken up, which is the same in both cases. In the case of blood-corpuscles in sucrose solution, the rate of hæmolysis is not constant, but sets in rapidly after a period during which but little hæmolysis takes place. In the case of blood-corpuscles in saline, the hæmolysis is a regular process. In the former case, the formula which expresses the relationship between the concentration of the ammonia and the time necessary for complete hæmolysis does not correspond with the laws of adsorption. The inhibitory influence of serum and peptone solutions on hæmolysis may be at least partly explained by the diminished adsorption of ammonia. When large amounts of blood-corpuscles are employed, the increased amount of ammonia adsorbed is not proportional to the increased quantity of blood, but diminishes with increasing amounts of it. Blood which has been in isotonic sucrose solution for twenty-four hours is more rapidly hæmolysed (and adsorbs more ammonia) than fresh blood. S. B. S.

Hæmolysis by Acetic Acid. ED. STADLER and H. KLEEMAN (*Biochem. Zeitsch.*, 1911, 36, 321—334).—The methods of experiment and the results obtained were similar to those in the case of ammonia (see foregoing abstract). In the case of acetic acid, the inhibitory influence of serum is very great, possibly owing to the combination of the serum with the acid. S. B. S.

Hæmolytic Extracts of Organs. P. SCHÄFER (*Biochem. Zeitsch.*, 1911, 35, 445—470).—It has been shown that if hæmolytic soap solutions are heated with proteins, the hæmolytic substance will be carried down with the coagulum, which will then become hæmolytic, whilst the supernatant fluid will become inactive. It has been suggested that the hæmolysins in the organs are soaps, and it is now found that they act like soaps in respect to the action of proteins. Activated cobra venom acts also in the same way, although it cannot be carried down so completely by the proteins, and the protein-toxin combination is less stable.

Experiments were also carried out with the hæmolysin obtained by extracting the pancreas with alcohol. No regular results were obtained, as sometimes the extract from fresh tissues was inactive, and only became active after autolysis, whereas in other cases the reverse was observed. Neither could any connexion be traced between the state of nutrition or the quality of the food (that is, whether the diet had been mainly protein, carbohydrate, or fat) on the hæmolytic power of the alcoholic pancreas extract; soap injected into the bloodstream of an animal rapidly disappears, as the injection causes no appreciable increase in the hæmolytic power of the serum removed a short time after the injection. S. B. S.

Relation of the Reaction of the Culture Medium to the Production of Hæmolysin. E. E. ATKIN (*J. Hygiene*, 1911, **11**, 193—201).—Bacteria differ greatly in their range of growth in bouillon of varying reactions. Roughly, the optimum of growth occurs when the reaction is neutral to phenolphthalein; but most micro-organisms have some power of overcoming the inhibitory effect of sodium hydroxide; the capacity to overcome the effect of hydrochloric acid is rarer. The production of hæmolysin by *Vibrio nasik* is not limited to an optimum reaction, but is coextensive with its range of growth in media of varying reactions, but the maximum is reached sooner and lost sooner in alkaline as compared to acid cultures.

W. D. H.

The Alterations in Hæmolytic Immune-substance which Occur During Immunisation. CARL H. BROWNING and G. HASWELL WILSON (*J. Hygiene*, 1911, **11**, 208—219).—Rabbits were injected intraperitoneally with the red corpuscles of ox-blood; the immune-substance in the serum at an early stage is deficient in the power of causing absorption of complement; in later stages this is not the case. W. D. H.

Effects of Ultra-violet Rays on Serum. W. M. SCOTT (*J. Path. Bact.*, 1911, **16**, 148).—The exposure of anti-toxic serum to ultra-violet rays destroys the major part of the antitoxin, but leaves the anaphylactic toxicity still appreciable. The procedure also renders the serum incoagulable by heat, and markedly increases the amount of protein precipitable by half saturation with ammonium sulphate.

W. D. H.

A Reversed Action of the Chorda Tympani on Salivary Secretion. HENRY H. DALE and PATRICK P. LAIDLAW (*J. Physiol.*, 1911, **43**, 196—198).—Several observers have noted the reversal of effects of stimulation of nerves after certain drugs. The present paper draws attention to the effect of cytisine, the alkaloid of laburnum seeds, which has an action similar to that of nicotine in reversing or lessening the usual action of stimulation of the chorda tympani nerve. W. D. H.

Lecithin and Diastatic Action. EMILE F. TERROINE (*Biochem. Zeitsch.*, 1911, **35**, 506).—In view of the recent investigations on this subject, the author reiterates his conclusions, namely: (1) Lecithin does not increase the rate of hydrolysis of monobutyrin by pancreatic juice, and increases only to a slight extent in more concentrated solution the rate of hydrolysis of oils. (2) It increases the lipolytic action of neither mucous membrane of stomach (in glycerol) nor intestinal lipase. (3) It has no action on the rate of hydrolysis of starch, the digestion of caseinogen or coagulated albumin, or the coagulation of milk by pancreatic juice. S. B. S.

Physiology of Digestion. III. The Secretion of Gastric Juice when the Chlorine Supply of the Body is Lessened. Rudolf Rosemann (*Pfluger's Archiv*, 1911, **142**, 208—234. Compare Abstr., 1907, ii, 706; 1910, ii, 1082).—Three experiments on dogs show that the secretion of gastric juice varies directly as the condition of nutrition in the animal; further, the supply of chlorine is most important, not only on the amount of acid in the juice, but for the secretion of the juice at all. The secretion commences again on giving chlorides. About 20% of the chlorine supply in the food is available for gastric juice secretion. W. D. H.

The Preparation of Solutions of Rennet Poor in, or Free from, Pepsin. Olof Hammarsten (*Zeitsch. physiol. Chem.*, 1911, **74**, 142—168).—A contribution to the vexed question of the identity or non-identity of the gastric enzymes. The main result of the research is that by precipitation of an acid infusion with caseinogen, the relation of the two enzymic actions is completely altered; the peptic is much more diminished than the rennetic. There can be no question here of the harmful action of reagents on the enzymes. The weakening of peptic activity cannot again be due to the appearance of inhibitory substances, but is only explicable on the assumption that the filtrate is poor in pepsin. From this it follows that the two enzymes are distinct, pepsin being precipitated with the caseinogen in greater proportion than rennin. W. D. H.

The Specific Inhibition of Rennet, and Differences between Rennets. Sven G. Hedin (*Zeitsch. physiol. Chem.*. 1911, **74**, 242—252).—By warming neutral infusions of the gastric mucous membrane of guinea-pig, calf, and pike with dilute ammonia and then neutralising, substances are formed which inhibit rennetic action. The inhibitory substances only inhibit the rennet of the animals used. The specific action of the inhibitory substances indicates that the enzymes they inhibit are specific also. W. D. H.

Digestive and Absorptive Defects. I. E. S. London, W. F. Dagaeff, B. D. Stassoff, and O. J. Holmberg (*Zeitsch. physiol. Chem.*, 1911, **74**, 328—359).—After removal of the whole or part of the stomach, various motor disturbances in the rest of the alimentary canal are noted, which are described in detail. The disturbances of secretory activity vary in relation to the sort of food given. Among the points mentioned are: (1) that protein and not fat leaves the stomach first after partial removal, and (2) that the duodenum enlarges into a reservoir when the excision is complete. Resection of the ileum leads to increased activity of the upper portion of the tube both as regards digestion and absorption, whereas resection of the jejunum produces a compensatory action in the large intestine. Obliteration of the pancreatic vessels produces little or no effect on digestion, and the same is true for occlusion of the pancreatic ducts. Total removal of the pancreas appears to evoke no compensatory activity. W. D. H.

Effects of Nutrition with Maize. III. Action of the Pancreatic Juice of the Dog on Zein and Gliadin. SILVESTRO BAGLIONI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 36—39. Compare Abstr., 1910, ii, 625).—Zein and gliadin are digested by pancreatic juice in the same way as animal protein. The biuret reaction in the intermediate stage of the process shows the presence of peptones, and later of amino-acids. From comparative experiments in which the free amino-acids formed were estimated by Sörensen's method, it is shown that gliadin is more readily digested than zein. R. V. S.

The Detection of Active Pepsin in the Intestinal Contents by means of Elastin. EMIL ABDERHALDEN and OTTO MEYER (*Zeitsch. physiol. Chem.*, 1911, 74, 67—100).—By means of adsorption with elastin, pepsin is always discoverable in the small intestine in important amounts. Peptic digestion is not confined to the stomach; the individual parts played by pepsin, trypsin, and erepsin in this part of the alimentary canal in protein digestion have still to be cleared up. It is perhaps their joint action which leads to the rapid disintegration of proteins into their amino-acids. The pepsin is no doubt adsorbed by elastin and connective tissues in the stomach, and carried thus in an active condition into the intestine.

W. D. H.

The Use of Elastin for the Detection of Proteolytic Enzymes. EMIL ABDERHALDEN and KARL KIESEWETTER (*Zeitsch. physiol. Chem.*, 1911, 74, 411—426).—Elastin absorbs enzymes, as Grützner showed that fibrin does; its special value is that it itself only very slowly undergoes any cleavage. By its use, the following facts were determined: (1) The fæces of ox, horse, dog, and man usually contain no digestive enzymes; (2) peptolytic enzymes were detected by the optical method and the biuret reaction in the following organs, or juices: horse liver, the juice from horse liver, the juice expressed from yeast, and horse's kidney. Some observations on the comparative digestibility of elastin, fresh egg-white, and boiled egg-white are given. The effects are not the same with the natural and artificial gastric juice. W. D. H.

Chemistry of Digestion and Absorption in the Animal Body. XL. The Degree of Cleavage of Different Proteins in the Alimentary Canal. E. S. LONDON and A. G. RABINOWITSCH (*Zeitsch. physiol. Chem.*, 1911, 74, 305—308).—Gastric digestion has only a limited power to cleave proteins into peptides; this power increases in the intestine. The amount of cleavage varies with different proteins, but there is no difference whether the proteins are obtained from the same species of animal or not. W. D. H.

Chemistry of Digestion and Absorption in the Animal Body. XLI. The Digestion of a Mixed Diet in Dogs and Men. R. S. KRYM (*Zeitsch. physiol. Chem.*, 1911, 74, 312—317).—In dogs, absorption of the chyme is most active at early stages in digestion, but it increases again a little at the end. Carbohydrates are absorbed first, then nitrogenous substances, and fats most slowly. In man some few observations show that absorption is similar to that in the dog. W. D. H.

A Reversible Phenomenon in the Action of Intestinal Juice on the Products of Casein Digestion. E. S. London (*Zeitsch. physiol. Chem.*, 1911, **74**, 301—304).—The intestinal chyme after feeding on casein is jelly-like; on removal from the body it becomes fluid in a few days under antiseptic conditions. The jellying is due to enzyme action, and is directly proportional in its velocity to the amount of intestinal juice; it runs parallel to the rate of formation of peptides, and is hastened by sodium carbonate. Its subsequent liquefaction is due, not to intestinal, but to other enzymes. The phenomenon is similar to plastein reactions. W. D. H.

The Action of Intestinal Juice on the Digestive Products of Various Proteins. E. S. London and S. K. Solowéeff (*Zeitsch. physiol. Chem.*, 1911, **74**, 309—310).—No single protein was found to be entirely decomposed by intestinal juice into peptides; the amount of cleavage was least for elastin; casein, gliadin, horse-flesh, gelatin, and dog's plasma follow in the order named. W. D. H.

The Specific Adaptation of the Digestive Juices. IV. The Relative Amount of Enzymes in the Intestinal Chyme on Different Diets. E. S. London and R. S. Krym (*Zeitsch. physiol. Chem.*, 1911, **74**, 325—327).—No adaptation of the amount of enzymes to the amount of the kind of food given was found to occur in the intestine; indeed, lipase is in excess when pure protein food is given. W. D. H.

Ereptase of the Intestinal Juice. Giuseppe Amantea (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 74—78).—The author has experimented with the secretion of isolated portions of the intestine of the dog produced with the aid of various mechanical and chemical stimuli. The juice is allowed to act on solutions of Witte's peptone or of Merck's casein, and the quantity of amino-acids formed is estimated by Sörensen's method. It appears that the secretion of the intestine proper does contain an ereptase. Differences can be observed between the activity of the secretions obtained with different stimuli, but they are not very marked, and the juice collected under the action of one and the same stimulus may exhibit considerable variation. The quantity of amino-acids produced is greater from peptone than from casein in almost all cases. R. V. S.

The Laws of Digestion and Absorption. X. The Disappearance of a Solution of Dextrose from the Stomach. E. S. London and W. F. Dagéeff (*Zeitsch. physiol. Chem.*, 1911, **74**, 318—321).—The emptying from the stomach of a 5% solution of dextrose follows the formula $x=k\sqrt{M/(t+p)}$, where p is $Mk^2/100^2$, and k is 10·35. The stomach empties in from thirty to sixty minutes. W. D. H.

The Laws of Digestion and Absorption. XI. Absorption of Proteins and Carbohydrates. E. S. London and O. E. Gabrilowitsch (*Zeitsch. physiol. Chem.*, 1911, **74**, 322—324).—The quantity of carbohydrate and protein absorbed is directly, and of water indirectly, proportional to the square-root of the quantity present, unless the concentration is abnormally great. The quantity of intestinal juice (N) which is secreted in dextrin-digestion varies directly with the square-root of the substance (M) dissolved: $N = k\sqrt{M}$; $k = 0 \cdot 1755$.
W. D. H.

The Bleaching of Flour. J. M. Hamill. **Chemical Changes Produced in Flour by Bleaching.** Gordon W. Monier-Williams (*J. Hygiene*, 1911, **11**, 142—166, 167—187).—These papers are abstracts of Local Government Board reports. The first is mainly technical, the second deals at greater length with the chemical changes produced, and the effect of bleaching on the digestibility of flour and bread. The digestibility of bleached flour is reduced. Salivary digestion was especially investigated. W. D. H.

Carbohydrate Metabolism and Glycosuria. Frederick W. Pavy and William Godden (*J. Physiol.*, 1911, **43**, 199—208).—Dextrose absorbed from the alimentary tract or intravenously injected in rabbits becomes fixed, and does not show itself either in blood or urine. This power of fixation is not unlimited, and is less when the sugar is injected rapidly, or when the amount of sodium chloride in the blood is increased. The fixing capacity, it is suggested, is due to bioplasmic incorporation carried out by lymphocytes, leucocytes, and growing bioplasm on other cells. W. D. H.

Carbohydrate Metabolism. II. The Prevention and Inhibition of Pancreatic Diabetes. Frank P. Underhill and Morris S. Fine (*J. Biol. Chem.*, 1911, **10**, 271—285. Compare this vol., ii, 910).—Removal of the pancreas from a dog may be followed by glycosuria within two hours. This is prevented by previous injections of hydrazine. The effect of a single hypodermic injection of 50 mg. of hydrazine sulphate per kilo. of body-weight may last two to four days. The amount of blood sugar in animals so treated and depancreatised is below the normal, or is at any rate not increased. If the injection is made during the course of pancreatic diabetes, the excretion of sugar in the urine is completely inhibited. After the administration of hydrazine, the presence of adrenaline in the adrenal bodies may still be demonstrated. In this respect hydrazine differs from phosphorus. The tentative hypothesis advanced can only be fully understood by the full presentment of it in the original paper; the underlying assumption, however, is that there exists an inter-relation between the pancreas, liver, and adrenals which normally keeps the amount of blood sugar constant. When the pancreas is removed, facilitation of carbohydrate katabolism is lost, and the opposing effect of the adrenals has full sway. Hydrazine, like phosphorus, is considered to diminish adrenal activity. W. D. H.

The Importance of Lipoids in Nutrition. Wilhelm Stepp (*Zeitsch. Biol.*, 1911, 57, 135—170).—If mice received food freed from lipoids by alcohol and ether, they died in a few weeks. This is not due to alteration in the saline constituents, or to the removal of fats. Fat added to the extracted food does not delay the fatal result; the addition of the alcohol-ether residue does. The important materials are lipoids, and are contained in the milk plasma. Lecithin and cholesterol alone are not the materials in question. Boiled milk supports life in mice as well as unboiled; but food free from lipoids, *plus* boiled milk, killed half the mice used; if unboiled milk is used instead, health remains perfect. W. D. H.

The Action of Some Non-protein Nitrogenous Compounds on Nitrogenous Metabolism of the Carnivora with Special Reference to Ammonium Acetate. Ernst Pescheck (*Pflüger's Archiv*, 1911, 142, 143—207).—If ammonium acetate is added to the food of dogs, even in comparative small amount and for a short time, the nitrogen is utilised. If it is intravenously injected, it has a strongly stimulating action, leading to noteworthy loss of nitrogen from the body. Ammonium tartrate has a harmful effect on nitrogenous metabolism. Asparagine caused nitrogen retention, but in a second experiment on the same dog, this was not confirmed.

W. D. H.

The Value of Different Amino-acids in the Organism of the Dog under Different Circumstances. Emil Abderhalden, Alberto Furno, Erich Goebel, and Paul Strübel (*Zeitsch. physiol. Chem.*, 1911, 74, 481—504).—Knoop has shown that in the dog, β-benzylpyruvic acid is transformed into anilinobutyric acid. This opens up the possibility of the transformation of one amino-acid into another, and thus the elucidation of many metabolic problems. As a preliminary to further work on such lines, the effect on the urine of fasting dogs was investigated; the principal experiments recorded in the present paper deal with glutamic and aspartic acids, asparagine and histidine; these were given alone or in conjunction with sucrose or pyruvic acid. The results given in full tables are very inconstant; sometimes even with the same substance there was a fall, sometimes a rise, either in total nitrogen, ammonia-nitrogen, or amino-acid nitrogen of the urine. As a rule, there was no appreciable effect at all, and the changes where they do occur are very slight.

W. D. H.

Creatine and Creatinine. I. The Rôle of the Carbohydrates in Creatine-Creatinine Metabolism. Lafayette B. Mendel and William C. Rose (*J. Biol. Chem.*, 1911, 10, 213—264).—A carbohydrate diet, absolutely nitrogen- and fat-free, produces a marked reduction in the elimination of total nitrogen and creatine in fasting rabbits. If it is continued for two or three days, creatine disappears from the urine. Alcohol produces no decrease; a pure fat diet produces no decrease; and a diet of mixed fat and protein also causes no reduction in creatine elimination. An increase in the elimination of total creatinine (that is, creatine *plus* creatinine) is always accompanied by an increase in the output of total nitrogen; it does not follow that the reverse is true; carbohydrates, in contrast to other foodstuffs, prevent the excretion of creatine, and are therefore indispensable for normal creatine-creatinine metabolism. The parallelism of total creatinine and total nitrogen output in inanition and with nitrogen-free diets is ascribed to a common source, namely, tissue or endogenous metabolism. The metabolism of exogenous or reserve protein is not accompanied by a production of creatine or creatinine. The intimate relation of creatine excretion (or the failure of its conversion into creatinine) to carbohydrate metabolism is discussed in full; experimental interference with the latter (such as phloridzin poisoning, which depletes the carbohydrate store, or phosphorus poisoning, which disturbs the glycogenic function) leads in dogs to an increased output of creatine. W. D. H.

How far can Protein Katabolism in Inanition be Diminished by Feeding on Carbohydrates? W. WIMMER (*Zeitsch. Biol.*, 1911, **57**, 185—236).—The experiments were performed on dogs, and it was found that feeding on carbohydrates can effect a sparing of protein to the extent of 55%; this is greater than the effect of gelatin. Starch and dextrose are about equal, provided the intake is divided into several meals per day. Pathological conditions appear to affect the result. W. D. H.

Protein Metabolism in the Dog. CHARLES G. L. WOLF and EMIL ÖSTERBERG (*Biochem. Zeitsch.*, 1911, **35**, 329—362).—The changes produced in the metabolism by giving quantities of protein, carbohydrate, and fat respectively insufficient for the body needs to a starving dog were investigated, the nitrogen and sulphur output and the distribution of these elements amongst various constituents by the urine being determined. It was found that the protein ingestion covers the sulphur lost by the body far more effectively than the nitrogen loss, and, in fact, in one case it was found that the body was retaining sulphur whilst losing nitrogen. The ratio of the amide- and urea-nitrogen to the total, tends to increase when protein is ingested; the ammonia-nitrogen remains more or less proportional to the total nitrogen. The creatinine-nitrogen is not affected, except that it appears to be somewhat less during the first period of protein ingestion than during starvation. The creatine appears on the third day of starvation, and disappears after ingestion of carbohydrates and proteins, but not of fat. The ratio of the residual nitrogen to the total diminishes after protein ingestion. The ratio of total sulphuric acid to total sulphur increases as the output of the latter increases in the urine; for example, after protein ingestion. The ethereal sulphur is independent of the food, and has no relationship to the indican excreted. Carbohydrate ingestion after starvation decreases the amide- and urea-nitrogen ratio, but increases the ammonia-nitrogen ratio. Like proteins, carbohydrates cause a disappearance of creatine. They also cause an increase, both absolute and relative, of the residual nitrogen and sulphur. Ingestion of fat hardly alters the distribution of the nitrogen, as compared with what exists during absolute starvation. S. B. S.

Metabolism of Development. III. Qualitative Effects of Pregnancy on Protein Metabolism in the Dog. JOHN R. MURLIN (*Amer. J. Physiol.*, 1911, 28, 422—454).—In pregnancy, nitrogen is retained, and the urea and ammonia in the urine are relatively low, the nitrogen which would normally be excreted in these forms being re-synthesised to make good the depletion of the blood proteins caused by the product of conception. The creatinine, uric acid, and undetermined nitrogen show in consequence a relative increase. The same is true for sulphur; the inorganic sulphate in the urine is decreased, being held back for fœtal development, and the "neutral sulphur" increased. On the days preceding parturition, creatine was found in the urine; this is indicative of tissue changes in the uterus. W. D. H.

The Influence of the Various Components of Diet and of the Ingestion of Various Iron Preparations on Iron Metabolism. MARTIN KOCHMANN (*Biochem. Zeitsch.*, 1911, 36, 268—274).—The experiments were carried out on the same lines as the previous work of the author on calcium and magnesium metabolism. Dogs were fed on meat diets containing a known quantity of iron. The effect on the iron metabolism of increase of proteins, or of the addition of sugar and carbohydrates to the meat diet, was investigated. The addition of all these constituents of diet to the original diet appeared to exert an unfavourable influence, in that it increased the negative balance. The minimal quantity of iron necessary for iron equilibrium depends therefore on the quantity and character of the diet. The administration of ferratin, metaferrin, and ferric phosphate can influence the iron metabolism favourably, converting a negative into a positive balance, or increasing a positive balance where this previously existed. No marked difference can be definitely stated to exist in the action of the three iron preparations, although the organic preparations appear to exert a more favourable influence. S. B. S.

The Heat Production in the Vital Oxidative Processes of Eggs I.—III. OTTO MEYERHOF (*Biochem. Zeitsch.*, 1911, 35, 246—279, 280—315, 316—328).—In view of the study of the relationships between various morphological changes (membrane formation, bifurcation, etc.) produced in the eggs of sea-urchins and other animals by both natural and artificial causes (fertilisation, treatment with narcotics, hypertonic solutions, etc.), and the amounts of oxygen utilised under different conditions, by Loeb and by Warburg (this vol., ii, 211), the author undertook the study of the amounts of heat produced under various conditions. The eggs were placed in a Dewar flask kept in a thermostat, and the heat changes during the vital process were measured by a Beckmann thermometer immersed in the vessel. Details are given as to the method of determining the calorimetric water value of the vessel, and of the various corrections to be applied, and the apparatus is figured. The oxygen used up was estimated in a second vessel kept in as nearly as possible under the same conditions as the first, with addition of a known quantity of eggs, a modification of Winkler's method being employed for this purpose.

The nitrogen in the eggs was determined by Kjeldhal's method, and the results expressed in terms of calories developed per hour per 140 mg. of nitrogen. It was found that, in the case of sea-urchin's eggs after fertilisation, this was 4·0—4·2 calories in the first hour, and in the following hours, 4·5—5, 5·3—5·8, 6·0—6·5, and 7·8—9, etc. The stage of development of the eggs during this interval was also noticed. The heat produced in the consumption of 1 mg. oxygen ("caloric quotient" of oxygen respiration) was also determined. This was found in cases of normal fertilisation to be 2·65—2·75. This same quotient was also determined under various conditions of artificial membrane formation. The results obtained are discussed in some detail by the author. S. B. S.

The Lipoids of Egg-Yolk. Cesare Serono and Antoinetto Palozzi (*Chem. Zentr.*, 1911, ii, 772; from *Arch. farm. sperim.*, 1911, **11**, 553—570).—One hundred grams of fresh yolk yield 14—17% egg oil, 11—12% lecithin, and 4% lutein. The last two were extracted with alcohol, and the first-named by extracting the alcoholic residue with ether. The residue after extraction with alcohol and ether was free from fatty acids. The egg-oil has a yellow colour, and smells like olive oil; it solidifies at 15°; it is neutral, and does not show absorption bands or optical activity, and does not contain cholesterol. Various constants (iodine number, etc.) are similar to those of olive oil. It is easily saponified. It contains 68·68% triolein and 30·04% tripalmitin. Lutein and lecithin were separated by acetone, in which reagent the lecithin is insoluble. The lecithin yielded palmitic and oleic acids and choline. Lutein crystallises out from acetone in fine needles and plates, and in large, fluorescent lamellæ. In the air it is rapidly oxidised by an oxydase in the yolk, and became reddish-yellow in colour. It is saponifiable with difficulty, and on decomposition yields free cholesterol and free fatty acids (cholesterol 39%, oleic acid 34%, and palmitic acid 9%). Lutein is regarded as an ethereal combination of cholesterol and fatty acids; glycerol was not detected. A synthetically prepared ester of similar composition was more resistant than lutein and less soluble in alcohol. W. D. H.

The Chemistry and Energy Dissipation in Sleeping Children. John Howland (*Zeitsch. physiol. Chem.*, 1911, **74**, 1—12).—A calorimeter of the Benedict-Atwater type was used for observations on three children, three to seven months of age. Details are given of the diet, excretions, heat production, etc., in each, and these results are compared with those obtained from ill-nourished or feeble children. The law that heat production is proportional to the surface area of the body is true only for those who are well nourished. W. D. H.

Choline in Ox-Brain. Max Kauffmann (*Zeitsch. physiol. Chem.*, 1911, **74**, 175—178).—Gulewitsch felt doubtful whether the small amount of choline he obtained from ox-brain was free, or, more probably, a decomposition product. If hydrolysis of lecithin or other phosphatide is prevented by the avoidance of hydrolytic agents, no free choline is discoverable. W. D. H.

Cholesterol Obtained from the Skull Contents of an Egyptian Mummy. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1911, **74**, 392—393).—The brain-pan of an Egyptian mummy contained a brown, wax-like mass, from which a number of crystals had separated. These are identified as cholesterol. E. F. A.

The Function of the Choroid Glands and its Relation to the Toxicity of Cerebro-spinal Fluid. S. P. Kramer (*Brain*, 1911, **34**, 39—44).—A normal saline extract of the choroid gland (choroid plexuses) injected into an anæsthetised animal intravenously causes a temporary fall of arterial pressure; no effect on the heart beat is noticeable. A similar effect obtained by the intravenous injection of certain specimens of cerebro-spinal fluid from pathological cases is attributed to excess of the choroid secretion. W. D. H.

Swelling Capacity of Nerve Tissue. Julius Bauer (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 112—116).—The influence of the addition of small quantities of hydrochloric, nitric, sulphuric, lactic, acetic, and boric acids to water on the swelling capacity of nerve tissue has been investigated. The data show that the swelling of nerve tissue of rabbits and cats is diminished by all six acids if the concentration is greater than $0·0005N$. Similarly, the swelling of human brain tissue is decreased in all cases if the concentration of the acid is greater than $0·001N$. These results show that acids have a dehydrating effect on the swelling of nerve tissue, as has been already found in the case of lipoids. Fischer's theory, according to which œdema is due to the increased swelling of tissue consequent on the formation of acid substances, cannot therefore be accepted in so far as brain and nerve tissue are concerned.

Salts diminish the swelling capacity of human brain tissue, and a similar influence is found in the case of non-electrolytes. In the case of very dilute acid solutions, the swelling is sometimes greater, sometimes less, than for pure water. H. M. D.

Fat Removal in Peripheral Nerve-degeneration. W. Kelman Macdonald (*J. Path. Bact.*, 1911, **16**, 71—74).—Nerve-degeneration was produced in rabbits by cutting the sciatic. The nerves were examined by the Marchi method. Six days after the operation, the fatty débris had not been carried beyond the confines of perineurium; five days later it had reached the septa between the nerve bundles. A few days later the amount inside the perineural sheaths was greatly lessened. Phagocytic and scavenger cells are the main agents in the transport. W. D. H.

Qualitative Analysis of Tissue Lipoids. J. Lorrain Smith and W. Mair (*J. Path. Bact.*, 1911, **16**, 131—134).—The material is fixed by formaldehyde, and methods are described for estimating the acidity of the chloroformic extract, the total alkali used in saponification, the cerebrosides, the cholesterol both free and combined as esters, and phosphorus to indicate the amount of phosphatide. The method of saponification used (barium hydroxide) completely saponifies fat and lecithin, but leaves the cerebroside almost untouched. Contrasting the brain of the child and adult, it was proved that phosphatides are more abundant, and cholesterol and cerebroside less, in the child. In cases of hemiplegic softening, the cholesterol, especially that in ester form, is increased, but the cerebroside and the phosphorus are reduced. In cases of general paralysis, cholesterol is normal in amount, but cerebroside and, to a less extent, the phosphorus are reduced.

W. D. H.

The Influence of Lecithin on Absorption by the Skin. S. BORSCHIM (*Biochem. Zeitsch.*, 1911, **35**, 471—477.—The hair was partly removed from rabbits, and the influence of lecithin in various preparations on the absorption of potassium iodide, eserine sulphate, tetanotoxin, and other substances, when rubbed into the hairless skin, was investigated, the urine being examined for these substances. Lecithin appears to promote very slightly the absorption of potassium iodide, but had no effect on the resorption of the other substances. The author used in a modified form Paolini's method for estimating colorimetrically the iodine in urine. S. B. S.

The Significance of Oxygen for the Growth of Mammalian Tissue. LEO LOEB and MOYER S. FLEISCHER (*Biochem. Zeitsch.*, 1911, **36**, 98—113).—The experiments were carried out by transplanting tissues to an artificial medium of blood-plasma, which was afterwards allowed to clot. The influence of oxygen on the formation of new tissue in this artificial medium was investigated.

A certain oxygen tension is necessary for growth under these conditions. In the complete absence of oxygen, the tissue dies, and it loses not only its capacity for growth, but also its phagocytic capacity. If the amount of oxygen ordinarily available is diminished, as, for example, by covering the tissue with the plasma coagulum, the growth of the cells and the number of surviving cells are diminished. Normal growths and carcinomata behave similarly, and no marked difference could be noticed between epithelial and connective tissue; the latter appears, however, to be somewhat more resistant when deprived of oxygen. Increase of oxygen tension in the atmosphere surrounding the plasma coagulum generally increases the peripheral surface of living tissue and also the processes of growth (mitoses).

S. B. S.

Creatine and Creatinine. II. Inanition and the Creatine Content of Muscle. LAFAYETTE B. MENDEL and WILLIAM C. ROSE (*J. Biol. Chem.*, 1911, **10**, 255—264).—In the rabbit and fowl in inanition, an increase occurs in the percentage of creatine in their muscles, and there is no reasonable ground for doubting the origin of urinary creatine and creatinine in endogenous metabolism. Contrary results reported by Howe and Hawk in the dog are severely criticised. The increase may be due (1) to a removal of the non-creatine portion of the muscle, or (2) to an increased formation of creatine. Reasons are given why the first is probably the correct view to take.

W. D. H.

Antipneumin. FR. BATELLI and MLLE. LINA STERN (*Biochem. Zeitsch.*, 1911, **36**, 114—143. Compare this vol., ii, 748).—Antipneumin is the substance which exists in many tissues, and has the capacity of diminishing primary respiration. It is precipitated with the nucleoprotein when an aqueous extract of the tissues is acidified with acetic acid (1 in 1500), and if the precipitate thus obtained be dried, a powder can be obtained containing antipneumin, which retains its specific action for a long period. Muscles and heart contain little, if any, antipneumin; the spleen is the richest in this substance. It is destroyed by heating to 65°, by moderate concentrations of acid and alkali, and by treatment with alcohol and acetone. It is not destroyed by peptic digestion, and is not dialysable. It is carried down generally with precipitates. It does not digest fibrin. Its action is inhibited by blood and by phosphates, and in investigating the content of any tissue in antipneumin, care must be taken to take into account the amount of phosphates present. Its inhibitory action on pnein is not immediate, but can only be detected after it has acted for some time. If tissue is allowed to remain in contact with an antipneumin solution and then washed, its respiratory capacity is not inhibited, and the antipneumin action appears therefore, at any rate after a short contact, to be reversible. There is no evidence that pnein and antipneumin are directly antagonistic. The action of the latter on primary respiration affects both the oxygen consumption and carbon dioxide output, so that there is little effect on the respiratory quotient. It has no action on the accessory respiratory processes (on the alcohol oxydase, urico-oxydase, or the oxidation of succinic acid). It inhibits the oxidation by the tissues, on the other hand, of citric acid (a primary oxidative process). It appears to regulate chiefly the post-mortal oxidative processes. S. B. S.

The Magnitude of the Work of the Liver. OTTO PORGES (*Biochem. Zeitsch.*, 1911, **36**, 342—343).—In reference to Verzár's paper with this title (this vol., ii, 746), the author claims that his own experiments (Abstr., 1910, ii, 785), carried out with a different technique, are of value in arriving at conclusions as to changes of respiratory quotient produced by throwing the liver out of general circulation. S. B. S.

Inversion of Sucrose by Bees. A. KORNDOERFER (*Chem. Zentr.*, 1911, ii, 777; from *Apoth. Zeit.*, 1911, **28**, 659).—Two bees were transferred in the autumn to an empty honey-comb and fed with a 50% solution of sucrose. After half an hour, the sugar transferred to the comb was removed; it retained 42—44% of invert sugar. A single passage of the sugar solution through the honey sack of the bee suffices to invert 80% or more. E. F. A.

Peptolytic Enzymes in Parasitic Worms. Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1911, **74**, 409—410).—Unless working under strictly comparable conditions the yield of tyrosine from silk-peptone is only a rough measure of the amount of peptolytic enzyme present. The intestinal contents of various intestinal worms gave wholly negative results by this and by the optical method. But if the worms were chopped up, the extracts showed the presence of peptolytic enzymes in large amounts, and the biggest yield was obtained from the intestinal walls of such worms. W. D. H.

The Shield of Chelone Imbricata. Hans Buchtala (*Zeitsch. physiol. Chem.*, 1911, **74**, 212—220).—Investigation of various epidermal horny appendages has shown great differences in their composition. The horny plate of the tortoise was subjected to hydrolysis and estimation of amino-acids with the following results. Glycine, 19·36; alanine, 2·95; valine, 5·23; leucine, 3·26; phenylalanine, 1·08; tyrosine, 13·59; cystine, 5·19, and glutamic acid, 0%. The high percentage of glycine and of tyrosine, the low percentage of leucine and cystine, and the absence of glutamic acid are remarkable. Of the total nitrogen, 94·84% is in the form of mono-amino-acids, 0·02% as melanin, 3·04% as ammonia, and 3·09% as diamino-acids.
W. D. H.

Experimental Glycosuria. VII. The Amount of Glycogenase in the Liver and in the Hepatic Blood as Affected by Stimulation of the Splanchnic Nerve. John J. R. Macleod and R. G. Pearce (*Amer. J. Physiol.*, 1911, **28**, 403—421).—Stimulation of the great splanchnic nerve of the dog increases the reducing power of the blood issuing from the liver, but no increase in the glycogenolytic power of the liver-extracts. The blood issuing from the liver possesses the same glycogenolytic power before and during stimulation of the nerve. The conclusion is drawn that modifications in the glycogenolytic activity of the liver do not depend on changes in the amount of glycogenase, but on changes in the conditions under which a constant amount of this enzyme is acting.
W. D. H.

Isolation of the Individual Acids in Bile. Fritz Pregl and Hans Buchtala (*Zeitsch. Physiol. Chem.*, 1911, **74**, 198—211).—The crude acids obtained by boiling ox bile with sodium hydroxide for twenty-four hours and then acidifying have been separated from each other by a modification of Langheld's process (Abstr., 1908, ii, 211). The results in the main confirm those of Langheld, the acids being obtained in the following percentages (calculated on the quantity, 674 grams, of the dry, crude acids): fatty acids, 10·8; cholic acid, 51·2; deoxycholic acid, 13·5; choleic acid, 11·9; uncrystallised acids, 12·6. Contrary to the previous experience of the authors and of Langheld, it was found that, with this particular bile, sodium cholate did not crystallise from the boiling alcoholic solution.

In the course of the research it became evident that the presence of the fatty acids prevents the isolation of the specific bile acids by any short process. However, by the following method, 50—70% of the specific bile acids can be obtained in a crystalline state directly from the aqueous solution of the bile after it has been boiled with sodium hydroxide (3·75 mols.) for twenty-four hours. The aqueous alkaline solution (after one extraction with ether to remove the cholesterol, if desired) is treated with ether, acetic acid (3 mols.) is added, and then hydrochloric acid (3·75 mols.) under stated conditions. The crystalline mass which separates consists essentially of cholic, choleic, deoxycholic, and a small quantity of the higher fatty acids, whilst the aqueous solution contains the greater portion of the fatty acids and of the deoxycholic acid. The crystalline mass is digested with alcohol, and is thus separated into a sparingly soluble residue containing cholic and choleic acids, and an alcoholic solution of deoxycholic and the fatty acids. The separation of the constituents of the several fractions does not present any difficulty.

Of the two preceding methods, the former is the more certain and more generally applicable; human bile has been examined by both processes, without success by the latter method, whilst by the former the crude acids have been almost entirely separated into the individual, crystalline constituents. C. S.

Compounds of the Aromatic Series as Cholagogues M. Petrowa (*Zeitsch. physiol. Chem.*, 1911, **74**, 429—435).—Sodium benzoate and salicylate, thymol, phenol, guaiacol, and menthol all cause a great increase in the secretion of bile, and all of them are excreted as ethereal sulphate. Thiocol (potassium *o*-guaiacolsulphonate) has no such action; it is itself an aromatic sulphonate, and therefore the liver can effect no further union with sulphuric acid. W. D. H.

The Bile of the Hippopotamus. Olof Hammarsten (*Zeitsch. physiol. Chem.*, 1911, **74**, 123—141).—Hippopotamus bile does not give the ordinary reactions for bile pigment; when freed from mucus it has a reddish-green colour. It contains two pigments, which give absorption spectra like that of cholehæmatin (found also in sheep and ox-bile). It contains 10·9% of salts soluble in water, but insoluble in alcohol; these are mainly chlorides; carbonates come next, with a small amount of sulphates and traces of phosphates. Of the material soluble in alcohol, 95·4% is precipitable by ether. It is poor in phosphatides, but contains a substance similar to jecorin. Cholesterol is absent, and the material soluble in ether, which is very scanty, is olein with a little solid fat. The bile is rich in glycocholic acid, and contains also taurocholates; about 6·4% of the sulphur is in ethereal sulphates. The cholic acid from the taurocholate is the usual kind; the glycocholic fraction yields a little cholic acid, but this is not quite certain; its chief acid is one not hitherto found, although it resembles hyocholic acid in some points; it contains 1·2% of sulphur. W. D. H.

Colostral Fat. St. Engel and A. Bode (*Zeitsch. physiol. Chem.*, 1911, **74**, 169—174).—The colostrum of cows has been collected immediately after calving, on the following day, and also at subsequent intervals. The fat has been extracted and examined for the iodine number and also for the saponification number, Reichert-Meissl value, and Polenske value by Arnold's method. In agreement with previous observations, it is found that the iodine number, initially about 43, decreases as the period of lactation increases. The saponification number varies considerably (217·9—226·4 on the second day) in fats from different cows, but increases as the lactation period increases. The Reichert-Meissl value increases considerably (from 23·4 to 30·2) between the first and second day, then increases more slowly, and after about a week sinks to the normal value, 29·0. The Polenske value increases with the period of lactation, attaining the value for milk fat after the first week.

According to the preceding constants, the colostral fat of a cow distinctly shows the characteristics of a milk fat, but less pronouncedly. The transition of the colostral fat into milk fat is gradual, only the Reichert-Meissl values showing a marked increase from the first to the second day. The colostral and the milk fats exhibit slighter differences in the case of a goat than of a cow. C. S.

Influence of Sodium Chloride on the Excretion of Bromides.

Cesare Paderi (*Chem. Zentr.*, 1911, i, 1867; from *Arch. farm. sperim.*, 1911, 11, 196—213).—Dogs on a normal diet of cooked horse-flesh received 5 to 10 grams of sodium chloride and 2·5 to 5 grams of potassium bromide; the giving of the bromide increased the excretion of sodium chloride in the urine, and the elimination of bromide was increased by the administration of chloride. If the diet was free from chlorides, bromism was more readily induced than in normal animals, and bromides accumulated in the blood. The explanation is based on osmotic phenomena. W. D. H.

The Amount of Alcohol Excreted by the Animal Organism under Various Conditions. II. Influence of Muscular Work on the Excretion of Alcohol in Expired Air and Urine.

Wilhelm Voltz and August Baudrexel (*Pflüger's Archiv*, 1911, **142**, 47—88. Compare this vol., ii, 218).—A continuation of previous researches on the same subject. The factor specially investigated was the influence of muscular work; this increases the frequency of respiration, and it is this that leads to a greater amount of alcohol finding its way into the expired air than during repose. There is also a considerable increase in the amount of the ingested alcohol which leaves the body by the urine, although it still remains less than the amount expired. Full numerical details are given. W. D. H.

Free Amino-acids in the Intestinal Contents of Certain Mammals.

Emil Abderhalden (*Zeitsch. physiol. Chem.*, 1911, **74**, 436—444).—About one-fifth of the total nitrogen in the intestinal contents of dogs, pigs, oxen, and horses is contained in the form of free amino-acids. A few estimations are given of those which can be estimated by simple crystallisation; the ester method lead to great loss. In the case of dogs, the intestinal contents from 100 dogs were collected together; the estimation of amino-acid nitrogen works out at about 0·1 gram per dog. The material has to be boiled to prevent further enzymic cleavage of polypeptides. W. D. H.

Creatine and Creatinine. III. Excretion of Creatine in Infancy and Childhood. William C. Rose (*J. Biol. Chem.*, 1911, 10, 265—270).—Creatinine excretion in young children is very low. The muscles of a new-born infant contain more creatine than embryonic muscles, but less than adult muscle. This coincides with Mellanby's statement that age is an important factor. It will account for the low creatinine excretion in infants, and furnishes further evidence for the origin of urinary creatinine in muscle metabolism. Creatine is usually present in the urine until the age of puberty. It is conceivable that the demand for carbohydrates by growing tissues is so great that the cells are left in partial carbohydrate hunger, and are thus unable to perform the "endo-katabolic" activities as perfectly as in later life. W. D. H.

Studies on Water-Drinking. IV. The Excretion of Chlorides when Large Amounts of Water are taken between Meals. S. A. Rulon, jun., and Philip B. Hawk (*Chem. Zentr.*, 1911, i, 1867; from *Arch. intern. Med.*, 7, 536—550).—The investigations were performed on healthy young men in nitrogenous equilibrium. In two cases the urinary chloride increased on the day the water was taken, and then returned to normal; this is explained on the supposition that the secretion of gastric juice was increased, and the excess of hydrochloric acid was absorbed and excreted as ammonium chloride; the water would also stimulate protein katabolism in the tissues. In one case the increase of chlorides in the urine occurred on the day after the excess of water was taken; here it is considered that the diluted blood would seek to recoup its chlorides from the tissues, and that with the fall in intake of water, these would be excreted. W. D. H.

Fasting Studies. IV. (Studies on Water-Drinking. VII.) Allantoin and Purine Excretion of Fasting Dogs. S. R. Wreath and Philip B. Hawk (*J. Amer. Chem. Soc.*, 1911, 33, 1601—1622).—A study has been made of the allantoin-nitrogen and purine-nitrogen excretion of three adult dogs which were subjected to fasts of from forty-eight to ninety-six days and of a pup which was subjected to a seven-days' fast. The data obtained for the allantoin-nitrogen excretion show considerable variations, which appear to be functions of the age and development of the animals. A decreased excretion of purine-nitrogen was observed in all cases. The effect of a large increase in the ingestion of water during the fast produced a marked increase in the output of allantoin-nitrogen and a much more pronounced decrease in that of the purine-nitrogen. The sum of the allantoin- and purine-nitrogen excreted was higher during the four days in which large quantities of water were ingested than during any other four-day period of the fast, and this indicates that the water stimulated protein katabolism. E. G.

The Excretion of Quinine by the Dog, and a New Method for the Estimation of this Alkaloid. JULIUS KATZ (*Biochem. Zeitsch.*, 1911, **36**, 144—189).—In quinine salts the acid can be estimated quantitatively by titration with alcoholic potassium hydroxide solution, using Poirrier's blue as indicator. This method can also be applied to estimation of other cinchona alkaloids. If an alcoholic solution of quinine is evaporated with hydrochloric acid on a water-bath in presence of sodium chloride, the salt

$$C_{20}H_{24}O_2N_2,2HCl$$

can be obtained free from excess of hydrochloric acid and the mono-acid salt. To obtain quinine from urine, the latter is treated with half its weight of ammonium sulphate and extracted with a mixture of 1 part of chloroform and 3 parts of ether. The extract can be cleared with magnesia usta.

The dog excretes in the urine smaller amounts of quinine than does the human subject; only a small part remains unabsorbed in the fæces. The quinine excretion ceases the fourth day after ingestion. The amount excreted is less when the quinine is administered subcutaneously, and still less when given intramuscularly, than after ingestion *per os.* After administration of aristochin, the excretion (of quinine) is at first smaller than after quinine, but with continued administration, increases; the excretion also continues for a much longer period after the ingestion of the drug has ceased. Subcutaneous and intramuscular injections of quinine cause vomiting. S. B. S.

The Iron in the Urine of Domestic Animals. MAX REICH (*Biochem. Zeitsch.*, 1911, **36**, 209—239).—The estimation was carried out by means of a slightly modified Neumann method. The normal urines were found to contain on an average 1 mg. iron per kilo., somewhat about the same amount as is found in human urine. There was not much difference in the iron content whether the animals were fed on an iron-rich or iron-poor diet in the cases of dog, pig, and sheep. The iron is present as an inorganic ferric compound in the colloidal state, and can be precipitated from the urine by calcium chloride.

S. B. S.

Purine Metabolism in Diseases of the Liver. S. LA FRANCA (*Biochem. Zeitsch.*, 1911, **35**, 434—444).—Patients with liver cirrhosis were fed on diets free from purines, or containing known amounts of purines (or caffeine), and the amounts of uric acid and purine nitrogen excreted in the urine were determined under these two conditions. It was found in Laennec's atrophic cirrhosis, that the purine destruction in the body was defective, whereas in Hanot's hypertrophic cirrhosis the purine destruction was more or less normal. S. B. S.

Auto-intoxication and Nephritis in Rabbits. W. HENWOOD HARVEY (*J. Path. Bact.*, 1911, **16**, 95—104).—That products of protein decomposition (*p*-hydroxyphenylethylamine and the like) when formed in excess in the alimentary canal and absorbed may be factors in the production of renal disease is confirmed by the present experiments on rabbits. Nephritis was produced in the majority of the animals dosed with such substances, either given by the mouth or intravenously injected over considerable periods. Many also developed degenerative changes in the aorta. W. D. H.

The Action of Cholesterol Derivatives with Lecithin in the Syphilis Reaction. CARL H. BROWNING and J. CRUICKSHANK (*J. Path. Bact.*, 1911, **16**, 135—136).—The addition of cholesterol to lecithin increases the amount of complement absorbed in the presence of syphilitic serum. A large number of cholesterol derivatives were investigated, but none was found equal to cholesterol itself.

W. D. H.

Pharmacological Behaviour of Certain Insoluble Preparations of Mercury. I. EDUARDO FILIPPI (*Arch. farm. sperim.*, 1911, **11**, 457—474; Reprint).—The action of mercury compounds (HgCl, HgI, HgI_2, HgO, and mercury salicylate) was studied by digesting them with various organs *in vitro*, at 38°; fifteen hours later, after filtration and centrifugalising, the organic substance was destroyed and the mercury estimated electrolytically; the amount of mercury per 100 grams of organ (liver, spleen, muscle, kidney, etc.) varied between 0·02 and 0·2. Mercury sulphide does not go into solution. The mercury which is dissolved from the other compounds is in part dialysable and precipitable by hydrogen sulphide, in part dissolved in a colloidal state, and in part firmly united to organic substances. The latter compounds increase in amount with more lengthy (eight days) digestion at the cost of the other portions.

W. D H.

The Influence of Potassium Iodide on the Accumulation of Mercury in the Liver. FERDINAND BLUMENTHAL and KURT OPPENHEIM (*Biochem. Zeitsch.*, 1911, **36**, 291—300).—Mercury was estimated by Salkowski's method, the tissues being partly destroyed by potassium chlorate and hydrochloric acid. From an aqueous extract of the residue the mercury was deposited on copper, from which it was expelled by heating in a test-tube. The condensed metal was rendered visible by converting it into the iodide with iodine vapour. The experiments were carried out on rats and rabbits with a variety of mercury compounds (nitromercuribenzoate, diaminomercuribenzoate, mercuric chloride, asurol, etc.). It was found that the liver was the only organ in which the mercury was constantly found. It was also observed that the rate of excretion after subcutaneous injection of compounds easily soluble in water was not always more rapid than in the case of those compounds which are only slightly soluble. If potassium iodide is administered simultaneously with the mercury compounds, the deposition of mercury in the liver was inhibited. S. B. S.

The Behaviour of Ethylene Glycol, Propylene Glycol, and Glycerol in the Animal Body. SOICHIRO MIURA (*Biochem. Zeitsch.*, 1911, **36**, 25—31).—When glycerol or ethylene glycol is given to animals either by the mouth or subcutaneously, no derivatives of glycuronic acid or other reducing substances are found in the urine. Propylene glycol, on the other hand, is excreted as a derivative of glycuronic acid, which may be isolated from the urine as barium propyleneglycolmonoglycuronate. W. J. Y.

The Action of Intravenous Injections of Concentrated Solutions of Sugar and Salt. G. G. WILENKO (*Arch. exp. Path. Pharm.*, 1911, **66**, 143—159).—Intravenous injection of concentrated salt solution in rabbits causes hyperglycæmia by stimulation of the central nervous system. The nerve stimulus is the cation. Another effect is first an increased and then a lessened permeability of the kidneys for sugar. This is determined by osmotic factors. The effect of concentrated solutions of dextrose on the kidney is the same, but less well marked. W. D. H.

The Behaviour of *o*-Iodoanisole in the Organism. RICCARDO LUZZATO and G. SATTA (*Arch. farm. sperim.*, 1911, **11**, 393—404; Reprint).—Doses of 5—6 grams of *o*-iodoanisole in dogs cause local excitation, but no toxic effects. It is excreted in part unchanged in the fæces; about 40% appears in the urine; a small fraction of the iodine is there in inorganic union; the greater part is present as ethereal derivatives, probably as esters of *o*-iodoquinol monomethyl ether (35% being present as sulphate and 65% as glycuronate).
W. D. H.

The Behaviour of Iodo-fat Derivatives of Cholesterol in the Dog's Body. EMIL ABDERHALDEN and EMIL GRESSEL (*Zeitsch. physiol. Chem.*, 1911, **74**, 472—480).—*α-Iodopropionylcholesterol* crystallises in tufts of needles, m. p. 115°; *β-iodopropionylcholesterol* crystallises in plates, m. p. 100°; *di-iodoelaidylcholesterol*, m. p. 90°, was not obtained in crystalline form. All three are badly absorbed, two-thirds of the iodine given being recovered in the fæces. Iodine passes into the urine for four or five days after the administration, and a considerable fraction of what is absorbed remains in the tissues. W. D. H.

Behaviour of Some Aliphatic Iodo-acids in the Organism. GIACOMO PONZIO (*Gazzetta*, 1911, **41**, i, 781—787. Compare Abstr., 1904, i, 548; 1905, i, 405).—In view of the use of calcium iodobehenate as a drug, the author has investigated the physiological action of some salts and amides of aliphatic iodo-acids formerly prepared by him. *Calcium α-iodopalmitate*, $Ca(C_{16}H_{30}O_2I)_2$, is an amorphous powder. *α-Iodopalmitamide*, $C_{16}H_{32}ONI$, is prepared: (1) from ammonia and 2-iodopalmityl chloride (obtained with phosphorus pentachloride); (2) from α-bromopalmitamide by heating it for some hours with an alcoholic solution of potassium iodide. The substance crystallises in large, lustrous laminæ, m. p. 108°. *α-Bromopalmitamide* crystallises in small, colourless plates, m. p. 85°.

Calcium α-iodostearate, $Ca(C_{18}H_{34}O_2I)_2$, is an amorphous powder. *α-Iodostearamide*, $C_{18}H_{36}ONI$, crystallises in large, lustrous laminæ, m. p. 112°. *α-Bromostearamide*, $C_{18}H_{36}ONBr$, crystallises in small, colourless plates, m. p. 91°.

The administration of the calcium salts is well supported by the organism, and they are absorbed, the iodine being liberated in the urine, but the amides pass through the gastrointestinal canal for the most part unchanged. R. V. S.

The Behaviour of Stereoisomeric Tartaric Acids in the Dog's Organism. CARL NEUBERG and SUMIO SANEYOSHI (*Biochem. Zeitsch.*, 1911, 36, 32—36).—When dogs were fed with either *d*- or *l*-tartaric acid, the same percentage of the total acid reappeared unchanged in the urine, whilst when racemic acid was given, the acid found in the urine was still optically inactive. There is thus no evidence that *l*-tartaric acid is used up in the body more quickly than *d*-tartaric acid (compare Brion, Abstr., 1898, ii, 618). W. J. Y.

The Method of Action of Phenylcinchonic Acid on the Purine Metabolism of the Dog. KONRAD FROMHERZ (*Biochem. Zeitsch.*, 1911, 35, 494—502).—The influence of the administration of atophan (phenylcinchonic acid) on the allantoin, uric and phosphoric acid excretions of dogs in different circumstances of nutrition was investigated. Somewhat varying effects were obtained. The author believes that the most probable action of the drug is the increase of the capacity of the kidneys for excreting the degradation products of nucleic acid. When this capacity has already reached its maximum, the action of the drug would naturally have no effect. S. B. S.

The Influence of Saponin on the Physiological Action of Digitoxin. J. J. POSTOÉEFF (*Biochem. Zeitsch.*, 1911, 36, 335—341). —The investigation was undertaken with the object of determining whether saponins increase the toxic action of digitoxin, Straub's method of perfusion through the frog's heart being employed. To produce the death of the heart, within a half hour, it was found that doses of 0·025 mg. and upwards were necessary. If 0·02 mg. saponin be present in the Ringer's solution (2 c.c.), then a dose of only 0·02 mg. digitoxin was capable of producing death (cession of ventricular beat) within this period. S. B. S.

The Action of Crystalline Aconitine on the Isolated Frog's Heart. CURT HARTUNG (*Arch. exp. Path. Pharm.*, 1911, 66, 1—57).— A detailed experimental study of the action of aconitine on the frog's heart. The effect is a depressant one, first the ventricular and then the auricular beats being extinguished. The heart-muscle is paralysed. W. D. H.

The Action of Crystalline Aconitine on the Motor Nerves and Skeletal Muscles of Cold-blooded Animals. CURT HARTUNG (*Arch. exp. Path. Pharm.*, 1911, 66, 58—70).—The effect of aconitine on nerves is first stimulating (unless the solution is very dilute), then paralysing. The question whether the drug acts also on the motor endings of the nerve in muscle is discussed. W. D. H.

Adrenaline Immunity. N. WATERMAN (*Zeitsch. physiol. Chem.*, 1911, 74, 273—281).—Various explanations of the so-called adrenaline immunity are discussed, such as a change in the substance in the myoneural junction on which adrenaline acts, a paralysis of the autonomic nervous system, and the relationship between adrenaline administration and an increase of the blood-sugar. No very definite conclusion is reached. W. D. H.

Influence of Caffeine on the Ureopoëtic System of the Liver. Giovanni Battista Zanda (*Chem. Zentr.*, 1911, i, 1602; from *Arch. farm. sperim.*, 11, 125—135).—Diuretin and caffeine increase the sugar and urea in the blood, and the urea in the liver. This increase may explain the diuretic power of these drugs.

W. D. H.

The Influence of Substances of the Digitalin Group on Blood-pressure in the Rabbit. Hernando (*Arch. exp. Path. Pharm.*, 1911, **66**, 118—131).—The rise of pressure produced by strophanthin and helleborein is variable, but is especially small in chloralised animals. If the pressure is first lowered by bleeding, the rise is more pronounced. The effect is mainly of cardiac origin, and chloral lessens the excitability of cardiac muscle. W. D. H.

The Action of Morphine, Codeine, Dionine, and Heroine, on Breathing. B. von Issekutz (*Pflüger's Archiv*, 1911, **142**, 255—272).—From experiments on rabbits, the conclusion is drawn that there is no qualitative difference in the action of the four drugs mentioned in the title on respiration. All of them lessen the number of inspirations, also their volume and energy, if the animal to start with is breathing normally. If, however, the breathing is superficial, these drugs increase the volume and the energy of the respiratory act. W. D. H.

The Influence of Tetrahydro-β-naphthylamine on Temperature and Respiratory Exchange. N. Mutch and Marcus S. Pembrey (*J. Physiol.*, 1911, **43**, 109—129).—This compound causes rapid respiration, convulsions, excitation of sympathetic nerves, and other symptoms which may end fatally. Particular attention was paid to the rise of temperature which occurs, and is due to increase of muscular action produced by action on the central nervous system. This is antagonised by anæsthetics. W. D. H.

Action of β-Iminazolylethylamine [4-β-Aminoethylglyoxaline]. Henry H. Dale and Patrick P. Laidlaw (*J. Physiol.*, 1911, **43**, 182—195).—This compound produces a vaso-dilator fall of blood pressure in carnivora, monkey, and fowl. This is a direct effect of the base. It slightly retards blood coagulation, accelerates the flow of lymph in the thoracic duct, and lowers body temperature.

W. D. H.

Biochemical Investigation of Aromatic Mercury Compounds. Ferdinand Blumenthal (*Biochem. Zeitsch.*, 1911, **35**, 503—505. Compare this vol., ii, 577).—A reply to Schrauth and Schoeller (this vol., ii, 687). S. B. S.

The Mechanism of Antagonistic Salt Action. JACQUES LOEB (*Biochem. Zeitsch.*, 1911, **36**, 275—279).—The author recapitulates several of his recently published results on the toxic action of sodium chloride on marine organisms, all of which show that the toxic action ceases to exist when potassium chloride and calcium chloride are present in the same relative proportions as they exist in blood and sea-water. He gives reasons for showing that this combination of salts is no mere nutrient medium, but ascribes their combined action to their effect on the colloids. The three salts in the proper relative proportions so act on the colloids (of the egg membrane, etc.) that these have just the correct permeability for salts and other substances which is necessary for the maintenance of the correct vital conditions. As the proteins alter in presence of different cations and anions (Pauli) as regards their physical character, the salts being quantitatively different in their actions in this respect, no other combinations can be substituted for the combination of the chlorides of sodium, potassium, and calcium as they exist in sea-water. S. B. S.

Nerve Excitability in Oxalate Poisoning. RICHARD CHIARI and ALFRED FRÖHLICH (*Arch. exp. Path. Pharm.*, 1911, **66**, 110—117). —The excitability of the vagus to faradic stimulation is lowered, and its susceptibility to atropine is increased, in oxalate poisoning. Calcium chloride in cases of slight poisoning by oxalates antagonises these effects. The excitability of autonomic nerves is affected in the same way, although the movements of the small intestine are unaffected. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Optional Forms of Lactic Acid Produced by Pure Cultures of Bacillus Bulgaricus. JAMES N. CURRIE (*J. Biol. Chem.*, 1911, **10**, 201—211).—Various strains of this bacillus from different sources in pure cultures produce different varieties of lactic acid. The *d*-lactic acid strain predominates. In some cases inactive lactic acid is formed, which probably necessitates the presence of both dextro- and lævo-acid-producing enzymes in the same organism. The bacilli of *B. Bulgaricus* type in human fæces and human saliva are identical. Some strains produce small amounts of succinic acid, which may account for the presence of this acid in Cheddar cheese.

W. D. H.

The Influence of Strychnine on Bacteria. WL. S. SADIKOFF (*Centr. Bakt. Par.*, 1911, i, **60**, 417—425).—Experiments showed that certain bacteria were able to grow in bouillon to which had been added 0·2—5·0% of strychnine phosphate, sulphate or chloride. The organisms were found to be more sensitive when grown on strychnine agar, but *Proteus*, *Bacillus subtilis*, *B. mesentericus*, *B. coli*, and *B. typhi* were able to grow in the presence of 0·5% of the phosphate. *Staphylococcus aureus* and some moulds were more resistant; the former organism becomes non-chromogenic when strychnine chloride is used instead of the phosphate. In like manner, the secretion of tryptase, invertase, and maltase is checked, or the enzymes are destroyed.

The non-toxic behaviour of these salts is believed to be due to the deposition of free strychnine by ammonia and basic amides formed in the cultures. H. B. H.

Action of Gypsum on Nitrification. SERAFINO DEZANI (*Chem. Zentr.*, 1911, ii, 157; from *Staz. sper. agrar. ital.*, 1911, **44**, 119—137).—Soil (1—2 grams) with magnesium carbonate (2 grams), a solution of an ammonium salt (200 c.c.), and gypsum (0·5 to 2·0°/$_{00}$), both with and without organic matter, was inoculated with *B. Nitrosomonas* and with *B. Nitromonas* respectively, and the ammonia, nitrites, and nitrates estimated from time to time. Similar experiments were made with an artificial soil and with soil (500 grams). Nitrification was not materially increased by the presence of gypsum.

N. H. J. M.

Sugar Tests and Pathogenicity in the Differentiation of Streptococci. J. M. BEATTIE and A. G. YATES (*J. Path. Bact.*, 1911, **16**, 137—138).—Forty-two strains were investigated. Gordon's tests do not differentiate those which are pathogenic and those which are not. W. D. H.

Fixation of Nitrogen by Yeasts and other Fungi. CHARLES B. LIPMAN (*J. Biol. Chem.*, 1911, **10**, 169—182).—Eighteen organisms, yeasts, pseudo-yeasts, and moulds were found to show a more or less pronounced power of fixing atmospheric nitrogen. The highest amount fixed was 2·94 mg. per gram of mannitol by pseudo-yeast Tulare No. 46b in solution of mannitol in distilled water. *Aspergillus niger* and *Penicillium glaucum* fix nitrogen as stated by previous observers. *Botrytis cinerea*, a parasitic fungus, has the same power. W. D. H.

Fermentations with Yeast in Absence of Sugar. III. CARL NEUBERG and LÁSZLÓ KARCZAG (*Biochem. Zeitsch.*, 1911, **36**, 60—68).—In earlier communications (this vol., ii, 320, 520) it was shown that a number of substances other than sugars give off carbon dioxide when treated with yeast.

In the cases of pyruvic, *d*-tartaric, and glycerophosphoric acids, it is now found that this evolution of carbon dioxide in presence of yeast is accompanied by a considerable disappearance of the substance. The other products of the fermentation have also been isolated in the cases of pyruvic and oxalacetic acid (next abstract).

The carbon dioxide is therefore due to a true fermentation of the substance, and not to an increase in the auto-fermentation of the yeast, as was obtained by Harden and Paine (Proc., 1911, **27**, 103) by the addition to yeast of a molar solution of sodium chloride or ammonium sulphate. On the other hand, the authors were only able to repeat the results obtained by Harden and Paine on rare occasions, neutral salts, as a rule, producing on the contrary an inhibition of the auto-fermentation. This difference in behaviour is ascribed to the difference between English and German yeasts. W. J. Y.

Fermentations with Yeast in Absence of Sugar. IV. A New Enzyme in Yeast-Carboxylase. CARL NEUBERG and LÁSZLÓ KARCZAG (*Biochem. Zeitsch.*, 1911, **36**, 68—75).—Free pyruvic acid and oxalacetic acid in solutions of 1% are fermented by yeast with production of carbon dioxide and acetaldehyde: $CH_3{\cdot}CO{\cdot}CO_2H = CO_2 + CH_3{\cdot}CHO$; $CO_2H{\cdot}CH_2{\cdot}CO{\cdot}CO_2H = 2CO_2 + CH_3{\cdot}CHO$. The acetaldehyde may be detected by distilling the mixture and isolating from the distillate by means of the *p*-nitrophenylhydrazone. These decompositions are not brought about when yeast which has previously been heated is employed, but are found to occur with yeasts which have been killed with acetone, toluene, etc. It is therefore due to an enzyme to which the name *carboxylase* is given.

When potassium pyruvate is fermented, the reaction goes somewhat differently, potassium carbonate being formed: $2CH_3{\cdot}CO{\cdot}CO_2K + H_2O = 2CH_3{\cdot}CHO + CO_2 + K_2CO_3$. In this case some of the carbon dioxide will be held in solution, forming potassium hydrogen carbonate, and the aldehyde will be polymerised in presence of alkali. The fermentation of potassium pyruvate is therefore more difficult to demonstrate. W. J. Y.

Fermentations with Yeast in Absence of Sugar. V. Carboxylase. CARL NEUBERG and LÁSZLÓ KARCZAG (*Biochem. Zeitsch.*, 1911, **36**, 76—81).—This enzyme was found to be present in all the different races of yeast tried; almost all yeasts fermented pyruvic acid, whilst all fermented oxalacetic acid. The action of the enzyme may readily be demonstrated by incubating at 38°, 12 c.c. of a 1% solution of the acid with 2 grams of yeast in a Schrötter's fermentation tube. After twenty to twenty-five minutes a quantity of carbon dioxide will have collected, and the liquid in the tube will smell of acetaldehyde, the presence of which may be confirmed by its *p*-nitrophenylhydrazone.

The enzyme is distinct from zymase. W. J. Y.

The Theory of Disinfection. REGINALD O. HERZOG and R. BETZEL (*Zeitsch. physiol. Chem.*, 1911, **74**, 221—241).—Various antiseptics (chloroform, mercuric chloride, phenol, etc.) were investigated, and yeast was the organism selected for experiment. Adsorption plays a part in the process, and this is reversible; it follows the logarithmic law. This is the first phase in disinfection; the second is the chemical action of the disinfectant on the micro-organism; the law for this part of the action is not a simple one, as determined by counting the dead cells, and requires further investigation. W. D. H.

Inhibiting Action and Germ-destroying Power of Free Sulphurous Acid, its Salts, and other Complex Derivatives. EKKEHARD HAILER (*Arb. Kais Gesundheits-Amt,* 1911, 36, 297—340).—An account of comparative tests with solutions of various concentrations on moulds, yeasts, and bacteria. The experiments are divided into two classes, the "static" series, in which the nutritive mixtures containing the organism were allowed to remain under the influence of varying concentrations of the respective inhibiting reagents, and the "kinetic" series, in which the organism was submitted for a certain time to the inhibiting reagent, a culture then transferred to the nutritive broth, and the presence or absence of life demonstrated. The resistance of the organism to the concentration of the disinfectant, as a rule, followed the order, that if the concentration of the germicide sufficient to kill the very sensitive bacteria be taken as unity, then yeast would require four times, and moulds five times, that concentration for their destruction.

The compounds employed were sulphuric and sulphurous acids, sodium and sodium hydrogen sulphites, and the sodium sulphite compounds of acetone, formaldehyde, acetaldehyde, and dextrose respectively, their action being compared with each other and with phenol. F. M. G. M.

The Respiration of Plants. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1911, 35, 228—245).—The destruction of the structure of the cells (by grinding in a mortar) causes in some plants an increased and in others a diminished respiration. The disintegration of the killed material, in contrast to the results obtained with the living material, has either no influence on the respiratory energy, as measured by the carbon dioxide output, or increases it. When the plants are killed, the anaerobic processes become more prominent; the more important the rôle played by such processes in the living plant, the less is the respiratory process of the plant interfered with when it is killed. The effects of various substances on the respiratory energy were also investigated. It was found that sugar solutions which had been fermented with zymin, and to a greater extent neutralised extracts of the corresponding quantity of zymin, or expressed yeast juice, stimulate the respiratory energy of pea and wheat seeds. Quinine has no effect on the respiration of sprouting pea seeds.

S. B. S.

The Nutrition of Green Plants with Formaldehyde and Formaldehyde-yielding Substances. THOMAS BOKORNY (*Biochem. Zeitsch.*, 1911, 36, 83—97).—Stronger solutions of formaldehyde are toxic to plants. From dilute solutions, however (0·001%), spirogyra, which has been rendered starch-free by keeping in the dark and treatment with calcium nitrate, can synthesise starch. Cress, also, which has been rendered starch-free, can form starch if kept under a bell-jar over sodium hydroxide solution to which has been added not too much formaldehyde (0·1%). With methylal, plants remained alive, but did not form starch until they were exposed to light. Algæ can form starch from the sodium bisulphite compound of formaldehyde if disodium or dipotassium phosphate is present, which renders the sodium sulphite set free harmless. With flowering plants, on the other hand, no definite positive result was obtained when this substance was used. Methyl alcohol stimulates the growth of pea-seedlings. S. B. S.

Amounts of Substances Yielding Hydrogen Cyanide in Some Fruit Seeds. PAUL HUBER (*Landw. Versuchs.-Stat.*, 1911, **75**, 462—482).—Native pear seeds contain no amygdalin, or not more than 0·0025%. Apple seeds were found to contain approximately the amounts of amygdalin found by Lehmann (0·46—1·21%). The seeds of sweet apples generally contain less hydrogen cyanide than those of sour apples. Seeds of apple and pear quinces cannot be distinguished by the amounts of amygdalin they contain.

Seeds of stone fruits contain considerably more hydrogen cyanide-producing substances than hitherto supposed. As much as 0·3% of hydrogen cyanide was obtained in some cases, corresponding with 5% of amygdalin.

No relation seems to exist between the amount of total nitrogen in the seeds and the amount of glucosides producing hydrogen cyanide. N. H. J. M.

Phytase in Lower Fungi. ARTHUR W. DOX and ROSS GOLDEN (*J. Biol. Chem.*, 1911, **10**, 183—186).—An enzyme which decomposes phytin into inositol and phosphoric acid was first noted in rice bran by Suzuki and his colleagues. It is probable that such an enzyme is present in all plants which contain phytin, or at any rate has a wide distribution. It has not been found in animal tissues; the present research shows that it occurs in various kinds of *Aspergillus*; the enzyme is present there in both the intra- and extra-cellular form. W. D. H.

The Inulinase of Aspergillus niger. J. BOSELLI (*Ann. Inst. Pasteur*, 1911, **25**, 695).—The secretion of inulinase by *Aspergillus* is the same whether inulin, sucrose, dextrose, lævulose, or sucrose and peptone are employed. The enzyme diffuses with ease into the culture liquid, especially when the culture is old.

The optimum acidity for the activity of the enzyme varies with the acid used and inversely with the temperature; at 51° the optimum concentration of sulphuric acid is *N*/200, and that of acetic acid *N*/12·5. At a given temperature the amount of change corresponds with the concentration of acid, optimum concentrations of acetic and sulphuric acids leading to equal changes. Slight alkalinity arrests the action of inulinase. The rate of change conforms to the logarithmic law. H. B. H.

Micro-chemistry of Plants. I. The Micro-chemistry of Birch Camphor. O. TUNMANN (*Chem. Zentr.*, 1911, i, 1656; from *Apoth. Zeit.*, 1911, **26**, 344—345).—When small, thin lamellæ of birch-bark are submitted to sublimation, the birch-camphor (betuline) is obtained as a crystalline sublimate; these crystals consist of long, fine prisms or needles, which are grouped together in masses. They are soluble in aniline, slightly soluble in aqueous chloral hydrate solution, acetic acid, and benzene, and insoluble in water, alcohol, light petroleum, carbon disulphide, chloroform, and ether. The crystals yield a yellow coloration when treated with sulphuric acid. The quantity of birch-camphor in birch-bark may be estimated by the micro-sublimation process, and tables are given showing percentages of camphor for different lamellæ. W. P. S.

Soluble Carbohydrate of Chestnut Flour. GIOVANNI LEONCINI (*Chem. Zentr.*, 1911, i, 1873; from *Staz. sperim. agrar. ital.*, **44**, 113—118).—The flour is extracted with water and a little lead acetate, and the filtrate polarised; about 26% of sucrose is present. Erythro-, amylo-, and acro-dextrin are absent. These are perhaps formed when the temperature at which the chestnuts are roasted is too high.
E. F. A.

Colour Changes Occurring in the Blue Flowers of the Wild Chicory, Cichorium intybus. JOSEPH H. KASTLE and R. L. HADEN (*Amer. Chem. J.*, 1911, **46**, 315—325).—The flowers of the blue variety of the wild chicory, *Cichorium intybus*, are blue when they first open, but in the course of a few hours undergo a remarkable series of changes, first becoming pink, then white, and, finally, brown. The present investigation was undertaken in order to ascertain the causes of this phenomenon.

It has been found that the colour changes are partly due to variations in the amount of acid contained in the pigment-cells and partly to the action of an oxydase occurring in the flower which oxidises and destroys the pigment. It is shown that the decomposition of the pigment can also be brought about by the oxydase of the potato as well as by various other oxidising agents, such as potassium ferricyanide and permanganate, *p*-benzoquinone, and hydrogen peroxide.

The flowers of the white variety of the wild chicory rapidly wither and turn brown, and in this case also an oxydase is present.
E. G.

Occurrence of Fraxin in Diervilla lutea. CHARAUX (*J. Pharm. Chim.*, 1911, [vii], **4**, 248—250).—The stalks and roots of the shrub *Diervilla lutea* (*D. Canadensis*) contain a glucoside which the author has identified as fraxin, a substance separated originally from *Fraxinus excelsior* and later from *Fraxinus ornus*, etc. A substance similar to saponin was also present. W. P. S.

Micro-Chemistry of Plants. II. Detection and Localisation of Andromedotoxin in Ericaceæ. O. TUNMANN (*Chem. Zentr.*, 1911, ii, 644; from *Apoth. Zeit.*, 1911, **26**, 555—556).—Thin sections of parts of the plant are shaken with water for ten minutes and then treated with concentrated hydrochloric acid; in the presence of andromedotoxin, a greenish-blue coloration is produced, which changes gradually to violet-red. With 25% phosphoric acid solution a violet-red coloration is also produced, and this coloration is still more intense when phosphoric anhydride is used. The compound is present in almost all parts of the leaves, the outer parts of the stalks, seed capsules, and buds of *Ericaceae*; it has a powerful toxic action.

W. P. S.

The Green and the Yellow Colouring Matters of the Florideæ. Harald Kylin (*Zeitsch. physiol. Chem.*, 1911, **74**, 105—122).—As a contribution to the solution of the vexed question whether the green colouring matter extracted from florideæ by alcohol is identical or not with the chlorophyll of higher plants, the author finds that the colouring matter from *Ceramium rubrum* contains magnesium (compare Willstätter and Isler, this vol., i, 392).

With regard to the yellow colouring matters in the florideæ, the author has isolated from *Ceramium rubrum* three substances; one of these is carotin, another is xanthophyll (probably identical with the xanthophyll of higher plants), whilst the third (fucoxanthin ?), which presents a great similarity to xanthophyll, but differs from it in its solubility in petroleum, is probably derived, not from the *Ceramium rubrum* itself, but from the diatomaceæ and fucoids with which it is unavoidably contaminated. C. S.

Composition of the Fat from the Seeds of Lophira Alata. Samuel S. Pickles and William P. Hayworth (*Analyst*, 1911, **36**, 493—494).—The fatty acids separated from this fat consisted of 50% of saturated acids comprising arachidic acid, m. p. 77·5°, palmitic acid, m. p. 62·5°, and a small quantity of another acid, and 50% of unsaturated acids consisting of about equal quantities of oleic acid and linoleic acid. W. P. S.

Composition of Para Rubber-seed Oil. Samuel S. Pickles and William P. Hayworth (*Analyst*, 1911, **36**, 491—492).—The composition of the mixed fatty acids obtained from a sample of Para rubber-seed oil was found to be: saturated (solid) acids, 14%, consisting of stearic acid, m. p., 69°, and an acid or mixture of acids, m. p. 56·5°; unsaturated (liquid) acids consisting of oleic acid, 32·6%, linoleic acid, 50·9%, and linolenic acid, 2·5%. W. P. S.

Composition of Pear and Apple Seeds. Paul Huber (*Landw. Versuchs-Stat.*, 1911, **75**, 443—461).—The dried seeds of two varieties of pears (1 and 2) and of apples (3) were found to have the following percentage composition:

					N			P as	
	Fat.	Sugar.	Fur-furoids.	Crude fibre.	as protein.	as bases.	Ash.	phos-phatides.	P as lecithin.
1.	24·84	5·13	6·72	10·90	4·961	0 205	3·83	0·048	1·23
2.	25·15	5·62	6·72	7·15	5·921	0·216	4·19	0·032	0·82
3.	24·03	3·42	6·66	3·96	4·87	—	3·79	0·038	0·99

The composition of the separated germs and husks is also given in each case. N. H. J. M.

Localisation and Distribution of the Essential Oil in "Bupleurum fruticosum" (Linn.). LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 111—117).—The essential oil is present in the form of minute drops in the epidermis of the leaves, and in the cells immediately beneath it, and is abundant in certain small vessels which terminate there. Young leaves contain much more than older ones. In the vessels of the stem, and in its epidermis (especially when young), the essential oil is present in considerable quantity, and is particularly evident in regions where growth is taking place. The root also contains it, but not in great amount. The oil is also present in the seed, to which it gives a strong, aromatic odour. R. V. S.

Oil and Cholesterols of the Soy Bean. HERMANN MATTHES and A. DAHLE (*Arch. Pharm.*, 1911, **249**, 424—435).—See this vol., i, 831, 858.

The Relation of Certain Non-leguminous Plants to the Nitrate Content of Soils. T. LYTTLETON LYON and JAMES A. BIZZELL (*J. Franklin Inst.*, 1911, **171**, 1—16, 205—220).—An account of numerous experiments intended to illustrate the relationship between soil, temperature, and nitrification, both in the presence and absence of growing crops. The results are tabulated, and the following facts deduced :

That the nitrate content of soil under timothy, corn, potatoes, oats, millet, and Soy beans was different for each crop when on the same soil.

There was a characteristic relationship between the crop and the nitrate content of the soil at different stages of growth.

During the most active growing period of the corn crop, nitrates were higher under corn than in cultivated soil bearing no crop ; under a mixture of corn and millet at this period, the nitrates were higher than under millet alone, although the crop yields were about the same in each case.

Both under corn and oats the nitrate content was higher during the period when the crop was making its greatest draft on the soil nitrogen than in the later stages of growth; nitrates under these crops and under millet failed to increase late in the season when nitrogen absorption had practically ceased, although uncropped soil showed a very large increase in nitrates at that time; this fact is accounted for on the supposition that plants in later periods of growth exert a retarding influence on nitrification.

Changes in the moisture content, or in the temperature of soil under crops during the growing season, did not materially affect the nitrate content except under the legume soy beans, but on uncropped soil an increased moisture content during September was accompanied by a marked increase in nitrates. F. M. G. M.

Analytical Chemistry.

Estimation of Moisture in Various Substances by means of Magnesium Methyl Iodide. TH. ZEREWITINOFF (*Zeitsch. anal. Chem.*, 1911, **50**, 680—691).—The process is briefly as follows: The substance (coal, starch, etc.) is treated with anhydrous pyridine and a solution of magnesium-methyl iodide in amyl ether is added. The operation is carried out in a kind of a Lunge nitrometer, which is fully described and figured in the original paper. The moisture, being rapidly absorbed by the pyridine, is at once acted on by the reagent, and the methane evolved, which represents the water, is then measured with the usual precautions. L. DE K.

Modified Cobalt Reaction for the Detection of Small Quantities of Hydrogen Peroxide. M. LEUCHTER (*Chem. Zeit.*, 1911, **35**, 1111).—To a 1% solution of crystallised cobaltous chloride is added an equal volume of a solution of 1·6 parts of borax, 20 parts of glycerol (D 1·24), and 100 parts of water. One to two c.c. of the mixture are placed in a very narrow test-tube, and an equal volume of the liquid to be tested is carefully poured over the surface. If hydrogen peroxide is present, a brownish-black ring is formed at the place of contact, and if much is present, a decided evolution of gas will be noticed.

The above reaction is also given by perborates, but not by persulphates. On warming, however, these also give the reaction. Addition of a few drops of sodium hydroxide solution also promotes the reaction sometimes. L. DE K.

Estimation of Fluorine [in Silicates]. M. KLEINSTÜCK (*Zeitsch. anal. Chem.*, 1911, **50**, 697).—A solution of zinc oxide in ammonium carbonate is recommended for the removal of the last traces of silica from the alkaline solution. L. DE K.

New Apparatus for the Estimation of Sulphur and Carbon in Iron and Steel. D. A. WENNMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 1861—1862. Compare this vol., ii, 938).—*Estimation of Sulphur.*—In the estimation of sulphur the material is often dissolved in concentrated acid, which necessitates the passage of the gases evolved through water. The author finds that it is not necessary to have a continuous stream of cooling water, and has therefore devised a special cooler for the gases, which is fitted into the decomposition flask by a ground-glass joint, the whole apparatus being made of glass. Everything is so arranged that the gases evolved from the flask have to pass through water contained in the cooler before escaping to the absorption vessels. There are also the necessary tubes for running the acid into the flask, and for passing a current of carbon dioxide through the apparatus towards the end of the estimation. A diagram is given of the apparatus, which is very compact.

Estimation of Carbon.—A condenser is fitted into the decomposition flask by a ground-glass joint, a special tube being sealed through the bottom of the condenser for leading gases free from carbon dioxide through the apparatus. A diagram is given. T. S. P.

Estimation of Sulphuric Acid in Soils. P. DE SORNAY (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, **29**, 133—136).—The soil (10 grams), with 1 gram of potassium nitrate and 5 c.c. of water, is dried on a sand-bath, ignited, treated with 25 c.c. of hydrochloric acid, and evaporated on a sand-bath until all the silica is rendered insoluble. It is then treated with 20 c.c. of hydrochloric acid and 5 c.c. of water, heated for thirty to forty-five minutes on a sand-bath, filtered, and washed with about 100 c.c. of water. Barium chloride is then added, and the estimation completed in the usual manner. N. H. J. M.

Rapid Estimation of Nitrogen. OSWALD CLAASSEN (*Chem. Zeit.*, 1911, **35**, 1130—1131).—Three grams of the dried and thoroughly powdered and mixed sample are heated in a Kjeldahl flask with 20 c.c. of sulphuric acid, 5 grams of potassium sulphate, and eight drops of mercury. Heat is applied first to the sides of the flask for ten minutes, after which the flask is placed in the usual position. The operation is finished within twenty to thirty minutes. In order to hasten the cooling, a small lump of ice may be introduced.

The soda solution used for the titration may be checked as follows. The ammonia evolved by boiling 1 gram of ammonium chloride with aqueous sodium hydroxide is collected in standard sulphuric acid, and the excess of acid is then titrated back. If the acid itself requires 146·1 c.c. of soda solution, and after the operation only 39·6 c.c., 106·5 c.c. of soda solution have been used up, corresponding with 0·262038 gram of nitrogen; 1 c.c. therefore equals 0·00245844 gram. L. DE K.

Apparatus for the Estimation of Nitrogen by Kjeldahl's Method. KRIEGER (*Chem. Zeit.*, 1911, **35**, 1063).—In order to avoid loss of ammonia during neutralisation, and bumping during distillation, the flask is provided with a tap-funnel, through which the alkali is introduced, the stem of the funnel having a branch through which steam may be passed.

A simpler method is to employ a large flask, of 500 c.c. capacity for 20 c.c. of sulphuric acid, and add a little mercury. After cooling, 250 c.c. of water are added, followed by 10 c.c. of 4% potassium sulphide and 50 c.c. of concentrated sodium hydroxide solution. Neutralisation and distillation are completed without loss of ammonia. C. H. D.

Analysis of Lime Salpetre, "Kalk Stickstoff," and "Stickstoff Kalk." E. DINSLAGE (*Chem. Zeit.*, 1911, **35**, 1045—1046).—*Lime Salpetre.*—The analysis (including the estimation of any nitrite) is conducted like that of an ordinary crude nitre. The moisture, however, cannot be readily estimated in the ordinary way, but may be determined within twenty minutes by heating 3—5 grams of the sample in a porcelain crucible over a small flame some 10 cm. distant from the crucible. Care must be taken that the mass does not melt.

"*Kalk Stickstoff.*"—The usual Kjeldahl process gives unsatisfactory nitrogen figures, but the following modification gives trustworthy results. One gram of the sample is boiled in a flask with 30 c.c. of a mixture of equal vols. of sulphuric acid and water, with addition of a few drops of mercury. The conversion into ammonia is complete in at most two hours; addition of potassium sulphate towards the last is superfluous. The ammonia is then distilled off as usual. The estimation of the various mineral constituents and pre-existing ammonia is carried out by the usual analytical methods.

"*Stickstoff Kalk.*"—The same process as for "Kalk Stickstoff" is recommended. This product is distinguished from the former by its dark colour and tarry odour, and by its chlorine content.

L. DE K.

Estimation of Phosphoric Acid by Direct Weighing of Ammonium Phosphomolybdate. NORBERT VON LORENZ (*Oesterr. Chem. Zeit.*, 1911, **14**, 1—5. Compare Abstr., 1908, ii, 777, 895, 983).—Experimental details of methods previously advocated for the direct estimation of phosphoric acid as ammonium phosphomolybdate in soils, manures, and vegetable ash are discussed. A detailed account is given of the author's method of preparing the required reagents, the amount of material to employ, and the modifications recommended in the respective cases of various soils, soluble phosphatic manures, basic slag, superphosphates, and bone meal.

F. M. G. M.

Estimation of Arsenic in Pyrites. GEORG HATTENSAUR (*Oesterr. Zeitsch. Berg. & Huttenwesen*, 1911, **59**, 175—178).—The author discusses Vilstrup's method for the analysis of pyrites (Abstr., 1910, ii, 458), and recommends that the arsenious sulphide be redissolved in hydrochloric (or hydrobromic) acid treated with bromine and subsequently heated to remove excess, the solution rendered ammoniacal, and the arsenic reprecipitated as magnesium ammonium arsenate; this is collected after twenty-four hours, redissolved, and estimated by any of the known methods, or the redissolved sulphide may be evaporated with nitric acid until free from chloride, the arsenic precipitated as silver arsenate, collected, ignited, and the metallic silver weighed.

F. M. G. M.

Detection of Small Quantities of Arsenic in Urine, Blood, and Other Organic Substances. GEORG LOCKEMANN (*Biochem. Zeitsch.*, 1911, **35**, 478—493).—The following processes are described: (1) The destruction of organic matter: for which fuming nitric acid and a mixture of potassium and sodium nitrates are employed. (2) The precipitation of the arsenic: which is brought about by adding ferric ammonium sulphate to the solution and precipitating therefrom ferric hydroxide by the quantitatively correct amount of ammonia solution. (3) The detection of arsenic in this precipitate by a specially constructed Marsh apparatus. The last traces of arsenic are removed from the reagents by the ferric hydroxide method, the full experimental details of which are given in the paper. S. B. S.

Estimation of Carbon in Irons and Steels in the Electric Furnace. HANS AUGUSTIN (*Zeitsch. angew. Chem.*, 1911, **24**, 1800—1803).—The process recommended is essentially the same as the one described by Lorenz (Abstr., 1893, ii, 491). The sprinkling over the iron with lead chromate cannot be recommended, but the use of copper oxide in the front part of the porcelain combustion tube is absolutely necessary to ensure complete oxidation of the carbon.

An electric furnace is described and figured, whereby it is possible to heat the iron at 1000° and the copper oxide layer at 800°. The combustion is carried out in a current of purified oxygen, and after passing through drying tubes containing sulphuric acid, the carbon dioxide is absorbed in the usual soda-lime tubes. L. DE K.

Analysis of Graphite. FRIEDRICH MAYER (*Chem. Zeit.*, 1911, **35**, 1024—1025).—The amount of carbon present in graphite may be estimated by taking the calorific value of the substance. In order to ensure the complete combustion of the graphitic carbon, 0·6 gram of the graphite is mixed with 0·4 gram of pure benzoic acid, and the calorific value of the mixture is determined in a Berthelot's bomb. One kilo. of graphitic carbon yields 7900 Cal., and 1 kilo. of benzoic acid, 6322 Cal. If the graphite under examination contains sulphur, an allowance must be made for its quantity. For this purpose, the sulphuric acid formed during the combustion is estimated by titrating the solution of the acid in the water contained in the bomb; for each c.c. of $N/10$ solution required for the titration, 7·06 Cal. are deducted from the result first obtained. W. P. S.

Detection of Carbon Monoxide by means of Blood. HARTWIG FRANZEN and O. VON MAYER (*Zeitsch. anal. Chem.*, 1911, **50**, 669—697).—The gas to be tested is shaken with blood (preferably ox-blood), which is then examined for carbon monoxide by one of the usual methods. The original Hoppe-Seyler sodium hydroxide process cannot be recommended, but the Salkowski modification of the same readily detects 1% of carbon monoxide in the blood. Salkowski's hydrogen sulphide method and Rubner's tannin process are less delicate, only showing 5% or above. The Kunkel and Welzel ferrocyanide method and their original tannin process are also capable of indicating as little as 1% of carbon monoxide. The full details of these processes, with some comments by the authors, are recapitulated in the original article. L. DE K.

Microchemical Analysis of Silicates. RICHARD CANAVAL *Zeitsch. prakt. Geol.*, 1910, **18**, 460—461).—A process by which the constituents of refractory minerals can be qualitatively determined. The finely powdered substance is thoroughly mixed with an equal volume of lead oxide, and carefully fused in small portions to a globule on an aluminium spoon; the cooled pulverised globule is then frequently evaporated with nitric acid, after which the silica, lead, and other constituents can be separated or identified by various processes described in the original. F. M. G. M.

Detection of Silicates, Fluorides, and Silicofluorides. PHILIP E. BROWNING (*Amer. J. Sci.*, 1911, [iv], **32**, 249—250).—A small lead cup about 1 cm. in diameter and depth is made by running the melted metal into a mould, and a flat piece of lead with a small hole in the centre is used as a cover. Into this cup is placed about 0·1 gram of powdered calcium fluoride, together with 0·1 gram or less of the silicate, and the mixture is carefully moistened with a few drops of sulphuric acid. Upon the upper side of the cover is placed a piece of moistened black paper, and upon this a small moistened pad of ordinary filter paper, so as to keep the black paper moist during the ten minutes' heating on a steam-bath. At the conclusion of the experiment a white deposit is found on the underside of the black paper over the opening in the cover if silica was present in appreciable amount. Conversely, the process may be used for the detection of fluorides by heating these with silica and sulphuric acid; silicofluorides are decomposed by sulphuric acid readily in the cold. L. DE K.

Qualitative Analysis of Metals without Employment of Hydrogen Sulphide or Ammonium Sulphide. G. P. PAMFIL (*Mon. Sci.*, 1910, [iv], **24**, II, 641—644).—The mixed metals are evaporated several times with nitric acid, whereby stannic oxide and antimony tetroxide are separated.

Silver chloride, mercurous chloride, and lead chloride are precipitated with hydrochloric acid; after boiling with ammonium chloride, bismuth oxychloride separates; the filtrate is rendered alkaline with potassium hydroxide, and ammonia eliminated by boiling; the solution is again cleared by boiling with hydrochloric acid, after which the addition of potassium hydroxide and hydrogen peroxide precipitates the oxides and hydroxides of manganese, cobalt, nickel, copper, mercury, iron, titanium, zirconium, uranium, and part of the magnesium; the solution is then acidified with hydrochloric acid and saturated with ammonia, when aluminium phosphate and hydroxide separate.

The solution is acidified, and on subsequent treatment with ammonium carbonate yields barium, strontium, and calcium carbonates, and when again acidified, followed by the addition of potassium ferrocyanide, furnishes zinc hydroxide; the further addition of hydrogen peroxide and ether precipitates the chromium, leaving only the arsenic and remainder of the magnesium, which are finally precipitated with excess of ammonium hydroxide. The further separation of the individual elements is carried out by known methods.

The presence of iron being found to vitiate the hydrogen peroxide test for titanium, the author recommends the employment of potassium persulphate in dilute sulphuric acid solution, accompanied by a control containing the equivalent colorimetrically in ferric sulphate to which hydrogen peroxide and a standard solution of a titanium solution can be added for comparison. F. M. G. M.

A Method of Qualitative Analysis. D. A. Roche (*Mon. Sci.*, 1911, [v], 1, I, 87. Compare preceding abstract).—An adverse criticism of Pamfil's method of analysing metals without the employment of hydrogen sulphide or ammonium sulphide; the author states that the possibility of other insoluble residues besides stannic oxide and antimony tetroxide remaining after treatment with nitric acid is not considered, and suggests the presence of silica, titanium oxide (TiO_2), and possibly barium sulphate; also, that the separation of lead is not complete, that the silver would be liable to be overlooked, and that phosphoric acid would be precipitated before the stage indicated by Pamfil. F. M. G. M.

Potassium: its Detection as the Cobaltinitrite. Leon T. Bowser (*J. Amer. Chem. Soc.*, 1911, 33, 1566—1569).—The sensitiveness of the author's method for detecting potassium as the cobaltinitrite (Abstr., 1910, ii, 346) can be greatly increased by carrying out the test in the following manner. Two tall beakers, of 50—100 c.c. capacity, are placed side by side on a mirror. In one beaker are placed 5 c.c. of the solution to be tested, and in the other, 5 c.c. of water, and to each are added 2·5 c.c. of the sodium cobaltinitrite reagent and 5 c.c. of 95% alcohol. If, on looking down through the solutions into the mirror, the image of the observer appears equally sharp in each case, potassium is not present, but if the image is dimmed by the liquid in the beaker containing the solution under examination, potassium is present to the extent of 2 or more parts per million. Care must be taken to ensure the absence of ammonia, since ammonium salts are readily precipitated by the reagent, 10 parts per million being sufficient to yield a visible cloudiness. It is also of importance that the solution should be either neutral or slightly acidified with acetic acid. E. G.

New Indicator for the Estimation of Alkalis in Blood. Paul Bernhardt (*Chem. Zentr.*, 1911, i, 1763; from *Wien. klin. Woch.*, 1911, 24, 606—607).—An indicator, consisting of a mixture of 2 volumes of 1% "alizarinsulphazid" solution and 1 volume of 1% indigo-carmine solution, is recommended for use in the estimation of alkalis in blood according to Engel's method (titration with *N*/75-tartaric acid solution); the indicator exhibits a dark green colour in acid solution, and reddish-violet in alkaline solution. W. P. S.

Estimation of Calcium and Magnesium in Hard Water. Günther Nothnagel (*Veroffentlichungen aus dem Gebiete des Militar-Sanitatswesens.*, Heft 45; *Arbb. Hyg.-chem. Untersuchungsstellen*, 1911, IV, Tl. 76—85. Compare Grittner, Abstr., 1902, ii, 696).—A review of the work of Winkler and Grittner, with numerous tables demonstrating the results obtained by various modifications in the experiments carried out by these and other workers.
F. M. G. M.

Estimation of Very Small Amounts of Calcium by means of Potassium Permanganate. Leon T. Bowser (*J. Ind. Engin. Chem.*, 1911, 3, 82—84).—The solution (5—10 c.c.) containing a minimum of 0·3 mg. of calcium is treated with a few drops of ammonium hydroxide and about 0·4 gram of ammonium chloride, boiled, and 0·2 gram of ammonium oxalate added, again boiled, and diluted with about its own volume of a 3% solution of ammonium hydroxide and allowed to remain several hours.

The precipitate is collected by suction on an asbestos pad in a tube of "Shimer" form, washed with 3% ammonium hydroxide, and the pad with adherent precipitate transferred to a beaker and treated with 1 c.c. dilute sulphuric acid (50%), titrated in boiling solution with excess of *N*/200-potassium permanganate, and the excess titrated back with *N*/200-oxalic acid. The amount of potassium permanganate consumed by the asbestos, water, and acid must be determined by blank experiments; the first titration of the asbestos oxidises all the impurities, and a second one should be made for the amount to be deducted in the future employment of that pad; one pad suffices for about twelve experiments. Special burettes graduated in 0·02 and 0·01 c.c. are employed, with the ends drawn out so that 10 drops are equivalent to 0·15 c.c. of the solution. The *N*/200-solution of permanganate is not oxidised as much as it should be by theory; therefore it must be standardised against a calcium oxalate solution of approximately the same concentration as that employed in the estimation. F. M. G. M.

Detection of Certain Elements which Form Insoluble Sulphates: Barium, Strontium, (Calcium) and Lead. PHILIP E. BROWNING and PHILIP L. BLUMENTHAL (*Amer. J. Sci.*, 1911, [iv], **32**, 246—248).—Ten c.c. of the solution are precipitated with hydrochloric acid, and to the filtrate are added 5 grams of ammonium acetate and an excess of 10% solution of ammonium sulphate. After warming the liquid, the sulphates are collected and washed with a saturated solution of ammonium acetate until free from lead; the filtrate and washings are then kept for further testing. After placing in the filter a little sugar carbon, the paper is rolled up and heated in a covered porcelain crucible to full redness for a few minutes. The fused mass is then heated with 5 c.c. of 50% acetic acid to decompose the sulphides formed. The filtrate is then tested for barium with potassium dichromate, and in the filtrate from the barium chromate the strontium and calcium are reprecipitated by boiling with sodium carbonate. The washed carbonates are re-dissolved in nitric acid, and the liquid is examined spectroscopically; if the amount is not too small, the nitrates may be separated by boiling with amyl alcohol.

L. DE K.

Estimation of Magnesium as Oxide. O. KALLAUNER (*Chem. Zeit.*, 1911, **35**, 1165—1166).—The author confirms the statements of Krause and others that magnesium chloride cannot be readily converted into oxide by simple ignition.

Berzelius's method (evaporation of the magnesium chloride solution with mercuric oxide, and ignition of the residue) gives technically correct results, provided that the operation is several times repeated, for even a double treatment with mercuric oxide gave in one of the author's experiments a residue which still contained chlorine. L. DE K.

Analysis of Cuprous Iodide. H. BARDT (*Zeitsch. anal. Chem.*, 1911, **50**, 695—696).—Five grams of the sample are repeatedly treated with dilute ammonia by decantation and filtration into a half-litre flask until the filtrate is free from copper. The residue is then treated with nitric acid in case it should still contain any copper.

An aliquot part of the ammoniacal solution is placed in a 500 c.c. electrolytic vessel, 5 grams of tartaric acid are added, and then again so much ammonia that there is an excess of about 1—1·5% present. From this solution, the copper is then separated electrolytically as usual. When completely deposited, the cathode is removed and carefully rinsed. The adhering copper is then dissolved in 30 c.c. of nitric acid, diluted to 500 c.c., and, after adding 5 c.c. of sulphuric acid, the solution is again electrolysed (*N.D.* 100—0·5 ampère), using the same cathode. Similarly, the copper is recovered from the nitric acid solution of the insoluble residue. Any copper present as sulphate may be extracted from the sample with water. To the liquid free from copper are added 20 c.c. of chloroform and then an excess of hydrochloric acid. The iodine liberated in then titrated with *N*/10-thiosulphate. L. DE K.

The Spectroscopic Recognition of Traces of Mercury in Nitrocellulose. Stability in Explosives. JEAN FLORIN (*Zeitsch. ges. Schiess. Sprengstoffwesen* 1911, **6**, 21—22, 63—66).—A detailed description of methods employed to demonstrate spectroscopically the presence of mercury in nitrocellulose. Illustrations of the spectroscope and other apparatus employed, with tabulated results and curves, are given in the original. F. M. G. M.

Time Curves for Cadmium Deposited from Organic Electrolytes. MARY V. DOVER (*J. Amer. Chem. Soc.*, 1911, **33**, 1577—1583). —Holmes and Dover (Abstr., 1910, ii, 1111) have shown that cadmium can be deposited in a satisfactory form from various organic electrolytes when the rotating spiral anode is employed and the current is less than one ampere, but that the character of the deposit varies considerably with the different electrolytes. Experiments have now been made to determine the rate of deposition and the quantity of the metal that can be deposited from each electrolyte in a sufficiently adhesive form to allow of accurate weighing. Curves have been constructed for each electrolyte, the time being plotted as the ordinates and the amounts of cadmium deposited as the abscissæ.

It has been found that the maximum quantity of cadmium which will form an adhesive deposit and the rate of deposition vary greatly with the different electrolytes. The data are recorded for cadmium acetate, formate, and lactate in each of the acetate, formate, and lactate electrolytes. The deposits are finer and more adhesive when the solution is decidedly acid, but if too much acid is used, the last traces of the metal cannot be deposited. E. G.

Estimation of Colloids in Arable Soil. JOSEF KÖNIG, JULIUS HASENBAUMER, and C. HASSLER (*Landw. Versuchs-Stat.*, 1911, **75**, 377—441).—The amounts of colloids in soils may be estimated by means of a solution of methyl-violet of such a strength that a distinct colour remains after absorption by the soil. Solutions containing 1, 2, and 3 grams per litre may be employed. Absorption of salts was estimated by means of a *N*/50-solution of tricalcium phosphate.

Potassium is chiefly absorbed by the colloidal clay, and it can be more or less completely liberated by oxidation with hydrogen peroxide or by an electric current. Phosphoric acid, on the other hand, is mainly chemically fixed by the production of insoluble phosphates of calcium, etc. The combination is rendered more complete by the action of heat, and even strong electric currents fail to dissolve the phosphoric acid completely.

A method is described for estimating the readily soluble constituents of soils by means of an electric current. The results, as regards potassium, are approximately the same as those obtained by steaming under pressure and oxidation. Results obtained by the latter method agreed well (in the case of potassium) with the amounts actually assimilated by plants. N. H. J. M.

Estimation of Ferric Oxide in the Presence of Alumina. KRIEGER (*Chem. Zeit.*, 1911, 35, 1054).—The weighed mixed oxides, which need not be powdered, are introduced into an Erlenmeyer flask and boiled gently with a mixture of 25 c.c. of sulphuric acid and 25 c.c. of water. After five to ten minutes the iron oxide has dissolved, as may be noticed from the colour of the undissolved alumina. When cold, another 50 c.c. of water and some zinc are added, and finally the iron is titrated with permanganate as usual. L. DE K.

Gravimetric Estimation of Nickel and Cobalt. L. DEDE (*Chem. Zeit.*, 1911, 35, 1077).—To the solution containing the nickel or cobalt is added a very slight excess of potassium hydroxide solution, and then a solution of potassium persulphate. When the supernatant liquid has become colourless, the precipitate is washed with cold water and then collected on a filter. After ignition the oxide is reduced by heating in a current of hydrogen, and the nickel, or cobalt, is then weighed as metal. Salts of ammonium should be absent. L. DE K.

Rapid Estimation of Nickel in Steel. G. RAULIN (*Mon. Sci.*, 1911, [v], 1, i, 84—86).—One gram of a steel containing about 10% nickel is dissolved in 10 c.c. hydrochloric acid diluted with an equal amount of water, boiled with 10 c.c. nitric acid, and treated with 200 c.c. water; ammonium hydroxide is added until the solution becomes red, but remains clear, followed by a calculated excess of potassium cyanide, and then by a further quantity of ammonium hydroxide, after which the solution is filtered and made up to a volume of 500 c.c. Half of this is removed, treated with 10 c.c. of ammonium sulphate solution, and five drops of potassium iodide solution, followed by titration with silver nitrate; 0·24% must be subtracted from the nickel found as due to the action of the cyanide. The solutions employed should contain respectively the following weight of each salt in grams to the litre: silver, nitrate 5·788; potassium cyanide, 4·45, accompanied by 0·5 of sodium hydroxide; potassium iodide, 200; and ammonium sulphate, 600. The duration of the operation is about half an hour. F. M. G. M.

Application of Methyl-orange in the Colorimetric Estimation of Titanium. André Gautier (*Rev. gén. Chim. pure appl.*, 1911, **14**, 16—17).—The stability of methyl-orange as a colorimetric reagent renders it suitable for employment in the estimation of titanium. The relative concentrations of the titanium and methyl-orange solutions which it is advisable to employ are tabulated in the original. F. M. G. M.

Assay of Platinum. Albert Steinmann (*J. Suisse Chim. Pharm.*, 1911, No. **32**, **33**, Reprint 8 pp.).—The usual process of cupellation with silver and lead and separation of the silver from the button obtained by boiling with sulphuric acid is not correct, as platinum, in the circumstances, is far from totally insoluble in the acid. The loss, however, is somewhat compensated by the platinum retaining some lead and silver.

The author has found that by using a slightly diluted acid (100 vols. strong acid, 22 vols. water) and heating at 240°, the solvent action of the acid on platinum is reduced to a minimum. The retention of lead and silver in the button may be prevented by adding a suitable amount of copper before cupellation. L. de K.

New Method for the Destruction of Organic Matter by Bromine, Specially Applicable in Toxicology. Georges Magnin (*J. Pharm. Chim.*, 1911, [viii], **4**, 302—306).—The substance to be destroyed is treated with bromine in a long-necked flask, and heated on the water-bath. The process is stated to be more rapid, and to give better results than the methods hitherto employed. W. O. W.

Estimation of Organic Matters in Waters from Sulphur Springs. Max Dittrich (*Zeitsch. anal. Chem.*, 1911, **50**, 697—700).—The usual method of permanganate titration cannot be applied to waters containing hydrogen sulphide unless the latter is first removed. The author recommends for this purpose a solution of cadmium sulphate. It is, however, necessary to analyse a sample freshly obtained, otherwise the sulphur is not completely removed, and too much permanganate will be consumed. L. de K.

Estimation of Caoutchouc as Tetrabromide; the Decomposition of the Bromide by Nitric Acid. David Spence, J. C. Galletly, and J. H. Scott (*Gummi Zeit.*, 1911, **25**, 801—803).—The experimental methods advocated by Korneck and Budde (this vol., ii., 545) for the estimation of bromine in caoutchouc tetrabromide are discussed, and a dozen experiments described which show that different results can be obtained by varying the experimental details; these include the presence or absence of silver nitrate during the decomposition and the employment of excess or otherwise, varying the concentration of the nitric acid and the temperature at which decomposition is carried out, and replacing sealed tubes by other forms of apparatus. F. M. G. M.

Hübener's Caoutchouc Tetrabromide. GERHARD HÜBENER (*Gummi Zeit.*, 1911, **25**, 634, 751—752); R. BECKER (*ibid.*, 677—678).—Polemical in reference to Hübener's methods for estimating bromine in caoutchouc tetrabromide. F. M. G. M.

A New Method of Estimating Alcohol Vapour. AUG. BAUDREXEL (*Woch. Brauerei*, 1911, **28**, 21—23. Compare Abstr., 1906, ii, 584).—A sketch of the apparatus employed, with an account of the method by which the author estimates minute quantities of ethyl alcohol colorimetrically by passing the vapour into a solution of potassium dichromate in sulphuric acid. F. M. G. M.

The Proportion of Dextrose to Lævulose in Certain Preserved Fruits. FAVREL and GARNIER (*J. Pharm. Chim.*, 1911, [vii], **4**, 253—255).—The authors find that apricot pulp, dried apricots, and prunes contain about twice as much dextrose as lævulose, and that, consequently, the detection of an excess of dextrose in preserves made from these fruits does not necessarily indicate that added dextrose is present. W. P. S.

Viscosity of Saccharine Solutions. PH. ORTH (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, **29**, 137—148).—The viscosity of saccharine solutions may be expressed by the following equations:

$$\log.(\log.\eta) = 0{\cdot}069498 - 2 + 0{\cdot}03381935(x + Kn) - 0{\cdot}009818782t$$

and $100K = 156{\cdot}89 - 0{\cdot}81586m + (0{\cdot}0187228m - 1{\cdot}38441)t$,

in which η is the viscosity compared with distilled water at $20° = 1$, x the amount of sugar % obtained by inversion (Clerget), n the non-sugar %, m the dry matter, and t the temperature. The equations hold good with percentages of sugar between 60 and 76, with dry matter between 65 and 82%, and at temperatures from 20° to 90°.

Viscosity increases very rapidly with diminished temperature, especially when the concentration is high. N. H. J. M.

Detection of Small Quantities of Disaccharides. CARL NEUBERG and SUMIO SANEYOSHI (*Biochem. Zeitsch.*, 1911, **36**, 44—55).—The method is applicable to those disaccharides which form phenylosazones.

Maltose may be detected in the presence of other disaccharides by converting into the osazones, dissolving in water, and treating with yeast maltase for two days. The maltosazone is converted by the enzyme into glucosazone and dextrose. The solution is filtered and treated with mercuric acetate, and the dextrose estimated in the filtrate by Fehling's solution after removal of the excess of mercury with hydrogen sulphide.

In this way 0·01 gram of maltosazone may be detected. *iso*Maltosazone is not attacked by yeast enzymes, but may be hydrolysed by heating with 1·5% sulphuric acid, when dextrose is set free and may be detected as before. Lactosazone and melibiosazone may be hydrolysed with emulsin or kefirlactase, or by heating with 1·5% sulphuric acid with formation of galactose and glucosazone. The method allows of the detection of these substances in presence of hexoses and of pentoses, the osazones of which will not be hydrolysed in the above manner. W. J. Y.

The Estimation of Carbohydrates by Oxidation with Permanganate in Alkaline Solution. W. GREIFENHAGEN, JOSEF KÖNIG, and A. SCHOLL (*Biochem. Zeitsch.*, 1911, 35, 169—193).—All carbohydrates, multivalent alcohols, the corresponding aldehydes and ketones, and polysaccharides are oxidised in alkaline solutions quantitatively to oxalic acid and carbon dioxide. The details of the method for estimating the oxidation products are given by the authors. If the oxidation is carried out with standardised permanganate solution and the reaction mixture is afterwards acidified, then by titration of the excess of permanganate with oxalic acid, the amount of oxygen used in the oxidation process can be determined. The terminal groups of the sugars appear to be oxidised in alkaline solution to carbon dioxide, the intermediate groups yielding oxalic acid. In the case of ethylene glycol and erythrol, the results obtained indicate the formation of polymerides as intermediate products. Formic acid was never detected amongst the oxidation products. S. B. S.

The Estimation of Starch. W. GREIFENHAGEN, JOSEF KÖNIG, and A. SCHOLL (*Biochem. Zeitsch.*, 1911, 35, 194—216).—The polarimetric method of Lintner's (polarisation after treatment with cold more concentrated hydrochloric acid) and of Ewer's (polarisation after treatment with warm more dilute acid) are applicable to all varieties of starch. The rotatory power by Lintner's process is about the same for all kinds of starch (+202°), whereas that by Ewer's differs for the different starches from maize, rice, wheat, rye, barley, and oats, but has a mean value of about 183°. In applying the method to fodder, etc., it is advisable to treat the material first with water, alcohol, and ether to remove other substances which effect the polarisation. Cellulose, hemicellulose, and pentosans have no effect in these processes. Condiments and foodstuffs can also be examined by the methods; in certain cases (for example, cinnamon) the material should be treated with hot alcohol before submitting it to either process. The conclusion is drawn that these processes are as valuable for examination of foodstuffs as the ordinary gravimetric methods. S. B. S.

Estimation of Volatile Acids in Wine. A. VERDA (*Chem. Zentr.*, 1911, ii, 643; from *Schweiz. Woch. Chem. Pharm.*, 1911, 49, 340—341).—The usual method of estimating the volatile acids in wine (titration of 200 c.c. of distillate obtained by distilling 50 c.c. of the wine with steam) appears to yield low results in the case of wines from Southern Italy; it is recommended, therefore, that the distillation be continued until the distillate no longer exhibits an acid reaction when tested with litmus paper, showing that the whole of the lactic acid present has distilled. W. P. S.

Estimation of Free Fatty Acids in Fats in the Presence of Soap and Alkaline-earth Soaps. DAVID HOLDE and JULIUS MARCUSSON (*Zeitsch. angew. Chem.*, 1911, 24, 1945—1948).—In order to prevent hydrolysis of the soaps, the following process is recommended for the estimation of free fatty acids in mixtures consisting of fat, mineral oil, soap, and calcium or magnesium soaps: Ten grams of the sample are boiled under a reflux apparatus with 50 c.c. of a mixture consisting of 9 vols. of "benzine" and 1 vol. of absolute alcohol until solution of the sample is attained. The hot solution is then filtered, and the filter is washed with a small quantity of the "benzine"-alcohol mixture. The filtrate and washings are now mixed in a separating funnel with 30 c.c. of 50% alcohol (by volume), shaken thoroughly, and titrated with *N*/10-alkali solution, using phenolphthalein as indicator; the end-point of the titration is indicated by the appearance of a pink coloration in the lower layer of the contents of the funnel (compare Abstr., 1910, i, 538). W. P. S.

Analysis of Lactic Acid. W. KLAPPROTH (*Chem. Zeit.*, 1911, **35**, 1026—1027).—The following process is recommended for the estimation of lactic acid and lactic anhydride in samples of commercial lactic acid. One gram of the acid is diluted with 20 c.c. of water and titrated with *N*/1-sodium hydroxide solution, phenolphthalein being used as the indicator. The quantity of alkali used corresponds with the lactic acid present, together with one-half of the anhydride. An excess of from 1 to 3 c.c. of the sodium hydroxide solution is now added, the solution is heated for five minutes on a water-bath, the excess of alkali is titrated with *N*/1-sulphuric acid, 1 c.c. of the latter is added in excess, and, after being heated for two minutes on a water-bath, the mixture is titrated with *N*/1-sodium hydroxide solution. The quantity of alkali used in these operations, after allowing for the sulphuric acid added, is equivalent to the second half of the lactic anhydride present. A simple calculation then gives the quantities of lactic acid and anhydride in the sample.

W. P. S.

[Estimation of Lactic Acid in Blood.] H. FRIES (*Biochem. Zeitsch.*, 1911, **35**, 368—385).—See this vol., ii, 994.

Estimation of Tartaric Acid in Apples, Pears, Cider, and Perry. G. WARCOLLIER (*Ann. Falsif.*, 1911, **4**, 485—490).—The author finds that, as a general rule, apples, pears, cider, and perry do not contain tartaric acid. For the estimation of this acid, when present, the method described by Kling (Abstr., 1910, ii, 359) was found to be the most trustworthy. The methods proposed by Berthelot and de Fleurieu, Pasteur and Reboul, Mestrezat (Abstr., 1906, ii, 635), and Muttelet do not yield satisfactory results.

W. P. S.

Detection of Small Quantities of Glycuronic Acid as Osazone. CARL NEUBERG and SUMIO SANEYOSHI (*Biochem. Zeitsch.*, 1911, **36**, 56—59).—The phenylosazone of glycuronic acid gives the naphtharesorcinol test (violet-colour when heated with naphtholresorcinol and hydrochloric acid). The colour may be extracted with benzene or chloroform, giving a violet solution. The presence of pentosazones, hexosazones, and disucrosazones does not interfere with the reaction, since no colour is extracted by the benzene or chloroform in these cases. If ether be used in place of benzene, the extract is always more or less violet with other osazones. In this way, 0·001 gram of glycuronic acid osazone may be detected. W. J. Y.

Estimation of Benzoic Acid. Otto Folin and Fred F. Flanders (*J. Amer. Chem. Soc.*, 1911, **33**, 1622—1626).—In an investigation of cranberries, it was found that the benzoic acid could be satisfactorily estimated by titrating a solution in chloroform, from which all the acids except benzoic had been removed, with sodium ethoxide solution.

In attempting to apply this method to the estimation of benzoic acid in ketchup, it was found that several other acids as well as benzoic acid are extracted by the chloroform, and, after numerous experiments, the following method was devised.

The ketchup (25 grams) is placed in a 50 c.c. beaker, 2 c.c. of concentrated nitric acid are added, and about 0·2—0·3 gram of sodium nitrite is introduced in small portions, the mixture being well stirred after each addition. The liquid is rinsed into a 500 c.c. separating funnel by means of 200 c.c. of saturated ammonium sulphate solution, and is then extracted five times with chloroform. The chloroform is transferred to another separating funnel, and shaken with 200 c.c. of a saturated solution of sodium chloride, slightly acidified with hydrochloric acid. It is then transferred to a third separating funnel, again shaken with 200 c.c. of the acidified salt solution, and then run off into a 500 c.c. Erlenmeyer flask and titrated with standard sodium ethoxide solution in presence of a few drops of alcoholic phenolphthalein.

The repeated washing with salt solution does not remove cinnamic acid, and any of this acid which may be present will therefore be estimated with the benzoic acid. The method is rapid and gives satisfactory results. It is also useful as a qualitative test. It is only necessary to shake the chloroform after titration with a small quantity of water, to separate and filter the aqueous solution, and add ferric chloride or apply Mohler's test. E. G.

Apparatus for the Estimation of the Melting Points of Fats. Leo von Liebermann (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 294—295).—The apparatus consists of a U-tube, the lower portion of which is filled with mercury; the fat under examination is poured in a molten condition into one of the limbs of the tube, and allowed to solidify. This limb is closed by a cork through which pass a thermometer, a platinum wire, and the stem of a small funnel; the bulb of the thermometer and the lower end of the wire are forced into the layer of fat, but do not touch the mercury. The other limb of the tube carries a platinum wire in contact with the mercury. A further quantity of mercury is now poured through the funnel so as to form a layer above the fat, and the tube is heated gradually in a water-bath after the two platinum wires have been connected with an electric bell and battery. When the fat begins to melt, the mercury above it passes downwards and causes the bell to ring by establishing a contact between the two wires. This point is taken as the "first melting point" of the fat; the point at which the fat becomes perfectly clear is the "highest melting point." W. P. S.

Estimation of Fat in Feeding-stuffs by means of Trichloroethylene. R. NEUMANN (*Chem. Zeit.*, 1911, **35**, 1025—1026).—Trichloroethylene is recommended as a solvent in the estimation of fat in such substances as oil-cakes, etc. Five grams of the sample are shaken for thirty minutes with 100 c.c. of the solvent, the mixture is then filtered, 50 c.c. of the filtrate are evaporated, the residue is dried, and weighed. The results obtained agree well with those yielded by the ordinary method of extraction with ether (compare Abstr., 1910, ii, 647). W. P. S.

Detection of Thujone [Tanacetone] in Absinthe. H. ENZ (*Chem. Zentr.*, 1911, ii, 576, 1556; from *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 337—440; 507—508).—For the detection of tanacetone in any liqueur, a portion of the latter is boiled with the addition of aniline phosphate, in order to destroy aldehydes, and then diluted with water until the alcoholic strength is reduced to 30% by volume. Five hundred c.c. of the solution are fractionally distilled, the distillate being collected in nine portions of 25 c.c. each. In the case of absinthe itself, it is better to reduce the alcoholic strength to 60%, and to collect 50 c.c. quantities of distillate. The portions of distillate, numbers six and seven, are then tested for the presence of tanacetone as described by Duparc (Abstr., 1909, ii, 188); these fractions are free from aldehyde, aniseed oil, and fennel oil. As certain essential oils, such as *Ol. hyssopii*, *calami*, *verbenae*, and *sabinae*, and also carvone and citral, give the same reaction as tanacetone, a liqueur which yields a positive reaction does not necessarily contain absinthe; a negative reaction, however, indicates the absence of absinthe.

The second paper is a reply to Philippe and Fellenberg (below). W. P. S.

Detection of Thujone [Tanacetone] in Absinthe. ERNST PHILIPPE and THEODORE VON FELLENBERG (*Chem. Zentr.*, 1911, ii, 797; from *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 418—420).—The authors point out several errors in Enz's process (preceding abstract). W. P. S.

Tannin Solutions. GEORG GRASSER (*Collegium*, 1911, No. 445, 46—52).—The author gives (in tabulated form) the results of treating various concentrations of tannin solutions with the following reagents: (1) Five % solution of tartar emetic: (2) the same with addition of ammonium chloride; (3) with ammonium acetate; (4) a solution containing 5% tartar emetic, 5% sodium chloride, 5% sodium hydrogen tartrate, and 20% sodium acetate; (5) ammoniacal zinc acetate solution; (6) an *N*/50-iodine solution, and (7) a solution of 10% sodium chloride and 1% gelatin. In very dilute solutions (0·006—0·001%) iodine gives a violet coloration, whereas the others have ceased to give any appreciable reaction, but this varies somewhat with tannins obtained from different barks. F. M. G. M. 5

General and Physical Chemistry.

Molecular Refraction of Azo-compounds. Henri Duval (*Compt. rend.*, 1911, 153, 874—875).—The position of substituents in the ring has very little effect on the molecular refraction of aromatic azo-compounds. In the case of azobenzene the index varies somewhat with the solvent, and increases slightly with the temperature; superfusion is without effect. Adopting Brühl's value for nitrogen, the calculated numbers for the molecular refraction with the *D*-sodium and α-hydrogen lines are lower than the actual values found with the lithium line, λ 670·5. W. O. W.

The Negative Pole Spectrum of Oxygen. F. Croze (*Compt. rend.*, 1911, 153, 664—665).—A new band, nearer the red than those previously recorded, has been detected in the negative pole spectrum of oxygen. It became visible when the negative electrode had the form of a hollow cylinder, and was resolved into eleven components all diffuse towards the violet. The wave-lengths and relative intensities are given; the most intense component is at λ 6791·3 Ångström units. The five bands now known show a general resemblance to those of nitrogen, but the series cannot be represented by the usual formula.

W. O. W.

The Green Carbon Band λ = 5635. Rudolf Komp (*Zeitsch. Photochem.*, 1911, 10, 117—134).—An arc generated by a current of 22—25 amperes at 220 volts was employed as source of light. The intensity of the green carbon band, which appears to be emitted most strongly by that portion of the arc which is in immediate contact with the electrodes, increases with the strength of the current and with the extent to which hissing takes place. In order to avoid cyanogen lines, the arc was surrounded by an atmosphere of carbon dioxide.

The wave-length measurements were made by means of a large concave grating of 6·5 metres radius and 20,000 lines to the inch, and are expressed in 0·001 Ångström units.

The green carbon band is similar in constitution to the second carbon band, which has been previously examined in detail, and this similarity indicates that the two bands have a common origin. Starting from the first head of the band, the spectrum exhibits two series of strong lines and two similar series of finer lines. Between the individual members of these series are a number of relatively weak triplets which seem to fall into six different series. The wave-lengths of the lines of these various series are discussed in reference to the validity of Deslandres' first and second laws. H. M. D.

Separation of Spectra in Compound Gases. G. Stead (*Phil. Mag.*, 1911, [vi], 22, 727—733. Compare this vol., ii, 830).—Further experiments are described in which the author has compared the anode and cathode spectra in the discharge through tubes containing ethane, ethylene dichloride, ethylidene dichloride, carbonyl chloride, mercury dimethyl, aniline, ethyl ether, methyl sulphide, and chloroform. The differences between the two spectra indicate that these are determined by the electro-chemical character of the component elements and by the inequality of temperature and of potential gradient at the two electrodes. It is supposed that the discharge of positive ions takes place throughout the negative glow; whilst negative ions lose their charges in the positive column. H. M. D.

Spectra of the Electrodeless Ring Discharge in Certain Gases. H. DONALDSON (*Phil. Mag.*, 1911, [vi], **22**, 720—727).—The influence of pressure, variation in the length of the spark-gap, and frequency of sparking has been investigated for the electrodeless ring discharge in hydrogen, air, carbon dioxide, carbon monoxide, oxygen, and argon. As in the case of the discharge between metal electrodes, it is found that the spectrum is dependent on the intensity of the electric field, although the results are not quite parallel.

In oxygen the continuous spectrum appears at the lowest intensities in the case of the ordinary discharge, whereas the ring discharge intensity lies between those which give rise to the compound line and the band spectra.

In carefully purified carbon monoxide the Swan spectrum appears at high intensities, whereas weak electric fields give rise to the carbon band spectrum only. It is suggested that these two spectra may be the high and low intensity spectra of the same substance.

The ring discharge in nitrogen and air shows no trace of the negative band spectrum, the change from the positive band spectrum to the line spectrum taking place directly. The general results agree with those found for electrode discharge in that the positive band spectrum appears to be brought about by the weakest fields and the line spectrum by stronger fields. H. M. D.

Resolution of the Spectral Lines of Lanthanum and Cobalt in the Magnetic Field. STEPHAN RYBÁR (*Physikal. Zeitsch.*, 1911, **12**, 889—900).—From observations of the influence of a strong magnetic field on the lines in the spark spectrum of lanthanum, it is found that the Zeeman effect for certain lines is very similar to that observed in the case of yttrium. The wave-lengths of those lines which exhibit close resemblance in their magneto-optical properties are as follows: La 4575·08, Y 3818·49; La 3921·71, Y 3628·89; La 4946·60, Y 3628·89; La 3381·10, Y 4398·21; La 3193·09, Y 4199·46; La 4986·99, Y 3950·51; La 3303·26, Y 4358·91 and 3195·80. The resolution in the last group of these lines is identical with that observed for the barium line $\lambda = 5997·4$.

The data for cobalt show resolution of the lines 3385·39, 3388·32, and 3463·01 into ten components, of 3495·89, 3550·75, and 3704·24 into eight, of 3491·51, 3561·06, and 3941·05 into seven, of sixteen lines into four, and of 106 lines into three components. H. M. D.

Distribution of Chemical Elements in the Earth's Crust. WLADIMIR J. VERNADSKY (*Bull. Acad. Sci. St. Petersburg*, 1911, [vi], 1007—1018).—[With B. A. LINDENER and E. D. REVUTSKY.]—Tables are given similar to those already published (Abstr., 1910, ii, 1013), and including the results obtained during 1910. In addition to the occurrence of cæsium, rubidium, thallium, indium, boron, etc., in a large number of minerals, that of copper, calcium, strontium, etc., in various artificial products, such as vanadium oxide, yttria, etc., is noted. T. H. P.

The Influence of Neutral Gases on the Absorption of Sodium Vapour. KARL FREDENHAGEN (*Physikal. Zeitsch.*, 1911, 12, 909—911).—The non-appearance of the principal series lines of the alkali metals when their salts are introduced into the hydrogen chlorine flame has been explained by Franck and Pringsheim (this vol., ii, 574) as due to the small concentration of free electrons. With the object of throwing further light on the nature of the process which gives rise to the principal series lines, the author has investigated the influence of inert gases on the absorptive capacity of sodium vapour. The admission of hydrogen, nitrogen, carbon dioxide, and helium to sodium vapour at 400° increases the absorptive power to a large extent, the magnitude of the influence of the different gases being approximately the same. In each case the intensity and breadth of the *D*-lines increases as the concentration of the admixed inert gas is increased.

Interferometer observations with the yellow helium and mercury lines indicate that the number of absorbing particles in the sodium vapour increases in the presence of the inert gases. This change in the number of the absorbing particles is correlated with the increased ionisation which has been found (compare this vol, ii, 571) to accompany the admixture of sodium vapour with small quantities of inert gases. H. M. D.

Absorption of Light by Silver Hydrosols. NILS PIHLBLAD (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 156—158).—The absorption of light by colloidal silver solutions of different degrees of dispersity has been examined for the mercury lines $\lambda = 404{\cdot}7$, $435{\cdot}9$, $491{\cdot}6$, $546{\cdot}1$, 577—579, 622, and 690. As the size of the particles is gradually increased, the maximum value of the extinction-coefficient moves towards the red end of the spectrum. For all solutions there appears to be, however, a more strongly developed maximum in the ultra-violet region.

From experiments with solutions of variable concentration, it is found that the light absorption takes place in accordance with Beer's law. H. M. D.

Absorption Spectra. IV. Influence of the Solvent and of Dilution on the Validity of Beer's Law. ALFRED W. STEWART and ROBERT WRIGHT (*Ber.*, 1911, 44, 2819—2826).—The absorbing power of a solution of iodine in alcohol increases at a greater relative rate than corresponds with the increase in dilution of the solution, probably because of the formation of an additive compound between iodine and alcohol. The opposite is the case with solutions of iodine in water; with increasing dilution the solutions become relatively more transparent.

An explanation of the behaviour of aqueous solutions can be given on the assumption that an oxonium derivative is formed which ionises when the solution is diluted; the ionised iodine atom causes practically no absorption, in contradistinction to the alkyl iodides, which show a strong selective absorption (compare Crymble, Stewart, and Wright, Abstr., 1910, ii, 470).

Solutions of iodine in mixtures of water and alcohol can be made more transparent by increasing, and less transparent by decreasing, the proportion of water.

An alcoholic solution of *p*-nitrotoluene behaves similarly to one of iodine, and in this case, also, is the formation of an additive compound possible. The addition of water, however, has simply the ordinary effect of dilution, and does not make the solution relatively more transparent, there being no possibility of an ionisation occurring.

Azobenzene is an indifferent substance, which neither forms additive compounds, nor is capable of ionisation, so that it conforms to Beer's law both in alcoholic and in aqueous-alcoholic solution. T. S. P.

Ultra-violet Absorption Spectra of Nitro-compounds.

Nicolai D. Zelinsky and N. A. Rosanoff (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1173—1183).—The absorption spectra of various nitro-compounds (including nitromethane and nitroethane, for which Baly and Desch [Trans., 1908, **93**, 1747] and Hedley [Abstr., 1908, i, 382] obtained divergent results) and their alkali salts have been investigated in the ultra-violet by Hartley's method (Trans., 1885, **47**, 685).

With nitromethane, in either aqueous or alcoholic solution, the absorption increases considerably in passing from the free nitro-compound to its sodium salt, corresponding with the unsaturated *iso*nitro-derivative.

With nitroethane, the selective absorption is changed into continuous absorption on the formation of the sodium salt. The character of the absorption is the same with nitromethane and nitroethane, but in the latter the absorption band is displaced towards the visible part of the spectrum, probably owing to the influence of the molecular mass; the maxima in the two cases are at $1/\lambda = 3720$ and $1/\lambda = 3640$ respectively. These results confirm those of Baly (*loc. cit.*).

α-Nitropropane gives similar absorption curves, the selective absorption of the free compound being displaced still more towards the visible spectrum, the maximum being at $1/\lambda = 3600$. β-Nitropropane gives a greater general absorption in the free state, and a greater selective absorption in the form of sodium salt, than is the case with the α-compound, the maximum lying at $1/\lambda = 3500$; the increased absorption is here evidently due to the yellow colour of the freshly-prepared sodium salt in either aqueous or alcoholic solution.

With tetranitromethane, the selective absorption is still more towards the visible portion of the spectrum, the maximum being at $1/\lambda = 2975$.

ω-Nitrophenylmethane gives a curve similar to those of the above primary nitro-compounds, the maximum being at $1/\lambda = 3465$; the characteristic behaviour of the aromatic series is not shown.

With ω-nitro*cyclo*hexylmethane, selective absorption occurs only with the salts, the maximum being at $1/\lambda = 3440$; the free compound shows marked general absorption.

Free nitro*cyclo*hexane shows two absorption bands with maxima at $1/\lambda = 3500$ and 3720; the salts exhibit general absorption. The same is the case with 1-nitro-1-methyl*cyclo*hexane, the maxima being at 3550 and 3740. 1-Nitro-1-methyl*cyclo*pentane gives, however, only one absorption band, with a maximum at $1/\lambda = 3570$.

These results confirm the view that the absorption is conditioned, besides by other influences, also by the molecular mass of the compound.

The introduction of nitro-groups into aliphatic compounds causes a considerable increase in the general absorption, along with which selective absorption also appears. The latter is a consequence, not of a quinonoid grouping (compare Hedley, *loc. cit.*), but of the vibration between the elements of the molecule (see Baly and Collie, Trans., 1905, **87**, 1332), resulting from the residual valency of the nitro-group. There should hence be no difference in general character between the absorption curves of mono- and dinitro-aliphatic compounds; this is contrary to the results of Hedley, who found no selective absorption for nitromethane, an observation which the author is unable to confirm.

The introduction of nitro-groups into the molecules of hydroaromatic compounds causes marked displacement of the absorption towards the visible part of the spectrum, and also the appearance of absorption bands not observed with the hydrocarbons themselves.

The introduction of nitro-groups into the benzene ring evidently neutralises the residual valency of the nucleus, and weakens the manifestation of molecular vibrations, since the number of absorption bands diminishes. In this respect, the hydroaromatic compounds are similar to the aliphatic compounds, owing to the absence of residual valency.

The conclusion is drawn that the magnitude of continuous and selective absorption is closely connected with the degree of tension prevailing in the molecule. This may depend on the extent of unsaturation of the compound itself, and also on the degrees of tension of its constituent elements. T. H. P.

Photosensitive Antimonite [Stibnite] Cells. William Sebastian Gripenberg (*J. Amer. Chem. Soc.*, 1911, **33**, 1761—1762).—Jaeger (Abstr., 1907, ii, 923) has shown that light has a powerful influence on the electrical conductivity of stibnite. The author has constructed a highly sensitive cell which consists of a lamella of natural stibnite about 0·3 mm. thick, pressed against a glass electrode plate covered with a large number of very fine electrodes of gold or platinum foil, parallel to one another and about 0·067 mm. apart. The width of this grating is 3 × 4 mm., this having about 14 electrodes per sq. mm. The required pressure on the lamella is effected by a small screw-press, into the frame of which insulated wires are fitted. The wires end in small elastic bars, which pinch the electrode-plate and make metallic contact with the bars of the grating.

Such cells have a resistance of from 10^5 to 5×10^6 ohms. The presence of a small oil-lamp in the neighbourhood of the cell causes the resistance to fall to 10% or even 1% of its original value. During the passage of the current, the cells are very sensitive to atmospheric influences, and must therefore be enclosed in vaselin. They can be used satisfactorily for an *E.M.F.* of 30 volts, but if used with very high voltages they are liable to get out of order. E. G.

Absorption and Secondary Radiation of Cathodic Rays. F. BUTAVAND (*Ann. Chim. Phys*, 1911, [viii], **24**, 421—432. Compare Schmidt, Abstr., 1910, ii, 7, 378; Schmidt and Cermack, Abstr., 1910, ii, 918).—When a group of β-rays falls on a plate of an elementay substance $I = I_0 e^{-\lambda d}$, where I is the intensity of a saturating current, I_0 that of the emergent group of rays, and λ the coefficient of absorption. λ is not proportional to the density, ρ, of the element. The expression $\lambda/\rho = kP^{1/3}$, where P is the atomic weight, gives values of k which fluctuate about a mean 1·85 when values of λ, ρ, and P are inserted for the various elements. Taking any one of the groups of the periodic table, the differences between 1·85 and the values of k found for the constituent elements are alternately positive and negative, so that k is a periodic function of the valency V. Substitution of values in the expression $\lambda/\rho = 1{\cdot}88P^{1/3}\ (1 \pm 1/10 \cos \omega V/8)$ gives values approximating to those calculated. For compounds, an analogous expression holds, namely, $\lambda/\rho = hp^{1/3}$, where p is the molecular weight and h a coefficient which is approximately constant for analogous compounds. For applications of this the original should be consulted.

β-Rays falling on a plate of an elementary substance give rise to secondary β-rays in all directions, and the intensity η of these secondary rays varies with the nature and substance of the plate, and increases with the atomic weight P of the element. Substitution of values in the expression $\eta = k'P^{1/3}$ shows that k' is approximately equal to $10k$. T. A. H.

Radioactive Properties of High Temperature Flames. HARRY CARTER (*Phil. Mag.*, 1911, [vi], **22**, 805—816).—To ascertain whether atomic disintegration takes place in reactions which are accompanied by the liberation of large quantities of energy, the author has examined the electric arc, the spark, and the oxy-hydrogen and oxy-acetylene blowpipe flames for β-radiation. The apparatus was arranged so as to avoid temperature variations of the electroscope and the presence of ionised air in its neighbourhood. In no case could any appreciable difference be detected between the rate of leak when the electroscope was exposed to the source and when shielded from its action.

H. M. D.

Radiation in Explosions of Coal Gas and Air. W. T. DAVID (*Phil. Trans.*, 1911, *A*, **211**, 375—410).—Measurements have been made of the radiation emitted during the explosion and subsequent cooling of mixtures of coal-gas and air. By the use of screens of fluorite, quartz, glass, and water for the bolometric apparatus, it was possible to estimate fairly accurately the total radiation emitted by the gas, the approximate proportions emitted by water vapour and by carbon dioxide, and also the amount of energy in the luminous radiation.

The bolometric records show that, for different gas mixtures at atmospheric pressure, the total heat lost by radiation to the walls of the vessel up to the moment of maximum pressure is approximately proportional to the product of the third power of the maximum absolute temperature by the time of explosion. The total radiation lost during the explosion and subsequent cooling is about 25% of the heat of combustion of the gas present in the explosion chamber. The radiation in the initial stages of cooling is a function of the time interval from ignition as well as of the temperature. The rate at which the radiation is emitted is a maximum some time before the attainment of maximum pressure, and probably occurs at the moment when the flame fills the explosion chamber. Weak explosive mixtures radiate very much more in the initial stages of cooling than stronger mixtures do when these have cooled to the same temperatures.

The total heat radiated by carbon dioxide is about twice as large as that radiated by an equal volume of water vapour at the same temperature.

When explosive mixtures of the same strength, but of different densities, are compared, it is found that the ratio of the heat which is lost by radiation up to the moment of maximum pressure to the heat of combustion decreases as the density increases, but denser mixtures emit much more strongly at the moment of maximum pressure and in the initial stages of cooling.

In the second part of the paper an account is given of experiments relating to the diathermancy and emissive power of the hot gaseous mixtures after explosion. H. M. D.

The Distribution of the Intervals of Emission of the α-Particles of Polonium. (Mme.) MARIE CURIE (*Le Radium*, 1911, **8**, 354—356).—The results obtained confirm those of previous observers (Rutherford and Gieger, Abstr., 1910, ii, 917; Marsden and Barratt, *Proc. Phys. Soc.*, 1911, **23**, 367). From a series of curves, obtained by means of the ionisation method in which the excursions of the electrometer needle are recorded on a moving photographic film, comprising 1080 intervals, it was found that the number of intervals, n, comprised between t and $t+\theta$, where θ represents a fixed time, varies according to an exponential law, $n=n_0e^{-t/\tau}$, where τ is the mean interval, and $n_0/\theta=N/\tau$, N being the total number of intervals. This is the same law as applies to the free path of the molecules of a gas, the mean free path corresponding with the mean interval between the emissions. F. S.

The Variation of the Activity of Some Radioactive Substances with Time. (Mme.) MARIE CURIE (*Le Radium*, 1911, **8**, 353—354.)—The α-rays of uranium oxide have been kept under observation for four years. The means of the measurements taken in each year agree within 0·5%, and the conclusion may be drawn that the activity has remained constant. The β- and γ-rays from a salt of barium containing radium, previously purified from radio-lead and its products, and contained in a thin-walled glass tube covered with aluminium foil, have been observed for twenty months. The tube forms the central electrode in a cylindrical ionisation chamber, and a correction is introduced for the changes of density of the air. An increase of the radiation amounting to about 2·5% per year has been observed, which is doubtless due to the formation of radio-lead. A preparation of Debierne's actinium many years old has been studied in the same way. The measurements are unaccountably irregular, but indicate a diminution of the penetrating rays in three years amounting to 10% of the initial activity. Either there must exist between actinium and radioactinium an intermediate substance of long-life giving β-rays, initially present in excess, or the period of average life of actinium is only of the order of thirty years. In the latter case the relation between actinium and the other radio-elements of uranium minerals ought to be capable of elucidation. Radio-lead submitted to a crystallisation of the chloride to remove radium-*E* and -*F*, and containing initially radium-*D* only, has been studied for five years. The penetrating rays attained the maximum in one month, the period of radium-*E* being 4·7 days, and the α-rays attained the maximum in two years. Both types of radiation remained fairly constant during the third year. During the fifth year a regular decay of the α-rays occurred, amounting to about 5% in 440 days. This would correspond with a period of average life of radium-*D* of about twenty-five years. The β-ray measurements are less precise, but indicate about the same rate of decay. All measurements have been effected by means of the quartz piézo-électrique, which remains, when properly mounted, absolutely constant, and is very suitable for these measurements. F. S.

Thorium and its Products of Disintegration. MAY SYBIL LESLIE (*Le Radium*, 1911, 8, 356—363).—The results confirm those of other workers as to the chemical nature of mesothorium. The material employed was thorite containing 40% of thorium oxide and 0·73% of uranium. In the electroscope employed the different values for the separate α-ray producing members of the series were: thorium 5·5%, radiothorium 9·4%, thorium-*X* 12·2%, emanation 48·6%, thorium-*A* 12·2%, thorium-*B* 12·2% (old nomenclature). This accords with the view that the emanation gives four α-particles per atom disintegrating, and that the α-rays due to thorium itself have a very low velocity corresponding with a range of only about 2 cm. The activity of oxide of thorium freshly separated from thorium decays at a rate which indicates that the period of radiothorium is only three or four months. F. S.

The Amount of Radium Emanation in the Soil and its Escape into the Atmosphere. JOHN JOLY and LOUIS B. SMYTH. (*Sci. Proc. Roy. Dubl. Soc.*, 1911, **13**, 148—161).—Observations have been made in the vicinity of Dublin, during the months of April and May, 1910, of the amount of radium emanation in the soil at various depths and on the amount exhaled per hour from the surface. The period covered began with wet and stormy weather and ended with a long spell of fine settled weather. The observations are in agreement with the view that the influence of rain is to choke the capillaries of the soil, retarding the escape of the emanation and therefore increasing the amount in the soil, whilst reducing that in the air. At depths below the surface of from 25 to 250 cm., the relative amount of emanation in the air in the soil was usually many thousand times that in the atmosphere. A very rapid escape of emanation from the soil was established, and it is considered probable that this exhalation is the chief, if not the only considerable, source of the emanation in the atmosphere. F. S.

Quantity of Radium Emanation Liberated From One of the Springs at Columbières-sur-Orb (Hérault). JACQUES DANNE and VICTOR CRÉMIEU (*Compt. rend.*, 1911, **153**, 870—871).—This spring evolves gas at the rate of 43,000 litres per day, with an amount of radium emanation corresponding with 860 mg.-minutes per twenty-four hours. This unusually large amount of emanation is readily available in an active form, since the gas contains 95% of easily removable carbon dioxide. W. O. W.

The Radioactivity of Mineral Springs. ERICH EBLER and M. FELLNER (*Zeitsch. anorg. Chem.*, 1911, **72**, 233—301).—The gas obtained from the Max mineral spring of Dürkheim contains $6\cdot1 \times 10^{-9}$ cubic mm. of radium emanation per litre. The spring evolves 30 litres of gas per hour. The activity of the sediment is, as usual, variable, and about one-half of the activity disappears when the sediment is gently warmed. An estimation of the radium present by Strutt's method gives, for two samples of sediment collected at different times, $3\cdot03 \times 10^{-10}$ and $1\cdot76 \times 10^{-10}$ gram radium per gram of sediment. Other radioactive substances, including radiothorium, are also present.

An analysis of the sediment, dried at 106°, shows that it contains 45·5% SiO_2, 9·9% residue insoluble in hydrofluoric acid, 10·7% As_2O_3, 7·1% CaO, 15·7% Fe_2O_3, and 2·5% Mn_3O_4, with small quantities of other substances. Sulphates are absent, and carbonates present only in minute quantity. Lead is present to the extent of 0·1%. Thorium and uranium are absent. The proportion of potassium increases with the time of agitation with the water, whilst that of sodium is unchanged. When treated with hydrochloric acid, 91% of the radium remains in the insoluble residue, being adsorbed by colloidal silica. Boiling hydrochloric acid extracts a substance from the sediment, which crystallises in polyhedral, yellow leaflets, 600 grams being obtained from 10 kilograms of sediment. This quantity yielded 33 grams of potassium nitrate, of similar activity to ordinary potassium salts.

The water itself contains $0\cdot97 \times 10^{-10}$ gram of radium per litre. The mother liquor obtained in the commercial crystallisation of salts from this water is distinctly radioactive, the activity being due to radium. Determinations of the activity of the sediment and of the mother liquor give a value of $0\cdot78 \times 10^{-10}$ gram of radium per litre of the original water, in good agreement with the foregoing.

Details are given of the chemical methods of investigating these and similar products. C. H. D.

The Radioactivity of the Mineral Springs of Tyrol. III. MAX BAMBERGER and KARL KRÜSE (*Monatsh.*, 1911, **32**, 797—813. Compare Abstr., 1910, ii, 570).—A table is given of numerous determinations of the activity in Mache units of mineral springs in Tyrol. The table contains details also of the temperature of the spring and of the rock in which it occurs. F. S.

The Radioactivity of the Air Over the Open Sea. CARL RUNGE (*Chem. Zentr.*, 1911, ii, 786; from *Nachr. K. Ges. Wiss. Göttingen, Math.-physikal. Klasse*, 1911, 99—109).—Under similar conditions the induced activity of the atmosphere was found to be about as great in the middle of the Atlantic Ocean as near the coast. In both cases the decay curve for the first two hours is that of radium alone, except that in the middle of the ocean the decay for the first half-hour is somewhat more rapid. After two hours the decay becomes slower, indicating the presence of thorium. F. S.

The Formation of Positive Ions by Heated Metals. Z. KLEMENSIEWICZ (*Bull. Acad. Sci. Cracow*, 1911, *A*, 417—424).—The emission of positive ions by electrically heated platinum, palladium, gold, iridium, copper, iron, and tungsten wires has been investigated. From measurements of the leakage current between the wire and a surrounding metal cylinder after different time intervals, decay curves were obtained for new wires, and also for wires which had been heated in a vacuum or left in contact with strongly compressed gases for several hours. In the case of platinum, observations were also made with the metal after anodic and cathodic polarisation.

The experimental data are in favour of the view that the positive ion emission is mainly due to absorbed gases. It is calculated that about 1% of the gas molecules which leave the heated metal are electrically charged. This fraction is approximately constant, and, as a consequence, the number of positive ions will be proportional to the solubility of the gas in the metal under investigation.

Experiments with palladium and iridium, superficially covered with the corresponding oxides, indicate that emission of ions is not an accompaniment of the formation or dissociation of these oxides. On the other hand, tungsten, copper, and iron show emission effects, both during oxidation and reduction. H. M. D.

Mobility of Positive Ions Produced from Heated Aluminium Phosphate in Gases at Low Pressures. GEORGE W. TODD (*Phil. Mag.*, 1911, [vi], 22, 791—804).—The mobility of the positive thermions from aluminium phosphate has been measured in air, carbon dioxide, sulphur dioxide, methane, and hydrogen at low pressures. As the pressure is lowered, the mobility increases in such a way that the product of pressure and ionic mobility remains approximately constant, but increases much more rapidly than this when the pressure is lowered beyond a certain critical value. This rapid increase may be due to the disintegration of the molecular clusters which form the ions under higher pressures, or to the existence of a positive ion in the free condition for short intervals of time. In air and carbon dioxide the data obtained at the lowest pressures show that the positive charge is carried by particles, the mass of which is smaller than that of the ordinary gas molecules.

Water vapour has only a small influence on the mobility of the positive ion in the region where the inverse pressure law holds, but has a large effect at smaller pressures. Under these conditions, the presence of water vapour causes the mobility to fall below the value which would correspond with the inverse pressure law.

The thermions emitted by heated aluminium phosphate appear to yield by collision with the gas molecules the same ions as are produced by the action of *X*-rays on the gas. H. M. D.

Positive Ionisation from Hot Salts. OWEN W. RICHARDSON (*Phil. Mag.*, 1911, [vi], 22, 669—703. Compare Abstr., 1910, ii, 923; this vol., ii, 9, 10)—The nature of the positive ions emitted by heated salts has been further examined by experiments with two different forms of apparatus and observations at different pressures and temperatures The values obtained for e/m indicate that the positive ions are metallic atoms which are not necessarily atoms of the metal in the salt under examination, but may be due to some other metal present as impurity. In the case of aluminium phosphate strong evidence has been obtained in favour of the view that the observed $e/m = 22$ is due to traces of foreign substance, for when the aluminium phosphate was prepared from ammonia, aluminium chloride, and phosphoric oxide, all of which had been subjected to distillation before use, a product was obtained which only gave about 1/150 of the emission given by Kahlbaum's aluminium phosphate,

In regard to the relative efficiency of different salts in emitting positive ions, it appears that the emissive power increases with the electro-positive character of the metallic constituent and with the volatility of the compounds which appear to be formed from the original substance at the high temperature. A number of facts cannot be satisfactorily explained unless it is assumed that the ionisation is not directly due to the heated salt, but to the action of vapours emitted by the salts on the hot platinum. This is the case for the changes in the emissive power which are observed when the pressure of the gas is altered and for the different effects which are obtained according to whether the salt is supported on a strip of platinum or is contained in a platinum tube. H. M. D.

Specific Conductivity of Fused Potassium Nitrate. A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1911, 78, 1—23).—The apparatus used was similar to that of Lorenz and Kalmus (compare Abstr., 1907, ii, 430). The thermostat contained fused potassium and sodium nitrates, and the temperatures were measured by means of a carefully calibrated platinum resistance thermometer. The determination of the resistance capacity of the apparatus and the corrections made are described in detail.

Measurements were made at intervals of temperature between 340° and 500° in vessels of common glass, Jena glass, and quartz respectively. The results for the different vessels are in fair, but not in exact, agreement; no satisfactory explanation for the deviations has been found. At high temperatures the conducting values are higher than those found by Lorenz and Kalmus, but are in fair agreement with those of

Goodwin and Mailey (*Phys. Review*, 1908, **26**, 28); at low temperatures, on the other hand, the author's results are lower than those of Goodwin and Mailey. The following numbers show the variation of the specific conductivity with temperature: 0·6334 at 340°, 0·8201 at 400°, 0·9687 at 450°, and 1·1099 at 500°. G. S.

Electrical Conductivity of Liquid Sulphur Dioxide Solutions at −33·5°, −20°, −10°, 0°, and +10°. EDWARD C. FRANKLIN (*J. Physical Chem.*, 1911, **15**, 675—697. Compare Abstr., 1909, ii, 957). —The conductivity of solutions of potassium iodide and bromide, tetramethylammonium iodide, ammonium thiocyanate, ethyl ammonium bromide, and dimethylammonium chloride in liquid sulphur dioxide has been measured, using the apparatus and methods previously described for liquid ammonia.

The conductivity-dilution curves closely resemble those given by liquid methylamine and liquid ammonia. On diluting the saturated solutions, the molecular conductivity rises to a maximum, then declines to a minimum at moderate dilutions, and finally rises continuously to the highest dilutions measured, approaching a maximum value in the normal way.

It is suggested that the high conductivity in concentrated solutions is due to autoionisation of the salt, whereas in dilute solutions ionisation by the solvent comes into play. The initial increase in conductivity on diluting saturated solutions is attributed to the considerable fall in viscosity which more than compensates for the fall in autoionisation. The temperature-coefficient of conductivity is positive for very concentrated and very dilute solutions, whilst for solutions of intermediate concentration the temperature-coefficient is generally reversed. The autoionisation in concentrated solutions and the almost complete ionisation at high dilutions are presumably unaltered by temperature changes which influence the conductivity only through the viscosity. At moderate dilutions the ionisation by the solvent may suffer a marked diminution, with rise in temperature.

It was observed in the course of the experiments that potassium bromide is more soluble in liquid sulphur dioxide the lower the temperature. R. J. C.

Electrical Conductivity of the System Ferric Chloride–Ammonium Thiocyanate. CORRADO BONGIOVANNI (*Boll. Chim. Farm.*, 1911, **50**, 694—697).—The conductivity of a red solution containing ferric chloride and ammonium thiocyanate is approximately equal to the sum of the conductivities of solutions of the separate salts of corresponding concentrations. The slight diminution in the degree of dissociation which occurs is probably due to mass action between the reacting salts, and consequent formation of a small number of undissociated molecules. Indeed, if the salts are taken in equivalent proportions, and in solutions sufficiently dilute to ensure complete dissociation, the specific conductivity of the red solution becomes very nearly equal to the sum of the separate conductivities.

These results confirm Magnanini's interpretation (Abstr., 1891, 1150) of this reaction (compare also Abstr., 1907, i, 833; 1908, i, 859), and are not in agreement with the view advanced by Tarugi (Abstr., 1905, i, 176). T. H. P.

The Electric Vacuum Furnace. OTTO GOECKE (*Metallurgie*, 1911, 8, 667—676).—The carbon tube electric vacuum furnace (Ruff and Goecke, this vol., ii, 897) has been further improved by the addition of a second carbon tube, enclosing the first and insulated from it by means of magnesia, to lessen the loss of heat by radiation. The crucible may be introduced and removed without removing the heating tube. A series of determinations of melting points in this furnace by means of the Wanner optical pyrometer gives results in good agreement with previous observations. A few new determinations have been made. Alumina has m. p. 2020—2035°, either in a vacuum or in nitrogen. Lime has not been fused in a vacuum, but in nitrogen it melts at 1990°, owing to a chemical reaction. Magnesia boils, without melting, at 2029°/7 mm., but volatilisation begins in nitrogen at atmospheric pressure at 1805°. C. H. D.

Differences in Potential of Apparent Contacts between a Metal and Electrolytic Solutions. J. GUYOT (*Compt. rend.*, 1911, 153, 867—869. Compare Abstr., 1908, ii, 656).—The apparent difference in potential established by ionising air between the surfaces of a salt solution and a metal plate above it varies with the logarithm of the ionic concentration of the solution. For solutions of the alkali chlorides, using reversible electrodes, the difference of potential is given by the expresssion $V = V_0 \pm 0{\cdot}053 \log c.1/p$. This is analogous to the Helmholtz formula for the electromotive force of a couple consisting of two reversible electrodes immersed in a liquid. W. O. W.

Polarisation of Solid Electrolytes. [The Phenomena of Passivity.] FRITZ HABER and J. ZAWADZKI (*Zeitsch. physikal. Chem.*, 1911, 78, 228—243).—When solid compressed silver salts (the chloride, bromide, iodide, and sulphate were used) are electrolysed between plates of silver, considerable polarisation occurs, and this is the greater the lower the temperature. With silver sulphate at room temperature, for instance, an *E.M.F.* of polarisation of 0·312 volt was observed two minutes, and 0·125 volt twenty minutes after breaking the current. At −80° a polarisation *E.M.F.* of 1·562 volts was observed one minute after breaking the current. Salts which have been kept compressed for some time give higher values than pastilles freshly prepared. By means of experiments with other electrodes it is made probable that the polarisation occurs only at the anode.

These results cannot be reconciled with the usual assumption that the primary change at the anode is the formation of silver ions from metallic silver. It is suggested that the transport of the current from solid electrolyte to anode is effected by the passage of electrons with simultaneous formation of oxidising substances (silver persulphate from silver sulphate, free halogen from halogen ions). These oxidising substances then attack the silver anode, this secondary reaction being greatly retarded by cooling. It is probable that the mechanism is the same in aqueous solution, but in this case the discharged ion in presence of the solvent reacts rapidly with the electrode. These results may have an important bearing on the phenomena of passivity. G. S.

Galvanic Elements with Carbon Anodes. P. BECHTEREFF (*Zeitsch. Elektrochem.*, 1911, 17, 851—877).—This is a very detailed investigation of the Jacques cell and of several modifications of it. The separate potentials of carbon on the one hand, and of a number of metals on the other, in fused sodium hydroxide are determined over a considerable range of temperature. The potential of carbon in fused sodium hydroxide referred to the calomel electrode is about 1 volt at 370°, and increases by 0·00184 volt per degree. The addition of small quantities of sodium nitrate or perchlorate diminishes the potentials. Permanganate has no effect, since manganate is always present. The potentials in fused mixtures of alkali carbonates are smaller by about 0·8 volt.

The metals iron, nickel, cobalt, silver, copper, constantan, gold, and platinum all become passive in fused sodium hydroxide, and give very exactly the same potentials. These are 0·5 volt at 550°, with a temperature-coefficient of 0·00096 volt per degree between 340° and 650°.

The observed *E.M.F.*'s of the Jacques cells (carbon | fused sodium hydroxide | passive metal) were at 350°, 0·633 volt; at 450°, 0·722 volt; at 550°, 0·804 volt; at 650°, 0·875 volt. These numbers agree well with those calculated from the separate potentials.

The polarisation of the electrodes is then studied. When the cell is yielding a current, the carbon is the anode and the passive metal the cathode, hence the anodic polarisation of the carbon and the cathodic polarisation of the metal are alone of practical interest.

Carbon is readily polarised anodically, a current of 0·06 ampere per sq. cm. reducing its potential by about 0·5 volt at 395°. The addition of sodium nitrate, perchlorate or chlorate diminishes the polarisation considerably, and the latter does not reduce the potential, but they all decompose about 400°, and are consumed. The depolarisation produced by the addition of selenium or tellurium to the electrolyte is of a different kind. The addition of 5% of selenium reduces the polarisation to very small values, and the effect is permanent. Neither selenites nor selenates have this effect; it is therefore ascribed to the presence of a selenide. Tellurium appears to be even more active.

In fused sodium hydroxide, silver and platinum give almost the same cathodic polarisation curves, whilst iron and nickel are much more strongly affected, probably because they become active. The most effective depolariser is sodium peroxide.

When carbon rods are used as anodes in fused sodium hydroxide to which 3% of selenium has been added, their loss of weight varies between 77 and 90% of that calculated, on the supposition that the electrochemical equivalent of carbon is 3.

As Haber had already observed, the Jacques cell gives a small and inconstant *E.M.F.* if the electrolyte is free from manganate. This is confirmed using fused lithium hydroxide as electrolyte in presence of a manganate; the *E.M.F.* is the same as with sodium hydroxide. A number of cells with aqueous solutions of sodium hydroxide containing a little potassium permanganate were also measured at temperatures down to 95°. Their *E.M.F.*'s lie on the continuation of the curve obtained with the fused electrolyte at higher temperatures. Above about 650° the *E.M.F.* of the cells falls off rapidly.

A number of cells of different types were tried at high temperatures; most of these gave small and inconstant *E.M.F.*'s Elements of the type carbon | fused boron trioxide | platinum, in which oxides of iron, nickel, cobalt, silver, or copper were added to the electrolyte gave *E.M.F.*'s between 1000° and 1300° of as much as 1 volt.

T. E.

Electrical Properties of Alkali Metals, Rhodium, and Iridium. WITOLD BRONIEWSKI and L. HACKSPILL (*Compt. rend.*, 1911, **153**, 814—816. Compare Abstr., 1910, ii, 821; Bernini, Abstr., 1908, ii, 255).—The alkali metals were of greater purity than those employed by other observers, and were distilled in a vacuum. The following expressions give the thermoelectric powers when copper is the second metal, for the temperature interval 0° to $-183°$. Cs $+0{\cdot}66 \;-0{\cdot}0010t$, Rb $-8{\cdot}26 \;-0{\cdot}0302t$, K $-11{\cdot}33 \;-0{\cdot}0376t$, Na $-4{\cdot}16-0{\cdot}0144t$. In the case of cæsium and rubidium, the variation of thermoelectric power with temperature was also registered photographically, using a Le Chatelier galvanometer. The curve for cæsium shows a break in the neighbourhood of the melting point of the metal, whilst that for rubidium shows an angular point.

Similar measurements were made with rhodium and iridium, using lead as the second metal. For the temperature interval -78 to $-100°$, the values for the thermoelectric powers are given by the expressions: Rh $+\;2{\cdot}17+0{\cdot}0005t$, Ir $+2{\cdot}44\;-0{\cdot}0014t$. At 80°, rhodium appears to undergo a molecular transformation analogous to that of copper, the electrical resistance being much below the expected value.

W. O. W.

Thermoelectric Forces in the Transition from the Solid to the Liquid State of Aggregation. PAUL CERMAK and HANS SCHMIDT (*Ann. Physik*, 1911, [iv], **36**, 575—588. Compare Koenigsberger and Weiss, this vol., ii, 578).—The variation of the thermoelectric potential of the elements tin–constantan, tin–iron, and lead–constantan with temperature has been examined at temperatures above and below the melting points of tin and lead. In each experiment two junctions were employed, one of these being kept at a constant temperature below the melting point, whilst the other was slowly heated or allowed to cool, so as to cause the tin or lead to change its state of aggregation. Potential and temperature measurements were made at suitable intervals, and curves have been constructed to show the connexion between thermoelectric potential and the difference between the temperatures of the two junctions. From the results thus obtained, it appears that the change from solid to liquid is not accompanied by any break in the thermoelectric potential, or by any alteration in the temperature-coefficient of the thermoelectric effect. H. M. D.

Anodic Behaviour of Nickel in Presence of Chromous Salts. C. Russo (*Gazzetta*, 1911, **41**, ii, 101—109. Compare this vol., ii, 181).—The theory that the anodic polarisation of nickel is due to the formation of a solid solution of oxygen at its surface does not exclude the possibility of polarisation even in a solution containing a strong reducing agent, because an oxidising layer can form in the vicinity of the electrode, and there is nothing but the diffusion of the reducing substance to prevent the oxidation of the electrode in consequence. Accordingly, the author finds that the presence of a chromous salt makes it more difficult for nickel to attain to the passive state, but does not prevent its doing so. To bring the condition about in a short time, a much stronger current is required than in the absence of a chromous salt, but if the current is then diminished, no loss of passivity is observed. The presence of the reducing agent also modifies but slightly the polarisation values. Further experiments have shown that the free acetic acid present in the solution containing the chromous salt used in the above electrolysis does not affect the polarisation in any way. This is due to its not taking part in the electrolysis, for in a solution of sodium acetate and acetic acid the polarisation does not follow the logarithmic law, whilst if this same solution contains sodium sulphate the logarithmic law is again valid. R. V. S.

The Flame Arising from the Nitrogen-burning Arc. Robert J. Strutt (*Proc. Roy. Soc.*, 1911, *A*, **85**, 533—536).—The structure of the high-tension alternating arc in hydrogen, nitrogen, oxygen, and air has been examined. In the case of the pure gases, the luminosity is entirely due to the true current-carrying arc, but in air the arc is accompanied by an envelope of yellowish-green flame, which may rise to a considerable height above the arc, and terminates above in quite a sharp point like a candle flame. The luminosity of the arc proper is very small in comparison with that of the flame, but, since the flame gives no violet rays, the arc may be seen alone by examination through a deep violet glass. It then appears to be of about the same size and form as the arc in pure nitrogen. By reduction of the air pressure the distinction between the arc and the flame can be made more evident. Under these conditions, a rose-coloured arc is seen, which is separated from the surmounting yellowish-green flame by a slight dark interval. The phenomenon is further accentuated if the reduction in pressure is accompanied by an increase in the percentage of oxygen.

The behaviour of the arc flame indicates that the luminosity effect is identical with the after-glow sometimes observed in Geissler tubes filled with air. This has been shown to be due to the oxidation of nitric oxide by ozone (*Proc. Phys. Soc.*, 1910, **23**). It has been observed since, that nitrogen peroxide gives the same result with ozone, and the author draws the conclusion that the yellowish-green flame of the arc is due to the interaction of ozone and oxides of nitrogen which are formed in the arc itself. H. M. D.

Formation of Hydrogen Cyanide in the High Tension Electric Flame. I. Moscicki (*Zeitsch. Elektrochem.*, 1911, **17**, 877).—Polemical. Lipinski obtained the information published (this vol., ii, 849) while working in the author's employment in a confidential capacity. T. E.

The Magnetic Properties of Some Nickel Steels. Edward Colver-Glauert and Siegfried Hilpert (*J. Iron Steel Inst.*, 1911, **83**, 375—411).—Alloys of iron with 5·86, 24·32, and 32·90% of nickel have been examined after slow cooling from 1250°, and also after quenching from 600°, 900°, and 1240°, and after cooling to $-50°$, $-100°$, and $-180°$, a magnetometric method being used. The 5% steel is unchanged by quenching from 600° or by cooling, whilst quenching from 900° renders it martensitic, and greatly increases the coercive force. If quenched from 1240°, it is only partly martensitic, and is magnetically softer. The 25% steel is apparently non-magnetic in the stable condition, but becomes magnetic at low temperatures, no sharp critical point being observed. This alloy, quenched from 1240°, becomes as magnetic at $-180°$ as that cooled slowly. It is suggested that a highly magnetic substance is formed at high temperatures, which dissociates between 600° and 900°, but may re-form on slow cooling. The structure of specimens quenched from 600° resembles that of natural meteoric irons, and when cooled to low temperatures becomes similar to that of quenched high-carbon steels. The 33% steel is little altered by quenching, and is not changed by cooling below zero. The structure is polyhedral, but etching with sulphurous acid develops a duplex structure, like that of the last alloy. It is improbable that γ-iron is non-magnetic. C. H. D.

Influence of the Magnetic Field on Passive Nickel and Iron. Horace G. Byers and Agnes Fay Morgan (*J. Amer. Chem. Soc.*, 1911, **33**, 1757—1761).—It has been shown by Byers and Darrin (Abstr., 1910, ii, 579) that when iron is used as an anode in various electrolytes, the current density required to produce the passive state is increased when the anode is placed in a magnetic field. It has now been found that the same is true in the case of nickel.

Magnetised steel is more difficult to render passive than the same steel which has not been magnetised, and soft steel is affected to a greater extent than hard steel. This is in accordance with the observations of Andrews (Abstr., 1893, ii, 16).

The positive pole of the magnets is rendered passive more easily than the negative pole. E. G.

Magnetisability of the Salts of Metals of the Iron Group. Rudolf H. Weber (*Ann. Physik*, 1911, [iv], **36**, 624—646).—In continuation of previous experiments (Abstr., 1906, ii, 331), the author has measured the magnetic susceptibility of chromous and chromic chlorides and of cobaltous and cobaltic sulphates. The atomic susceptibilities of the metals in these compounds are respectively: Cr in $CrCl_2$, 0·01078, in $CrCl_3$, 0·00625; Co in $CoSO_4$, 0·01019, in $Co_2(SO_4)_3$, 0·00486. As in the case of manganese, the susceptibility of bivalent chromium and cobalt is greater than that of the tervalent metal, whereas the reverse is true for iron. H. M. D.

Use of the Magnetic Field in Determining Constitution. XI. PAUL PASCAL (*Bull. Soc. chim.*, 1911, [iv], **9**, 868—873. Compare this vol., ii, 850).—An extension of the study of anomalous cases (*loc. cit.*) to colouring matters. The magnetic susceptibilities of the aminoazo-compounds even after fusion and rapid cooling indicate that they possess the azo- and not the quinonoid structure. Similarly, the magnetic susceptibility of magenta is in accordance with Rosenstiehl's formula.

The hydroxyazo-compounds exist in two forms having different densities: the one is yellow to orange-coloured and stable in the cold, the other reddish and stable on heating. Both co-exist in some cases. Consequently, the magnetic susceptibilities observed for the hydroxyazo-compounds vary with the treatment to which the substances have been subjected. In the fused state, or after fusion and rapid cooling, the magnetic susceptibilities are high, and are in accordance with a quinonoid constitution. After deposition from solution or after fusion and slow cooling, the magnetic susceptibilities are low, and indicate that the paler coloured forms have the azo-constitution.

The magnetic susceptibility of aurin indicates that it is quinonoid in structure.

The formulæ assigned by Torrey and Hunter (Abstr., 1907, i, 1030) to the two forms of the silver derivative of tribromophenol are in harmony with their magnetic values. T. A. H.

Magnetic Study of the Rôle of Water in the Constitution of Solid Hydrates. (Mlle.) E. FEYTIS (*Compt. rend*, 1911, **153**, 668—671. Compare this vol., ii, 367).—The coefficient of magnetisation of salts in the anhydrous and in the hydrated condition has been measured to ascertain whether water of crystallisation has any effect on magnetic susceptibility. For the sulphates of cobalt, samarium, and gadolinium, the property is strictly additive, the observed values for the anhydrous substances agreeing with the numbers found by deducting the coefficient for water from that of the crystalline, hydrated salt. In the case of copper sulphate, however, although the $4H_2O$ lost at 100° is without influence on the magnetic properties of the anhydrous compound, the remaining molecule, regarded as water of constitution, does not obey the law of additivity, since the coefficient for the anhydrous salt is identical with that of the monohydrate.

W. O. W.

Expansion Pressure of a Normal Liquid. L. GAY (*Compt. rend.*, 1911, **153**, 722—724. Compare Abstr., 1910, ii, 935, 1043; this vol., ii, 850).—The author develops the expression:

$$\log \pi = \log (RT/V-b) + b(V-b) - (EL - RT + PV)/RT,$$

wherein π is the expansion pressure of a liquid at constant temperature, T, of molecular volume, V and co-volume, b, L being the ideal molecular latent heat. Application to benzene shows that this furnishes a simple method for characterising normal liquids, or for determining the co-volume and internal pressure. Biron's determinations of the vapour density of benzene (Abstr., 1910, ii, 393) and Young's values for vapour pressure (Trans, 1889, **55**, 486) were employed. The results were in close agreement with theory.

W. O. W.

Specific Heat and the Theory of Finite Increments of Energy. WALTHER NERNST and F. A. LINDEMANN (*Zeitsch. Elektrochem.*, 1911, **17**, 817—827. Compare this vol., ii, 465, 466). —The difference between the atomic heats calculated by Einstein's formula and those observed at low temperatures is discussed. The suggestion that all the atoms of a substance do not have the same frequency of vibration is dismissed, because all the atomic heat curves may be superposed by using a suitable temperature scale, and because Rubens and Hollnagel's measurements of the infra-red absorption bands of sodium and potassium chloride and potassium bromide show these to be quite narrow (Abstr., 1910, ii, 172). The author's new formula: $C_v = 3R/2\{(\beta v/T)^2 e^{\beta\nu/T}/(c^{\beta\nu/T}-1)^2 + (\beta v/2T)^2 e^{\beta\nu/2T}/(c^{\beta\nu/2T}-1)^2\}$, where $\beta = 4{\cdot}865 \times 10^{-11}$ and v is the frequency of vibration of the atom, is shown to agree well with the observations down to 23^{c} absolute when the values of v observed optically by Rubens and Hollnagel are used. The example of diamond is especially interesting, because both theory and observation indicate that its specific heat becomes practically zero at so high a temperature as 42^{c} absolute.

The physical interpretation of the equation above given is discussed at some length.

The possible application of the equation in the exact determination of atomic weights is also pointed out. As an example the atomic weight of silver is calculated from the specific heat–temperature curve to be 107·55.

T. E.

Mean Specific Heat of Crystallised and Fused Silicates at 20—100°. KARL SCHULZ (*Centr. Min.*, 1911, 632—640).—The following determinations were made in a water calorimeter with the silicate heated at about 100°, and the water at about 20°. The glassy materials were obtained by fusing the crystallised silicates in an electric oven.

	Crystallised.	Amorphous.
Lead metasilicate ($PbSiO_3$)	0·07807	0·07886
Adularia from St. Gotthard	0·1855	0·1895
Microcline with albite from Arendal	0·1865	0·1919
,, ,, ,, ,, Miask	0·1845	0·1884
,, ,, ,, ,, Sætersdalen ...	0·1878	0·1909
Spodumene* from Branchville, Conn.	0·2161	0·2176

* M. p. about 1380°.

In every instance the specific heat is greater for the amorphous material than for the corresponding crystallised material. L. J. S.

Phosphoryl Chloride as a Cryoscopic Solvent. GIUSEPPE ODDO and ANNA MANNESSIER (*Gazzetta*, 1911, **41**, ii, 212—223. Compare Walden, Abstr., 1910, ii, 1036).—Phosphoryl chloride, m. p. about −1°, containing some hydrate, has a cryoscopic constant 70·2 (compare Oddo, Abstr., 1901, ii, 492). By fractional distillation over phosphoric oxide and repeated fractional crystallisation the melting point can be raised to 1·37°. The higher values given by Besson and by Thorpe must be erroneous, and the values −1·782° and +1·782°, attributed to Oddo by various writers, including Walden (*loc. cit.*), were never obtained by him. Phosphoryl chloride of the highest melting point cannot be kept. For cryoscopic purposes, purification by dehydration, distillation, and a few crystallisations is sufficient; it then has m. p. 0·4—0·9°, and the cryoscopic constant of this product is 72·1. This constant was obtained from experiments with acetic anhydride, *n*-propyl ether, acetone, *n*-hexane, *cyclo*hexanone, and sulphur chloride. Determinations with aromatic substances gave much more widely varying numbers, owing to substitution, and the mean was considerably higher. Hence the value 76·8, found by Walden, must be considered too high. The latent heat of fusion of phosphoryl chloride (calculated from $K=72·1$) is 20·9 cal. R. V. S.

Cryoscopy in Fused Sodium Thiosulphate. A. BOUTARIC (*Compt. rend.*, 1911, **153**, 876—877).—The freezing point of the salt $Na_2S_2O_3,5H_2O$ is 48·5°, and the temperature at which the solid pentahydrate and dihydrate are in equilibrium with the liquid is 48·2°. When the fused pentahydrate is employed as solvent for carbamide, sucrose or sodium chlorate, nitrate or sulphate, the molecular lowering of the freezing point is 44°. For potassium chlorate, nitrate, chloride and sulphate, and for ammonium nitrate, the lowering is practically double this number, corresponding with almost complete ionisation of these salts. W. O. W.

Cryoscopic Behaviour of Quaternary Aromatic Ammonium Salts in Bromoform, and the Cryoscopic Measurement of a Velocity of Decomposition. EDGAR WEDEKIND and F. PASCHKE (*Ber.*, 1911, **44**, 3072—3080. Compare Abstr., 1910, ii, 597).—From cryoscopic measurements it is found that quaternary ammonium salts of the type $CH_2Ph·NMePhRX$ (where R= methyl, propyl, *iso*butyl or allyl, and X= Br or I) are considerably associated in bromoform solution, the association factor being approximately 2. The association cannot be attributed to the residual affinity of an unsaturated element, since it is found that phenylbenzylmethylallylammonium *d*-camphorsulphonate also exists in the form of double molecules.

The velocity of decomposition of phenylbenzylmethylallylammonium bromide in bromoform solution has been determined by measuring the gradual alteration in the depression of the freezing point. The initial constants thus obtained are in agreement with those determined by the polarimetric method.

Further evidence of the decomposition of quaternary ammonium salts is furnished by the gradual diminution in the electrical conductivity of their solutions in chloroform; thus, after one hundred and fifty minutes at 25°, a 1·2% solution of phenylbenzylmethylallylammonium iodide has a specific conductivity of only two-thirds of the initial value. F. B.

Volatility of Sulphur Compounds. MARCEL DELÉPINE (*Compt. rend.*, 1911, **153**, 725—727).—From collected data on the boiling point of numerous organic oxygen compounds and their sulphur analogues, it is shown that generally speaking substitution of sulphur for oxygen raises the boiling point, except in the case of water and the lower alcohols, phenols, and acids. W. O. W.

Internal Pressure of Liquids and the Determination of the Absolute Zero. ÉMILE H. AMAGAT (*Compt. rend.*, 1911, **153**, 851—857. Compare Abstr., 1909, ii, 549).—Leduc has recently stated (this vol., ii, 792) that the internal pressure of a gas diminishes with rise of temperature, but calculations from Chappuis' data leave this open to doubt, especially when it is borne in mind that the values are referred to a hydrogen thermometer instead of to one containing a perfect gas.

Leduc's conclusion is necessary to the maintenance of the theory that the internal pressure for gases of the same molecular complexity is proportional to the square of their molecular weights. When the value of the function $T.dp/dt - p$ is calculated for hydrogen, it is necessary to pre-suppose the existence of a much greater variation of the internal pressure coefficient than can possibly exist, in order to bring the case into harmony with the theory. The values agree more closely with the present author's law of volumes when 273·0° is taken as the absolute zero than when the zero is taken as 273·1°. Conversely, assuming the truth of this law (that π and π', the components of internal pressure, vary inversely as the square of the volume for molecular distances sufficiently great), calculation of the absolute zero gives 272·983° as the absolute zero for hydrogen, and 272·999° and 272·996° for nitrogen and oxygen respectively. It is shown that the critical density of diatomic and triatomic gases increases regularly with the critical pressures in such a way that the ratio p/d^2 varies within somewhat narrow limits.

W. O. W.

Boiling Point of Water. EARL OF BERKELEY and MALCOLM P. APPLEBEY (*Proc. Roy. Soc.*, 1911, *A*, **85**, 477—489).—The boiling point of water, as determined by Buchanan's method (the so-called Landsberger-Sakurai method), has been compared with the hypsometer point. The small temperature differences involved were measured electrically by means of two platinum resistance thermometers. The sensitiveness of the measuring apparatus was such that the error attaching to the determination of the temperature difference was not more than 0·0001°.

The temperature at which water boils when a current of steam is passed through it depends on several factors, of which the chief are the height of the liquid and the rate of passage of the vapour bubbles.

As compared with the hypsometric temperature, the boiling point rises with the height of the liquid if the steam is passed through at a constant rate. When the temperature differences are plotted against the height of the column of water, hyperbolic curves are obtained which cut the temperature axis at the origin at an approximate right angle. The curves can be represented by an equation of the form $t = kah^2/(h+\beta)$, in which t is the temperature difference, h the height of liquid, k, a, and β constants which depend on the form of the apparatus and the rate of bubbling.

For a given height of liquid, the boiling point falls with increase in the rate of passage of the steam. This apparently anomalous result is attributed to the influence of (1) the increased rate of bubbling on the agitation of the liquid, leading to increased loss of heat at the surface, and (2) the coalescence of the bubbles, leading to a diminished rate of heating. H. M. D.

Boiling Points of Some Saturated Aqueous Solutions.

EARL OF BERKELEY and MALCOLM P. APPLEBEY (*Proc. Roy. Soc.*, 1911, *A*, **85**, 489—505. Compare Abstr., 1904, ii, 648).—The electrical temperature-measuring apparatus employed in the experiments with water (preceding abstract) has been applied to the accurate determination of the boiling points of saturated salt solutions according to Buchanan's method.

Since the effect of changes in barometric pressure on the temperature equilibrium is greater for saturated solutions than for water, boiling-point measurements were made at different pressures, and a barometer-coefficient determined for each salt. This coefficient, which represents the excess of the effect of a pressure of one millimeter of mercury on the temperature of the boiling saturated solutions over that on the hypsometer temperature, is dependent on the solubility of the salt and on the temperature-coefficient of the solubility. For sodium sulphate its value is 0·00052°, whilst for potassium nitrate the coefficient is 0·0217°.

From the hyperbolic curves which express the relationship between the boiling point and the height of the column of boiling salt solutions, boiling points corresponding with a very thin layer of solution are calculated by suitable methods of extrapolation. These values are then corrected by means of the corresponding barometer-coefficients, and in this way boiling points obtained for normal pressure.

The boiling-point data are applied to the calculation of osmotic pressures by means of Porter's equation; the values so obtained show that all the salts are dissociated with the possible exception of thallous nitrate. Data representing the composition and density of saturated solutions of strontium nitrate are given in an appendix. H. M. D.

Partial Pressures of Water and Alcohols in Aqueous Alcohols. V.

ANTONY G. DOROSCHEWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 962—973. Compare Zawidzki, Abstr., 1901, ii, 6; Vrevsky, Abstr., 1910, ii, 1038).—By means of experimental data obtained by Regnault, Konowaloff, and Vrevsky, the author deduces the two following theorems:

(1) In any aqueous alcoholic solution, the ratio between the partial pressures of the water at any two temperatures is equal to the ratio between the vapour pressures of pure water at these temperatures, or the change of the partial pressure of water with temperature is identical in all mixtures of alcohol and water, independent of the composition of the solution or of the nature of the alcohol.

(2) The ratio between the partial pressures of an alcohol in its aqueous solution at any two temperatures is identical for all solutions, and is identical with the ratio of the vapour pressures of the pure alcohol at the same two temperatures.

It is shown that the differences between the compositions of the vapours evolved from one and the same aqueous alcohol solution at different temperatures are a direct consequence of these two theorems. If P and p denote the vapour pressures of the alcohol and water at the temperature t, and P_1 and p_1 the corresponding magnitudes at t', then, if the ratio P/P_1 is greater than p/p_1, the increase of the partial pressure with rise of temperature is greater for the alcohol than for water. The values of this ratio for water and for various alcohols in the case of various pairs of temperatures are given in the following table:

	20°/30°.	30°/40°.	40°/50°.	50°/60°.	70°/80°.	80°/90°.	90°/100°.
Water	0·540	0·574	0·597	0·618	0·638	0·657	0·691
Methyl alcohol......	0·592	0·613	0·634	0·656	—	—	—
Ethyl ,, ...	0·564	0·585	0·607	0·628	0·647	0·662	—
Propyl ,, ...	0·517	0·546	0·597	0·599	0·623	0·647	0·691

It follows that with rise of temperature the vapours from aqueous methyl and ethyl alcohols become richer in water, whilst with aqueous propyl alcohol the opposite is the case. T. H. P.

Condensation of Vapours. Felix Becker (*Zeitsch. physikal. Chem.*, 1911, **78**, 39—70).—The phenomena attending the condensation of vapours which are in equilibrium with the crystalline form as stable phase have been investigated. The condensation was effected in the usual way by sudden adiabatic expansion, and the formation of fog was detected by a very sensitive method depending on the reflection and refraction of light by the particles. The substances chiefly used were nitrophenol, menthol, camphene, camphor, borneol, *iso*borneol, benzophenone, and iodine.

Substances which in the liquid form can be considerably supercooled condense at first as liquid drops, but substances which cannot easily be supercooled in the liquid form pass directly from vapour to crystalline form. The amount of reduction of pressure which is just sufficient to produce condensation on adiabatic expansion, and its dependence on the temperature, have been investigated, and it is shown that the condensation of a vapour to liquid drops occurs the more readily the denser the vapour, whereas the formation of crystals is retarded by increasing density of vapour. From the minimum depressions just sufficient to produce condensation, the supercooling which the vapours have undergone is determined, and hence a curve is constructed showing the limits within which the vapour can be realised on crossing the sublimation curve.

Iodine is exceptional, inasmuch as on considerable reduction of pressure it condenses as visible particles, but with smaller depressions (as shown by thermal observations) it condenses as invisible particles. None of the other substances investigated shows an intermediate stage in condensation.

The supercooling before condensation occurs is the same whether the vapour is or is not in contact with a smooth glass wall, and hence the latter has no influence on the condensation.

Water vapour condenses as liquid drops for temperatures down to – 4° and reductions of pressures up to 400 mm., so that the limit ice-liquid lies at still greater reductions of pressure. G. S.

Pressure-Temperature Sections. J. P. WHITE (*Zeitsch. physikal. Chem.*, 1911, **78**, 71—85).—A space figure is constructed for a two-component system for the case in which the components form a solid compound which as regards volatility lies between the two components, the assumptions being that the components are completely miscible in the liquid state and not miscible in the solid state, and that the volatility of the liquid mixtures diminishes continuously according to the proportion of one of the components. By means of this figure and the simple space figure of Roozeboom, the pressure-temperature sections for varying conditions are completely investigated. G. S.

New Methods of Resolving Mixtures of Liquids with Adjacent Boiling Points or Constant-boiling Mixtures. A. GOLODTZ (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1041—1060).—The method used by the author consists in adding to the mixture of two liquids a suitable proportion of a third component which forms with one of the original constituents a constant-boiling mixture with a boiling point lower than those of all the other elements of the mixture, that is, of the liquids themselves, and of any other possible combinations; the ternary mixture thus obtained is then rectified. This method can be applied either when the boiling points of the two liquids are very close, or when they form a mixture with a constant boiling point.

Several examples are given, one which is of technical importance being as follows: If 195 grams of 65·5% aqueous acetic acid are mixed with 272 grams of toluene, and the mixture distilled through a Hempel column, the first fraction of 337 grams, b. p. 84—85·5°, will contain practically all the toluene and water and only 4·1% of the acid; the last fractions, amounting to 107 grams, contain 96·01% of acetic acid, and the final one of these, 64 grams, 99·9% of acid.

T. H. P.

A Simplified Combustion Calorimeter. ROBERT WRIGHT (*Chem. News*, 1911, **104**, 201—202).—The calorimeter consists of a glass bell-jar carrying on its flange a lead weight heavy enough to sink the jar when filled with oxygen. The fuel is contained in a nickel crucible supported on a small tripod, which is part of the brass base plate. This base plate is cut from heavy sheet brass, and provided with broad tongues at the edge to clamp it to the base of the jar; tongues are also cut in it which turn up and form the tripod.

The oxygen for combustion is led through a tube of Jena glass, which slides through a cork in the neck of the jar, and is enlarged at the lower end. The outside of the jar is fitted with a ring of brass wire gauze projecting at right angles to the sides.

The combustion is carried out in the usual way with calorimeters of this type, the factor of the instrument being found by burning a substance of known calorific value. T. S. P.

Thermochemical Investigations. IV. Heats of Combustion of Terpenes and Styrenes and Prediction of Heats of Combustion. KARL AUWERS, WALTER A. ROTH, and FRITZ EISENLOHR (*Annalen*, 1911, **385**, 102—116. Compare Abstr., 1910, ii, 586). —It has been found that the heats of combustion of the terpenes and the styrenes already published (*loc. cit.*) are about 0·5% too low, in consequence of the difficulty of ensuring the complete combustion of slightly volatile liquids in the bomb calorimeter. A new series of estimations, performed in a modified apparatus, is being carried out. The results, which show that the theoretical deductions stated previously are still correct, were being held back until the series was completed. However, the appearance of Lemoult's paper (this vol., ii, 583) forces an immediate answer from the authors. Lemoult's heats of combustion of styrene, α-methylstyrene, and $\alpha\beta$-dimethylstyrene differ from those obtained by the authors by a constant amount, about 1·2%. This suggests that the discrepancy is due to a constant error (probably in the value of the water-equivalent of the calorimeter). The confidence with which Lemoult relies on his experimental values on account of their agreement with "calculated" values may be misplaced, because, although in some cases the observed and the calculated values are concordant, in others the difference is more than 1%, that is, more than ten times the experimental error. C. S.

Vapour Pressure and Integral Heat of Solution for Saturated Solutions. ALEXANDER SPERANSKI (*Zeitsch. physikal. Chem.*, 1911, **78**, 86—109. Compare Abstr., 1909, ii, 378).—The differences in the vapour pressures of pure solvent and saturated solution have been determined by the tensimeter for saturated solutions of oxalic acid, succinic acid, and a number of inorganic salts in water, and for saturated solutions of acetanilide in chloroform, and *m*-dinitrobenzene in benzene and in chloroform, and from the results, the vapour pressures of the saturated solutions between 20° and 60° have been calculated. Except in the case of sodium thiosulphate, the vapour pressures increase as the temperature rises. In accordance with the principles of thermodynamics, the ratio p_1/p_2, where p_1 is the vapour pressure of the solution and p_2 that of the solvent, diminishes with rise of temperature, except for the solution of sodium carbonate monohydrate.

For all the solutions, the relationship between vapour pressure and temperature is satisfactorily represented by Bertrand's formula:

$p=k[(T-\lambda)/T]^n$, where k and λ are constants. From the analogy between vaporisation and dissolution, it might be anticipated that Bertrand's formula in the form $C=G[(T-\lambda)/T]^n$, where C is the solubility, would represent the variation of the solubility with temperature, and this is shown to be the case. The formula $\log p=a \log C+b$, where C is the solubility in grams per 100 grams of solution, and a and b are constants, is valid for most of the solutions investigated.

It is further shown that the formula $\log p_2/p_1=a+b/T$ is valid for certain solutions, a and b being constants. Combining this with the formula $[d \log p_2/p_1]/dT=l/RT^2$ (Kirchhoff's formula), where l is the integral heat of solution, it follows that l must be nearly constant, and hence that the van't Hoff formula $\log(p_1/p_2)= -l/2T$ can be used to calculate the integral heat of solution for saturated solutions at temperatures exceeding 30—40°. G. S.

Dependence of the Integral Heat of Solution on the Temperature. A. WOITASCHEWSKY (*Zeitsch. physikal. Chem.*, 1911, **78**, 110—122. Compare Speranski, preceding abstract).—It is shown that all the formulæ representing the variation of the vapour pressure of a pure liquid with the temperature also apply to the variation of the vapour pressure of a saturated solution with temperature. On this basis, the conclusion is drawn that the integral heat of solution diminishes with the temperature when it is positive, and increases with temperature when it is negative; in other words, the absolute magnitude of the integral heat of solution always diminishes with the temperature. Kirchhoff's formula (compare Speranski, previous abstract) is not directly applicable to the experimental data. G. S.

The Theory of Solution and Heats of Dissolution. ALBERT COLSON (*Compt. rend.*, 1911, **153**, 812—814).—The author points out that the heat of dissolution of a gas should be equal to the sum of its latent heat of vaporisation and the heat of polymerisation of the dissolved molecule. This is known to be true in cases such as that of acetic acid, in which the degree of polymerisation is the same for the dissolved substance as when it is in the gaseous condition. The term *dissolecule* is employed to denote a polymerised molecule in solution. W. O. W.

A General Relation between the Physical Properties of Substances; Application to Densities. G. TER-GAZARIAN (*Compt. rend.*, 1911, **153**, 871—874. Compare Abstr., 1908, ii, 666; 1909, ii, 551).—It has been shown previously that for members of a homologous series, the densities corresponding with temperatures distant the same number of degrees from the critical temperature differ only by a factor which increases with the molecular weight and varies according to the series. It has now been found that this holds good, not only for densities, but also for coefficients of viscosity, heights of capillary ascension, rectilinear diameters, and the latent heat of vaporisation calculated by Mills' method. The best published data were employed for the verification of this generalisation. W. O. W.

Weight of a Falling Drop and the Laws of Tate. X. Drop Weights of Some Further Associated and Non-associated Liquids, and the Surface Tensions and Capillary Constants Calculated from Them. J. LIVINGSTON R. MORGAN and F. T. OWEN (*J. Amer. Chem. Soc.*, 1911, **33**, 1713—1727. Compare Abstr., 1908, ii, 356, 668; this vol., ii, 372, 584, 585, 698, 699, 857).—On applying the equation $w(M/d)^{2/3} = k_B(t_c - t_0 - 6)$ to the drop weights in order to find a value of t_0 independently of the temperature of observation and using in all cases the value of k_B found for benzene ($t_c = 288·5°$), it has been found that methyl hexyl ketone, phenylacetonitrile, benzaldehyde, piperidine, di*iso*amyl, *iso*amyl acetate, and nitrobenzene have a normal molecular weight, whilst methyl ethyl ketone, diethyl ketone, propionitrile, and acetone are abnormal and therefore associated.

The values of the surface tensions of these liquids in dynes, γ, and of the capillary constant, a^2, calculated respectively from the drop weights and drop volumes, agree well with the values obtained from the capillary rise.

Equations are given expressing the variation of the surface tension and the capillary constant, as found from the drop weight, for all the liquids mentioned. E. G.

The Viscosity of Suspensions and the Determination of Avogadro's Number. M. BANCELIN (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 154—156).—Measurements have been made of the viscosity of aqueous suspensions of gamboge and gum mastic. The experimental data are in accord with Einstein's formula, according to which the ratio between the viscosity of the suspension and the suspending medium is independent of the size of the suspended particles, but varies in a linear manner with the mass of the particles contained in unit volume of the suspension.

Experiments with various aqueous solutions indicate that the relationship between the viscosity of the solution and of the solvent can be represented in certain cases by a formula of the same type. This is true for solutions of glycerol, sucrose, and sulphuric acid, but not for solutions of phenol or carbamide.

The validity of Einstein's viscosity formula for suspensions of molecular dimensions permits of the deduction of the number of molecules in unit volume. From the data for sucrose solutions this is found to be 70×10^{22}, which agrees satisfactorily with Perrin's value deduced from observations on the Brownian movement.

H. M. D.

Molecular Complexity in the Liquid State. PHILIPPE A. GUYE (*J. Chim. phys.*, 1911, **9**, 505—518. Compare Turner and Merry, Trans., 1910, **97**, 2069).—Association in the liquid state was held by Turner and Merry to be due to electrical rather than chemical forces. The author is unable to find any essential difference between the two points of view, since chemical forces are almost certainly electrical in origin. Moreover, polymerisation in the liquid state is related to polymerisation in the vapour by the mass action law (Abstr., 1910, ii, 841). Surface tension, boiling point, vapour tension, and latent heat measurements do not indicate the molecular complexity of liquids apart from the surface film, and where easily oxidisable substances, such as phenylurethane and diphenylamine, are measured in contact with air the result may be wholly misleading. All the liquids giving higher values of Ramsay and Shields' coefficient than $k=2{\cdot}2$ are substances of high molecular weight and high boiling point, and in these cases the high surface pressure may considerably influence the molecular condition in the surface film. The only trustworthy methods are those such as Traube's volume method, which is independent of the surface film.

The recent observations of Walden on tristearin, tripalmitin, and *iso*butyl ricinolate are to be interpreted as showing marked dissociation of these substances in the surface film. The author suggests that the dissociation products are alkylene and acid. R. J. C.

Stability of Oil–Water Emulsions. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 159—164).—The author discusses the conditions which determine the stability of emulsions and the rate at which clearing takes place under the influence of electrolytes. It is calculated that an emulsion of an oil of density $0{\cdot}7$, which contains $0{\cdot}1\%$ of the disperse phase and consists of particles of diameter $0{\cdot}4\mu$, is subjected to an upward force amounting to $1{\cdot}10^{-11}$ dyne per particle, whereas according to Lewis's data for the magnitude of the electric charge, the electrical force of repulsion between two neighbouring particles amounts to $2{\cdot}3\times10^{-8}$ dyne. The very much greater magnitude of the electric force is in harmony with the exceptional stability of such highly disperse emulsions.

In accordance with Stokes's formula, the rate of clearing of particles of a given size on the addition of an electrolyte must depend to a large extent on the difference between the densities of the disperse phase and the dispersive medium. In this connexion, observations are recorded relating to the condition of oil–water emulsions at intervals of twenty-four, forty-eight, and one hundred and twenty hours after the addition of an electrolyte. The clearing process involves three stages: (1) the electric discharge of the particles; (2) the formation of larger complexes; (3) the mechanical separation of these from the dispersive medium, and of these, the second and the third represent changes which in general require considerable time for their completion.

H. M. D.

The Nature of Solvates and the Relationships between Adsorption and Dissociation. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 189—195).—The view is put forward that solvates may be regarded as absorption compounds between solute and solvent. For the special case of aqueous solutions of salts, reference is made to the connexion between the ionisation of a given salt and its degree of hydration, and it is pointed out that Noyes's formula $C(1-\gamma)=K(C\gamma)^r$ connecting the degree of ionisation (γ) with the concentration (C) can be written in the form $C\gamma=K_2(C-C\gamma)^p$, which is of the same type as the adsorption formula $x=K(C-x)^n$.

Not only is the form of the equations identical, but more or less quantitative relationships are also shown to exist between the two groups of phenomena. The exponents in the two equations are of the same order of magnitude, and their variation is confined to rather narrow limits. Both ionisation and adsorption exhibit maxima, have small negative temperature-coefficients, and show similar deviations from the exponential formula at high concentrations. These facts are in favour of the hypothesis that the hydration of salts in aqueous solution may be looked on as an adsorption of the solvent by the solute. H. M. D.

Adsorption of Neutral Salts. Hilary Lachs and Leonor Michaelis (*Zeitsch. Elektrochem.*, 1911, **17**, 917—919).—The statement in the previous paper (this vol., ii, 190) that the anion and cation are adsorbed in equivalent amount by blood charcoal from a neutral aqueous solution of potassium chloride is erroneous. As a matter of fact Cl′ ions only, and no K˙ ions, are adsorbed. It would therefore be anticipated that the solution, after adsorption of Cl′ ions, must contain free potassium hydroxide, but it has not been possible to obtain a quantitative proof of the presence of alkali. It is probable that the potassium is present as carbonate or other salt the negative component of which originates from impurities in the charcoal.

From an acidified solution of potassium chloride no K˙ ions are adsorbed, but in the presence of bases, such as ammonia and piperidine, K˙ is adsorbed. The adsorption of K˙ is most favoured when the solution is about *N*/50 with reference to ammonia. On the other hand, pyridine has no influence on the adsorption of K˙, so that the effect of bases depends partly on the nature of the cation. As it has previously been shown that Cl′ ions are not adsorbed from an alkaline solution of potassium chloride, the potassium must be taken up as the hydroxide.

The authors consider that these observations support their view that adsorption in such cases is a purely electrical phenomenon. G. S.

Adsorption Compounds (Van Bemmelen). Ugo Pratolongo (*Gazzetta*, 1911, **41**, ii, 382—412).—The author has carried out three series of experiments with the products which are precipitated when a solution of sodium aluminate is added to a solution of sodium silicate. The first series had for its object the determination of the variation in the composition of the precipitates formed, according to the relative concentrations of the solutions. The second set deals with the variation in the solubility of one of the compounds (of sodium aluminate and sodium silicate), according to the amount of the solid substance present. In the third series of experiments, determinations are made of the variations in the amount of ammonium chloride or potassium chloride adsorbed by the product used in the second series, according to the relative amounts of liquid and solid phases present. In these experiments the adsorption is measured by means of the equilibria reached (*a*) when the concentrations of the salt solutions is increasing, and (*b*) when the concentrations of the salt solutions is decreasing. The results indicate that a solid phase of the type employed can give rise to a trivariant system, in which the solid phase behaves as though it had a variable concentration.

The system also presents the phenomenon of chemical hysteresis (evidenced in the third set of experiments), that is to say, permanent modifications may be formed. R. V. S.

Adsorption in Solution. I. Retention of Acids by Sheep's Wool. GEORG VON GEORGIEVICS and ARTUR POLLAK (*Monatsh.*, 1911, **32**, 655—675).—The wool used was very carefully purified by treatment in turn with boiling distilled water, hot soap solution, boiling 2% hydrochloric acid (on the weight of wool), lukewarm very dilute ammonium carbonate, warm water containing very little acetic acid, and boiling distilled water.

The retention of acids by wool is an adsorption phenomenon which within certain limits takes place according to definite laws. In general, mineral acids are more strongly adsorbed than fatty acids. The concentration of the acid has considerable influence on the adsorption; an acid may be adsorbed more strongly than another acid from dilute solution and less strongly in more concentrated solution. There is no proportionality between the strength of an acid and its adsorption by wool; this is contrary to the conclusions of Walker and Appleyard with silk (Trans., 1896, **69**, 1334). There is absolutely no connexion between the adsorption and the amount of dissociation of an acid.

Less acid is adsorbed by wool from a mixture of acids than the arithmetical mean of the adsorption from two acids used singly. This negatives the possibility of simple salt formation between the acid and the thread substance. E. F. A.

Substantive Dyeing. W. G. SAPOSCHNIKOFF (*Zeitsch. physikal. Chem.*, 1911, **78**, 209—227).—Both the dyes and the materials were carefully purified, and, in contrast to the technical method, no salts were added. The dyeing was effected by boiling the material with a solution of the dye for two hours, a reflux condenser being used. The material was then washed, and the amount of dye taken up determined by fusing it with sodium hydroxide and nitrate, and estimating the sulphur as sulphate, the amount of sulphur in each dye being determined in like manner. The results of five series of experiments, in each of which the conditions were widely varied, are quoted.

It is shown that the results are represented satisfactorily by the adsorption formula: $\log C_f = \log\beta + 1/a.\log C_b$, where C_f and C_b are the final concentrations of dye in the material and in the bath respectively, and a and β are constants, or by the related formula: $C_f^2 + AC_f - A.10k = 0$, where A is a constant and $10k$ represents the dyeing limit, the greatest concentration of dye which the material can remove from the bath. A comparison of two experiments, for which all the characteristics are different, leads to the formula: $C_b/C'_b = [(10k - C_f)K'_w]/[(10k' - C'_f).K_w]$, that is, the end concentrations of the baths are directly proportional to the differences between the dyeing limit and the effective dyeing, and inversely proportional to the bath moduli, which are functions of the original dye concentration in the bath.

The above laws are followed whether the materials retain their natural structure (cotton wool) or have undergone treatment (mercerised cotton). Under equivalent conditions mercerised cotton becomes dyed about 10% more deeply than the natural wool.

G. S.

Dissociation Constant K_2 of Sulphuric Acid and Oxalic Acid. JOHANNES E. ENKLAAR (*Chem. Weekblad*, 1911, 8, 824—829).—By means of the hydrogen electrode and a dilute solution of sodium hydrogen sulphate, the author has determined the mean value of the second dissociation constant of sulphuric acid at 18° to be $K_2 = 0{\cdot}018$. For oxalic acid the value K_2 was calculated from the dissociation curve of oxalic acid, and the concentration of the hydrogen ions ($1{\cdot}5 \times 10^{-3}$) in a solution containing 0·05 gram of sodium hydrogen oxalate per litre, and was found to be $K_2 = 4{\cdot}7 \times 10^{-5}$. Another calculation based on the electric conductivity yielded the value $K_2 = 1{\cdot}3 \times 10^{-5}$. Both the values obtained for oxalic acid are therefore of the same order as the dissociation constant of acetic acid, $K = 1{\cdot}8 \times 10^{-5}$.

A. J. W.

Osmotic Pressure. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1911, [iv], 9, 857—862).—A mathematical investigation of osmotic pressure on the basis of an analogy between gravitational attraction and osmotic pressure. The details are unsuitable for abstraction. It is shown (1) that osmotic pressure is not directly proportional to the mass of the dissolved substance, which is in harmony with Fouard's experimental results; (2) that from the general equation arrived at in this investigation the known formulæ expressing the behaviour of dilute solutions under various conditions are deducible.

T. A. H.

The Theory of Solutions. ALBERT COLSON (*Compt. rend.*, 1911, 153, 719—721).—The author considers that the experimental data on osmotic pressure are not sufficiently in agreement with theory to support the hypothesis as to the analogy between osmotic and gaseous pressure, that is, to warrant the identification of R and ρ in the expression $PV = RT$, and $\omega V = \rho T$ when ω is the osmotic pressure.

W. O. W.

Osmotic Measurements of Salt Solutions and Arrhenius' Theory of Ions. EUGÈNE FOUARD (*Compt. rend.*, 1911, 153, 769—772. Compare this vol., ii, 267).—A theoretical discussion based on measurements of osmotic pressure made by the apparatus already described. The author draws attention to the divergences between his results and those required by the ionic theory.

W. O. W.

Direct Measurements of the Osmotic Pressure of Casein in Alkaline Solution. Experimental Proof that Apparent Impermeability of a Membrane to Ions is Not due to the Properties of the Membrane but to the Colloid contained within the Membrane. BENJAMIN MOORE, HERBERT E. ROAF, and ARTHUR WEBSTER (*Biochem. J.*, 1911, **6**, 110—121. Compare Moore and Roaf, Abstr., 1908, ii, 204).—The osmometer used in the experiments has been described in previous papers. At the commencement of an experiment, the osmometer chamber contained a certain concentration of caseinogen and of sodium hydroxide, and the outer liquid was a solution of sodium hydroxide of the same concentration as that inside the cell. The observed osmotic pressure was very low at first, but the exterior sodium hydroxide slowly diffused inwards through the membrane, and simultaneously the osmotic pressure increased. The inward passage of sodium hydroxide is against the gradient of osmotic pressure. The alkali in the osmometer unites in some form with the colloid, and it is this union which causes the osmotic pressure. The purpose of the membrane is the purely mechanical one of holding together the colloidal aggregates, and its apparent impermeability to the ions is quite fictitious. Free ions pass through quite readily, but ions associated with colloid are retained on the colloid side and produce pressure. The high concentration of crystalloid within and the low concentration without is due to a specific affinity between crystalloid and colloid. The maximum of osmotic pressure per 1% of colloid is reached at about 0·047*N* of free alkali, and further increase of alkali lowers osmotic pressure. In the course of the experiments pressures as high as 686 mm. were observed.

These considerations are applied to the elucidation of the osmotic behaviour of living cells, which is discussed in detail. G. S.

Permeability of Porcelain and Copper Ferrocyanide Membranes. F. E. BARTELL (*J. Physical Chem.*, 1911, **15**, 659—674. Compare Bigelow and Bartell, Abstr., 1909, ii, 979).—The rate at which water passes through unglazed porcelain and through an electrolytic copper ferrocyanide membrane under the influence of pressures up to 5885·7 mm. and 2957·9 mm. respectively was found to obey Poiseuille's laws relating to capillary tubes.

The porcelain membranes gradually became less permeable during the experiments, apparently owing to fine particles being torn off and forced into the capillary passages. On this account each series of determinations was immediately repeated in reverse order, and the average of each pair of values at the same pressure was taken as the rate for the membrane half way through the experiment. The permeability of the copper ferrocyanide membrane deposited in porcelain was only about 4% of the permeability of the 4·5 mm. porcelain plate, and no clogging of the membrane occurred.

The rate of permeation varied directly as the pressure at a constant temperature, and inversely as the viscosity of water when the temperature was altered and the pressure kept constant.

The fact that the same laws govern the passage of water through capillary tubes as through porcelain and ferrocyanide membranes is not necessarily in favour of the theory that these membranes are capillary in structure, since the passage of liquids through molecular interstices may be found to be amenable to the same mathematical treatment.

R. J. C.

The Influence of Affinity in Solutions. Michael Rózsa (*Zeitsch. Elektrochem.*, 1911, 17, 934—938).—When to a mixed solvent of the components A and B a third substance, C, readily soluble in A but only slightly soluble in B, is added, the freezing point of the mixed solvent is very often raised. For example, the addition of water to the mixed solvent benzene-alcohol raises the freezing point of the latter to an extent depending on the proportion of water added. The explanation given is that C forms chemical compounds with A or B, the number of molecules of solute being thus diminished. In this way the existence of molecular compounds of alcohol-water, phenol-water, alcohol-glycerol, alcohol-lactic acid, phenyl-glycerol, phenol-lactic acid, water-sulphuric acid, and water-stannous chloride has been proved. The quantitative composition of these compounds has not been determined.

The results appear to show the existence of considerable affinity between solvent and solute in dilute solution, and also that the influence of the solute extends over the whole of the solvent.

G. S.

Solubility of Sparingly Soluble Salts. Maurice Prud'homme (*J. Chim. phys.*, 1911, 9, 517—537. Compare Kohlrausch, Abstr., 1908, ii, 814).—The molecular conductivity, Λ, of a solution is approximately related to the dilution by the expression $\Lambda = cu^{1/n}$, where c and n are constants. The minimum value, V, of the dilution u for which ionisation is complete can be calculated, the ultimate molecular conductivity being represented by Λ_V instead of the more usual Λ_∞.

It follows that $\Lambda_V - \Lambda_v = (V/v)^{1/n}$, where v is the dilution of a saturated solution. The author shows that with twenty-one common bivalent salts n has a value very near 3·06. Taking $(\Lambda_V - \Lambda_v)/\Lambda_V = r$ and $1/\Lambda_V = R$, the above equation may be written $rv^{1/3·06} = RV^{1/3·06} = k$. The value of k deduced from Berkeley's accurate data for thallium chloride is 0·40154. From these equations it is possible to deduce the solubility of a salt, knowing the conductivity of its saturated solution and the value of Λ_V obtained from Kohlrausch's tabulated values of the ionic conductivities.

The solubilities of a number of sparingly soluble sulphates, carbonates, oxalates, etc., deduced in this way agree very well with the solubilities calculated by Kohlrausch in the majority of cases, but when the salts are hydrated, the author's method gives too high a value for Λ_v, and hence too low a value for the solubility.

With the very sparingly soluble salts cuprous thiocyanate, mercuric iodide, lead chromate, silver bromide, and silver iodide, the dilution in saturated solution is higher than that required to give complete ionisation, that is, $v > V$. The author's solubility values are then to be preferred to those of Kohlrausch. In all cases where $V > v$ the empirical formula $v = 0{\cdot}904 \times (\Lambda_{\infty} = 1/10^3\chi)^{1{\cdot}0086}$ may be used to calculate the solubility. This equation is independent of the conception expressed by V, and requires only the determination of the conductivity of the saturated solution. R. J. C.

Effect of Salts on the Solubility of Other Salts. I. ARTHUR A. NOYES and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1911, **33**, 1643—1649).—The well-known solubility principles, based on the law of mass-action, that (1) the product of the concentration of the ions of a salt, present as solid phase, has the same value in dilute solutions of other salts as it has when present alone, and that (2) the concentration of the non-ionised portion of a salt, present as solid phase, has the same value in dilute solutions of other salts as it has when present alone, are not accurate, but are subject to deviations, those of the first lying in the opposite direction to those of the second. The work described in this and the following papers has been undertaken with the object of studying the character and magnitude of these deviations, and, for this purpose, the concentration of the non-ionised portion and the product of the concentrations of the ions of the salt with which a solution is saturated have been calculated.

It is shown by reference to curves in which the solubilities of lead chloride, thallous oxalate, silver sulphate, and calcium hydroxide are plotted against the concentration of added salts, namely, lead nitrate, potassium oxalate, potassium sulphate, and sodium hydroxide respectively, that, in the case of uni-bivalent salts, the solubility-product principle is not even approximately true when a salt with a common bivalent ion is added. The ion-concentration product increases greatly, since the large addition of the bivalent ion is not compensated by any great decrease of the univalent ion of the salt with which the solution is saturated. E. G.

Effect of Salts on the Solubility of Other Salts. II. ARTHUR A. NOYES, C. R. BOGGS, F. S. FARRELL, and M. A. STEWART (*J. Amer. Chem. Soc.*, 1911, **33**, 1650—1663. Compare preceding abstract).—Determinations have been made of the solubility of potassium perchlorate in presence of potassium chloride and potassium sulphate at 25°, of thallous chlorate and sulphate in presence of each other at 20°, and of thallous sulphate in presence of thallous nitrate, sodium sulphate, and sulphuric acid at 25°. Conductivity measurements were made in order to obtain the various ionisation values.

The results show that the solubility of potassium perchlorate is reduced by the presence of potassium chloride or sulphate. The chloride has less influence on the solubility than the sulphate, which corresponds with its lower degree of ionisation.

The solubilities of thallous chlorate and sulphate are reduced when both salts are present as solid phases.

The solubility of thallous sulphate is greatly diminished in presence of thallous nitrate, a salt with a common univalent ion, and this decrease agrees qualitatively with the principle of the constancy of the ionic solubility product. Sodium sulphate, on the other hand, does not effect the expected reduction, the solubility being lessened by only 0·3% in a 0·1*N*-solution of this salt, and is actually increased by a 0·4*N*-solution. The solubility is also increased by sodium hydrogen sulphate and by sulphuric acid. E. G.

Effect of Salts on the Solubility of Other Salts. III. Solubility of Thallous Chloride in Solutions of Potassium Nitrate, Potassium Sulphate, and Thallous Sulphate at 25°. WILLIAM C. BRAY and W. J. WINNINGHOFF (*J. Amer. Chem. Soc.*, 1911, 33, 1663—1672. Compare preceding abstracts).—Experiments have been made to ascertain the effect of thallous sulphate and of potassium nitrate and sulphate on the solubility of thallous chloride. These are supplementary to the work of Noyes (Abstr., 1892, 1143) on the solubility of thallous chloride in presence of thallous nitrate, thallous chlorate, and several chlorides. The solubility and conductivity measurements were made at 25°.

The solubility of thallous chloride is increased by the presence of potassium nitrate or sulphate, salts without a common ion, as would be expected on account of the formation of thallous nitrate and sulphate by metathesis. The solubility is greatly decreased by thallous sulphate, a salt with a common ion, and this decrease is in qualitative agreement with the principle of the constancy of the ionic solubility product. The solubility curves for salts with a common ion seem to lie more closely together than would be expected from the widely different ionisation values. E. G.

Effect of Salts on the Solubility of Other Salts. IV. Quantitative Discussion of the Solubility of Uni-univalent Salts in the Presence of Other Salts. WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1911, 33, 1673—1686. Compare preceding abstracts).—The results of the work recorded in the two preceding papers are discussed quantitatively by a method which consists essentially in calculating, by the aid of the ionisation values, the concentration of the non-ionised portion and the product of the concentrations of the ions of the salt with which the solution is saturated, both when it is present alone and when another salt is present.

According to the mass law, the concentration (BA) of the non-ionised portion and the solubility product $(B^+)(A^-)$ should be constant in any saturated solution. It is shown, however, that in every case the former decreases considerably and the latter increases slightly as the total concentrations of the salts and of the ions in the saturated solution increase.

These variations can be expressed approximately as a function of the total ion concentration (Σi) in the solution by the exponential equations $(BA) = k_u(\Sigma i)^{m_u}$ and $(B^+)(A^-) = k_i(\Sigma i)^{m_i}$, in which k_u, k_i, m_u, and m_i are constants which were separately determined for each substance in the presence of each added salt. In the case of thallous chloride, in which the range of concentration of the added salts was very large, the equations do not fully express the results, but different values of m_i or m_u must be assumed at different concentrations. The values found for these exponents are recorded. Those for m_i at the concentration 0·016N are small and less than those at higher concentrations, and this indicates that the solubility product would be practically constant in the case of less soluble salts in presence of small quantities of other salts.

The values of m_i are much smaller than those of m_u at low concentrations, and hence the deviation from the theoretical dilution law $(B^+)(A^-)/(BA)=k$ is due more to abnormal behaviour of the non-ionised substance than to abnormal behaviour of the ions.

These results indicate that the ratio of the activity (Lewis, Abstr., 1908, ii, 16) to the concentration of univalent ions is nearly constant below 0·016N, but that at higher concentrations it decreases with increasing concentration, at first slowly and then more rapidly. The corresponding ratio for the non-ionised portion increases very rapidly with increasing concentration throughout the whole range of concentrations investigated.

The nearly uniform effect exerted on the concentration of the non-ionised portion and on the solubility product by the salts of two different valence types, and by those with and without a common ion, confirms the assumption that the ionisation relations of uni-univalent salts are primarily determined by the total equivalent ion-concentration. There are, however, consistent differences of secondary order in the effects of the different kinds of salts, and especially between the uni-univalent and uni-bivalent types. E. G.

Laws of "Concentrated" Solutions. III. Ionisation and Hydration Relations of Electrolytes in Aqueous Solution at 0°: (A.) Cæsium Nitrate, Potassium Chloride, and Lithium Chloride. Edward W. Washburn and Duncan A. MacInnes (*J. Amer. Chem. Soc.*, 1911, 33, 1686—1713. Compare this vol., ii, 862).—Determinations have been made of the depressions of the f. p., densities, relative viscosities, and equivalent conductivities of solutions of cæsium nitrate, potassium chloride, and lithium chloride at 0°, and of concentrations up to N in the case of potassium and lithium chlorides, and to 0·5N in that of cæsium nitrate. These salts were selected, since cæsium nitrate is only slightly or not at all hydrated, whilst lithium chloride combines with large quantities of the solvent, and potassium chloride occupies an intermediate position.

The cryohydric point for cæsium nitrate is $-1·254°$.

When the f.-p. curves for the three salts are compared with that of the normal solute, that is, one which is neither associated, dissociated, nor hydrated, potassium chloride is found to agree exactly up to about 0·5N, lithium chloride deviates decidedly in the direction of hydration, whilst cæsium nitrate deviates markedly in the opposite direction. The conclusion is drawn that deviation from the behaviour of a normal solute cannot serve as the basis for the calculation of the degree of hydration of an electrolyte. Another method for making this calculation is indicated, which has shown that about 9 mols. of water are combined with 1 mol. of potassium chloride, and about 18 mols. with one of lithium chloride in 0·5N solutions.

The f.-p. data for cæsium nitrate are compared with those of Biltz

(Abstr., 1902, ii, 310), and his statement that this salt obeys the law of mass action cannot be entirely confirmed. E. G.

Ultramicroscopic Observation of a Temperature Coagulation. THE SVEDBERG and KATSUJI INOUYE (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 153—154).—The influence of temperature on the coagulation of colloidal solutions of platinum in ethyl ether has been investigated by means of the ultra-microscope. When the number of particles observable in the ultra-microscope is plotted as a function of the temperature, two straight lines are obtained indicating a sudden change at 28—29°. This critical temperature agrees with that found previously as the result of microscopic observations.

H. M. D.

The Coagulation and Gelatinisation of Silicic Acid. NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 164—175).—The influence of electrolytes and of sucrose, separately and conjointly, on the gelatinisation of colloidal solutions of silicic acid has been investigated, and in reference to these experiments the author discusses the mechanism of the gelatinisation process. The colloidal particles are supposed to consist of membranes having a capillary structure. In consequence of the negative charge on the particles, water cannot enter into the capillary network until means are provided for the removal of the charge. Neutralisation of the charge is effected in presence of electrolytes by the positive ions, and gelatinisation can then take place as a result of the intrusion of water. If non-electrolytes only are added to the colloidal solution, the osmotic forces are unable to bring about gelatinisation, because of the impermeability of the membranes so long as the particles are electrically charged.

Experiments have also been made on the coagulation of silicic acid by colloidal ferric hydroxide. Quantitative measurements show that the oppositely charged colloids are precipitated in approximately constant proportions, excess of either remaining unchanged in the colloidal condition. The quantitative proportions appear to be related to the valencies of silicon and iron. H. M. D.

Application of the New Theory of Allotropy to the System Sulphur. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 263—270).—As in the case of acetaldehyde, it is shown that the relationships exhibited by the equilibria between the different forms of sulphur can be accounted for if it is assumed that sulphur represents a pseudo-ternary system. H. M. D.

Phenomena of Condensation for Mixtures of Carbonic Acid and Nitrobenzene in Connexion with Double Retrograde Condensation. PHILIPP KOHNSTAMM and J. CHR. REEDERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 270—278).—The influence of nitrobenzene on the condensation of carbon dioxide has been examined, and data are recorded which show the pressures characteristic of the three-phase systems at different temperatures in the neighbourhood of the liquid-liquid plait points. H. M. D.

Thermal Analysis of Quaternary Systems. II. NICOLA PARRAVANO and G. SIROVICH (*Atti R. Accad. Lincei,* 1911, [v], **20**, ii, 331—337. Compare this vol., ii, 973).—A mathematical solution of the problem of constructing the diagram of a quaternary system by the study of plane sections taken through a vertex of the tetrahedron and parallel to an edge. R. V. S.

Calculation of Equilibrium Constants from Cryoscopic Measurements. J. B. GOEBEL (*Zeitsch. physikal. Chem.*, 1911, **78**, 244—254).—The method described in the previous paper (Abstr., 1910, ii, 268) is extended to solutions of binary and ternary electrolytes in which polymerisation occurs. For the deduction of the numerous equations, the original paper must be consulted. As examples of binary electrolytes, organic acids are chosen, and in the case of acetic acid the concentration of double and triple molecules in aqueous solution is calculated. As an example of a ternary electrolyte, sodium sulphate is chosen. The value of $k = C_1^2/C_2$, where C_1 represents simple Na_2SO_4 molecules and C_2 double molecules, is 0·22. It is shown in the last case that the molecular conductivities can also be calculated from the formulæ. G. S.

Basicity of the Organic Acids Containing Alcoholic Hydroxyl Groups. G. CALCAGNI and LUIGI BERNARDINI (*Atti R. Accad. Lincei,* 1911, [v], **20**, ii, 261—267, 309—312).—The authors have investigated the influence of alcoholic hydroxyl groups on the basicity of organic acids, the experimental method adopted being the measurement of the conductivity of solutions of the acids (at five different dilutions) during gradual neutralisation with a weak base (ammonia). The acids examined were glycollic, lactic, α-hydroxybutyric, hydroxy*iso*butyric, malic, tartaric, and citric acids, and the results are given in the form of tables and in curves, in which the ordinates are the specific conductivities and the abscissæ the proportions of ammonia present. The curves of neutralisation first pass through a minimum, then rise until neutralisation is complete, and afterwards run parallel to the axis of abscissæ. In the polybasic acids, the pauses corresponding with the neutralisation of the individual carboxyl groups are not prominent. On the whole, the influence of the hydroxyl groups does not show itself at all in the curves, but this may be due to the considerable dilutions employed. All the acids dealt with can be titrated very well with phenolphthalein and potassium hydroxide. R. V. S.

The Alkalinity of Aqueous Solutions of Carbonates. FRIEDRICH AUERBACH and HANS PICK (*Arbeit. K. Gesundheitsamte,* 1911, **38**, 243—274).—The alkalinity of aqueous solutions of sodium carbonate, sodium hydrogen carbonate, and mixtures of these salts in different proportions has been determined at 18° by a colorimetric method in which the colour effects produced by addition of various indicators are compared with the colours exhibited by standard solutions of known hydrogen ion concentration.

From the data thus obtained, the second ionisation constant of carbonic acid, $k_2 = [H^{\cdot}][CO_3'']/[HCO_3']$, is found to be $6{\cdot}0 \times 10^{-11}$. This is in agreement with McCoy's value (Abstr., 1903, ii, 413), and also with that yielded by the data of Shields (Abstr., 1893, ii, 418) and Koelichen (Abstr., 1900, ii, 395). The divergent constants given by the two latter authors are due to errors of calculation.

From the above constant, the degree of hydrolysis of sodium carbonate solutions of different concentration has been calculated. The hydrolysis of sodium hydrogen carbonate solutions is nearly independent of the concentration, and corresponds with $[OH'] = 0{\cdot}0015$ at 18° and 0·0025 at 25°, the concentration being expressed in millimols. per litre. In contrast with the large temperature-coefficient indicated by these numbers, the degree of hydrolysis of sodium carbonate varies very little between 18° and 25°. H. M. D.

Velocities of Reaction of Acetone and Lutidone with Phenylhydrazine and Hydroxylamine Under Various Conditions.

IWAN SCHÖTTLE (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1190—1194).—The author's experiments were made in aqueous solutions at 16—18°, the concentrations of the ketone and phenylhydrazine (or hydroxylamine) being decinormal.

The progressive addition of small quantities of hydrochloric acid produces a continuous diminution in the velocity of interaction of acetone and phenylhydrazine.

Acetic acid first produces a very considerable fall in the velocity of this reaction, but as the proportion of the acid is increased, the velocity also increases until it attains approximately the original value in 100% acetic acid.

It has been found by Thiele and Schneider (Abstr., 1909, i, 929) that unsaturated cyclic ketones, similar in structure to lutidone, do not form phenylhydrazones, but combine with the phenylhydrazine. The author, however, confirms the statement of Petrenko-Kritschenko and Mosseschwili (Abstr., 1902, i, 190) that lutidone gives a phenylhydrazone.

The formation of lutidonephenylhydrazone is accelerated by hydrochloric acid, but in presence of acetic acid (10% or 40%) the velocity of the reaction is zero.

The interaction of acetone and hydroxylamine is retarded by sulphuric acid, but hastened by potassium hydroxide. The latter completely suppresses the reaction of ketones with phenylhydrazine. The velocity of reaction of lutidone with hydroxylamine is zero under all conditions (compare Petrenko-Kritschenko, and Stamoglu, Abstr., 1903, i, 197). T. H. P.

Case of Autocatalysis and Simultaneous Negative Catalysis.

ANTONIO QUARTAROLI (*Gazzetta*, 1911, **41**, ii, 64—69. Compare this vol., ii, 1086).—The reaction between nitrates and anhydrous formic acid is a process of autocatalysis in which nitrogen trioxide is the positive catalyst. Until a trace of this substance has been formed, the velocity of the reaction is very small, but the nitrogen trioxide cannot accumulate in quantity, because it also reacts with formic acid. In agreement with this view it is found that oxidising agents, transforming the nitrogen trioxide into nitric acid, act as negative catalysts. Traces of potassium chlorate, hydrogen peroxide, potassium permanganate, or carbamide hinder the reaction or prevent it entirely, so that there results the paradox that oxidising agents may prevent oxidation (compare Ihle, Abstr., 1896, ii, 460).

R. V. S.

Catalytic Esterification of Dibasic Acids in the Wet Way. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1911, **153**, 881—884. Compare this vol., ii, 600, 637).—By boiling a mixture of malonic acid (1 mol.) and alcohol (2 mols.) with 1—2% of its volume of sulphuric acid for an hour, the amount of ester formed is 67·5%, or 82·4% if twice the amount of alcohol is used. The yield is not increased by using 10% of sulphuric acid, but 5% of anhydrous aluminium sulphate or potassium hydrogen sulphate may be substituted for the acid without impairing the result. In practice the yield is less, owing to the solubility of the ester in the washing waters, but this loss is not so serious with the higher alcohols; thus, *iso*butyl alcohol (4 mols.) gave an actual yield of 75·4%, and *iso*amyl alcohol (4 mols.) 85·6%, of ester. With succinic or oxalic acid and *iso*amyl alcohol under the same conditions, the yields were practically theoretical. In the case of phthalic acid, it is necessary to employ 15% of sulphuric acid to obtain good results.

W. O. W.

Atomic Weights of the Dominant Elements. GUSTAVE D. HINRICHS (*Compt. rend.*, 1911, **153**, 817—818. Compare Abstr., 1893, ii, 317; 1907, ii, 945).—The author has previously elaborated a method for the simultaneous calculation of the atomic weights of each of the elements engaged in a particular reaction, and has published a résumé of over 1000 results derived from 340 reactions used in accurate atomic-weight determinations (Abstr., 1909, ii, 653). These are now classified according to their limits of precision. The first class consists of those determinations of the highest accuracy in which the maximum difference between the experimental and absolute values does not exceed 0·012; this comprises 454 values distributed amongst ten elements (O, Cl, Ag, C, Na, S, Br, H, Na, K). These are called the dominant elements, and in the author's opinion their true atomic weights are identical with their absolute atomic weights, the latter being whole numbers.

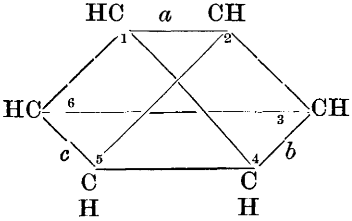
W. O. W.

The Cyclic Molecule. A New Hypothesis on Benzene. Allotropy and Polymerism. ANÍBAL CHACÓN (*Pamphlet*, pp. 43). —A theoretical paper in which a new hypothesis is put forward as to the constitution of benzene. The author gives the formula (I) for benzene, the molecule of which he considers as consisting of three "sub-nuclei" (*a*, *b*, *c*), corresponding with three molecules of acetylene, which mutually saturate one another.

In his formula the author considers that the *ortho*-position is 1 : 6, the *meta*-position 1 : 3 or 1 : 5, and the *para*-position 1 : 2. By his hypothesis he explains the fact of two isomeric benzene hexachlorides, assigning to them formulæ II and III for α and β respectively.

He then proceeds to give structural formulæ for naphthalene, anthracence, and phenanthrene, and for heterocyclic compounds, such as pyridine, the pyrone derivatives, etc.

Finally, he deals with allotropy and polymerism, explaining the polymerism of cyanic acid into cyanuric acid, and of cyanogen into para-cyanogen by the formation of cyclic molecules. He explains the allotropy of oxygen, sulphur, phosphorus, etc., on the same lines, giving, for example, for red phosphorus formula IV.



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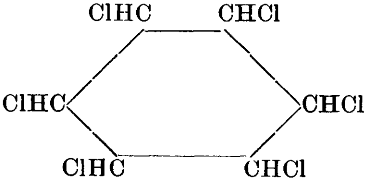

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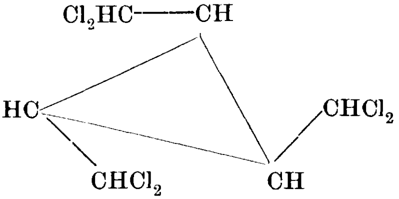

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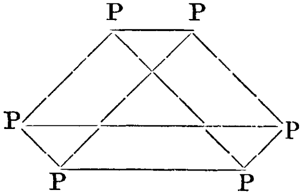


(IV.)

Finally, he enunciates the following conclusions :

(1) A simple substance can exist in two or more states, differing from one another by the number of atoms which the molecule contains in each of the states.

(2) Certain compounds are capable of giving rise to other compounds, the molecules of which are formed by two or more primitive molecules mutually saturating one another, this saturation being produced by pre-existing unsaturated valencies, or, if saturated, by alteration in the direction of the valencies.

(3) The atoms or molecules of elements and the molecules of compounds mutually saturate one another in the cyclic form, when they are assembled to the number of three, to constitute an allotropic or polymeric molecule. W. G.

A New Funnel. II. Philip Blackman (*Chem. News*, 1911, **104**, 211).—The funnel previously described (this vol., ii, 796) is further improved by rounding off the bends (for example, where the neck of the funnel connects with the upper part) instead of having them sharp. T. S. P.

A Funnel Support. II. Philip Blackman (*Chem. News*, 1911, **104**, 211).—The funnel support previously described (this vol., ii, 796) is better made of aluminium and not of glass. T. S. P.

Simple Apparatus for Filtering under Increased Pressure. Alfred Lohmann (*Zeitsch. Biol.*, 1911, **57**, 183—184).—The apparatus consists of a strong cast iron vessel provided with a removable lid, which can be firmly fixed and through which a tube passes connected to a cylinder of compressed gas. In the lower part of the vessel is placed a filter plate, and the vessel narrows to a tube, from which the filtrate can be drawn off. The pressure in the upper part of the vessel can be increased until the desired rate of filtration is obtained. E. F. A.

Apparatus for Extraction at High Temperatures. B. SCHURAVLEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1189—1190).—On an annular expansion on the outside and near the top of a Soxhlet extractor rests a narrow glass bell, mouth downwards. Steam is supplied to a perforated annular tube placed beneath the mouth of the bell, into which the steam rises and thus heats the extracting liquid. If the latter requires a higher temperature than is thus attained, the steam may be superheated, whilst if a lower temperature is desired, a portion of the steam is diverted by means of a three-way cock in the steam-delivery tube. In order that the condensed steam may not find its way into the flask containing the extracting liquid, round the lower tube of the extractor is fitted a slightly conical, rubber disk which carries the water off to one side. T. H. P.

Inorganic Chemistry.

Formation of Hydrogen Peroxide in the Electrical Discharge. ADOLPHE BESSON (*Compt. rend.*, 1911, **153**, 877—879).—Kernbaum's results (Abstr., 1910, ii, 818) are considered inconclusive, and might be attributed to formation of ozone or oxides of nitrogen. A more rigorous examination of the production of atmospheric hydrogen peroxide has been undertaken, employing conditions of temperature and pressure analogous to those obtaining in the higher regions of the atmosphere, and using a very dilute solution of potassium chromate, which is a specific reagent for hydrogen peroxide. Negative results were obtained on passing the silent electrical discharge through water vapour alone, below 0° and at 30—760 mm. In presence of oxygen, however, the production of hydrogen peroxide is very marked, but only at 385—770 mm. In presence of air, the results are less decisive, owing to formation of oxides of nitrogen which destroy the hydrogen peroxide. Nevertheless, the formation of this substance has been detected when the air was in large excess and in rapid circulation.

W. O. W.

Synthesis of Concentrated Hydrogen Peroxide by means of the Silent Electrical Discharge. FRANZ FISCHER and MAX WOLF (*Ber.*, 1911, **44**, 2956—2965).—The authors describe a special apparatus by means of which oxy-hydrogen gas can be submitted to a silent electrical discharge, the gas pressure being maintained at 3 cm. of mercury. The discharge passes through a U-tube, which is cooled by liquid air. Under these conditions a yield of 2·25—2·56% of the total possible hydrogen peroxide was obtained, the yield being calculated on the quantity of oxy-hydrogen gas passed through the

U-tube. No hydrogen peroxide was formed when the U-tube was only cooled to −20°.

The pressure of 3 cm. was chosen, because the gaseous mixture is not then explosive. The next experiments were made at the ordinary pressure, in one case the gaseous mixture consisting of 3% hydrogen and 97% oxygen; in the other case, of 3% oxygen and 97% hydrogen. In the former case, ozone was alone produced, and in the latter case the percentage yield of hydrogen peroxide varied with the temperature. At 22° it was 6·4%; at −20°, 33·6—34·1%; at −80°, 54%, and at the temperature of liquid air, 59—87·5%. In one case, the hydrogen peroxide solution produced was 86·9% by weight. .In these experiments 500 c.c. of the mixture took 1·5—3 hours to pass through the discharging apparatus.

When a mixture of 1 vol. of oxy-hydrogen gas and 4 vols. of carbon dioxide was submitted to the discharge in a tube cooled by a mixture of ether and solid carbon dioxide, the yield of hydrogen peroxide was 4%.

The authors find that the limits of explosibility of mixtures of oxygen and hydrogen at the ordinary pressure are: 5·45% hydrogen and 94·55% oxygen; 5·3% oxygen and 94·7% hydrogen, the percentages being expressed in volumes. T. S. P.

Products Containing Absorbed Iodine. LAMBERTO CORRIDI (*Arch. Farm. sperm. Sci.*, 1911, 12, Reprint 13 pp.).—When animal charcoal is placed for twenty-four hours in solutions of iodine, this element is absorbed, and a certain amount is retained by the charcoal even after many hours at 120°. The charcoals prepared in this way contain (according to the solvent used) 4·87—7·50% of iodine, no trace of which is evolved on keeping. The iodine is slowly removed, however, by organic solvents for iodine, by water, dilute acid, and especially by dilute alkali and by animal tissues. Hence the iodine charcoal should be of service in medicine. R. V. S.

Formation of Ozone by Electrolysis with Alternating Current. EBENEZER H. ARCHIBALD and H. VON WARTENBERG (*Zeitsch. Elektrochem.*, 1911, 17, 812—816).—Dilute sulphuric acid is electrolysed in a cooled U-tube with platinum electrodes. The anode consists of a short platinum tube of 1 mm. diameter fused into glass tubes and cooled by the flow of water through it. An alternating current, the strength of which can be varied independently, is passed between the electrodes in addition to the direct current used for electrolysis. The effect of the superposition of the alternating current is to depolarise the electrodes. The anode potential falls rapidly as the ratio between the strengths of the alternating and direct currents increases up to about 3, and more slowly thereafter. With the anodic current density 1·5 ampere per sq. cm., for example, the anode potential was reduced by 3 volts when the ratio of alternating to direct current increased from 0 to 4. The increase in the strength of the alternating current is accompanied by an extraordinary increase in the quantity of ozone formed at the anode. A very small fraction of the ozone is produced by the alternating current alone. The higher the current density the smaller is the effect of the superposed alternating current. The strength of acid which gives the largest quantities of ozone appears to diminish as the current density increases. The most favourable conditions observed were: area of anode 0·333 sq. cm.; direct current 0·25 ampere, alternating current 1·5 ampere, sulphuric acid of density 1·478. The ratio $O_3 : O_2$ produced by direct current was 0·37, but owing to the large quantity of electrolytic gas produced by the alternating current the escaping gases only contained 6·23% of ozone. T. E.

Reversible Light Reaction of Sulphur. ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1911, **78**, 208).—In a previous paper (this vol., ii, 878) the heat of formation of $S\mu$ has been put equal to the alteration of the free energy by light. This is not strictly justifiable, but at present the data for accurate calculation of the free energy are not available. G. S.

A Simple Hydrogen Sulphide Apparatus. E. RATTENBURY HODGES (*Chem. News*, 1911, **104**, 189).—The apparatus consists of two stout conical flasks fitted with rubber stoppers, and connected by a T-piece, one flask being inverted over the other; the projecting arm of the T is bent downwards. The top flask contains the iron sulphide resting on a wooden grid, previously soaked in paraffin wax, and the lower flask the acid. It is only necessary cautiously to invert the apparatus in order to get a flow of gas. W. G.

Industrial Preparation of Pure Nitrogen. GEORGES CLAUDE (*Compt. rend.*, 1911, **153**, 764—766. Compare Abstr., 1906, ii, 16). —The apparatus for the separation of air into oxygen and nitrogen by a process of partial liquefaction and fractionation has been improved by arranging that the gaseous phase rich in nitrogen is liquefied in the colder liquid circulating at the base of the rectification column, instead of in the bath of oxygen. The liquid phase through which the gas passes then contains only 0·4% of oxygen, whilst the nitrogen escaping from the top of the column contains not more than 0·2% of oxygen, a degree of purity sufficient to meet the requirements of the cyanamide industry. W. O. W.

Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. I. Ammonolysis of Hydrazine Sulphate. ARTHUR W. BROWNE and T. W. B. WELSH (*J. Amer. Chem. Soc.*, 1911, **33**, 1728—1734).—Franklin (Abstr., 1905, ii, 581) has drawn attention to certain reactions in which liquid ammonia acts in a manner analogous to that of water in hydrolysis, and for which he has therefore proposed the term "ammonolysis." Experiments have now been undertaken to investigate the behaviour of the nitrogen hydrides and their derivatives in liquid ammonia.

Hydrazine sulphate is decomposed by liquid ammonia at −33° in accordance with the equation: $N_2H_4,H_2SO_4 + 2NH_3 = (NH_4)_2SO_4 + N_2H_4$. The resulting solution of hydrazine in liquid ammonia may be decanted or filtered from the solid substance, which consists of ammonium sulphate or a compound of this salt with ammonia, and a method is thus suggested for the preparation of hydrazine from its sulphate.

It is shown that the same reaction takes place to a limited extent when hydrazine sulphate is submitted to the action of ammonia gas at the ordinary temperature. E. G.

Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. II. Ammonolysis of Certain Hydrazine Salts.

Arthur W. Browne and A. E. Houlehan (*J. Amer. Chem. Soc.*, 1911, **33**, 1734—1742. Compare preceding abstract).—The behaviour of hydrazine monosulphate, $2N_2H_4,H_2SO_4$, and of hydrazine oxalate, diselenate, and mono- and di-phosphate in liquid ammonia has been investigated.

It has been found that the monosulphate, dioxalate, and diselenate are decomposed with formation of hydrazine and the corresponding ammonium salts, whilst the mono- and di-phosphate are not affected. When hydrazine monosulphate is treated with ammonia gas at the ordinary temperature, ammonolysis occurs to some extent, and a liquid, consisting essentially of a solution of hydrazine monosulphate in free hydrazine, can be separated from the mixture by centrifugal action. E. G.

Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. III. Action of Ammonium Trinitride on Certain Metals.

Arthur W. Browne and A. E. Houlehan (*J. Amer. Chem. Soc.*, 1911, **33**, 1742—1752).—Ammonium trinitride can be prepared by passing dry ammonia into an ethereal solution of azoimide. When a solution of this salt in liquid ammonia is treated with lithium, sodium, potassium, calcium, or magnesium, vigorous action ensues with the formation of the respective trinitrides, and the liberation of ammonia and hydrogen in accordance with the equation: $M + NH_4N_3 = MN_3 + NH_3 + H$. In the case of zinc, aluminium, and tin, no perceptible action takes place, whilst with platinum a very slow reaction occurs.

A modified form of the Schiff nitrometer has been devised for use in this work, in which weighed quantities of two solids may be brought together in liquid ammonia in absence of air and moisture, and the gases evolved may be collected, measured, and preserved for subsequent analysis; this also permits of the residual solid being weighed and preserved, or prepared for analysis. E. G.

New Method for the Preparation of Nitrous Oxide and its Application to the Analysis of Nitrates.

Antonio Quartaroli (*Gazzetta*, 1911, **41**, ii, 53—59. Compare this vol., ii, 1079).—Nitrates react with pure, crystallisable formic acid quantitatively, according to the equation: $2KNO_3 + 6H{\cdot}CO_2H = N_2O + 4CO_2 + 5H_2O + 2H{\cdot}CO_2K$. The reaction affords a convenient mode of preparation for nitrous oxide, the gas evolved being collected over 20% potassium hydroxide solution at 40°. The gas is free from other oxides of nitrogen provided that the reaction is commenced by warming the mixture with a naked flame until the first bubbles appear. Gas is then rapidly evolved for some minutes without further heating. If the initial warming is gentle (for instance, in a water-bath at 25°), an intense blue coloration appears, and red fumes are seen which are not produced when the warming is carried out quickly.

The method also permits of rapid and accurate estimations of nitrates, the procedure being as follows. In a test-tube provided with a gas delivery tube are placed 5 c.c. of formic acid and the weighed sample (about 0·2 gram) of nitrate. The reaction is commenced by sudden heating, as above described, and the gas is collected in a graduated vessel over mercury, a correction being applied for the air originally contained in the apparatus. From the volume of carbon dioxide and nitrogen, the percentage of nitrate can be estimated; the carbon dioxide is then absorbed by means of potassium hydroxide, and from the volume of nitrogen remaining, a second calculation is made as a check. The method has been tried for the nitrates of sodium, potassium, ammonium, calcium and lead, and experiments with chemically pure nitrates indicate an average error of about 0·3 in the nitrogen percentage found. It is recommended for the analysis of commercial sodium nitrate, the impurities in which do not affect the accuracy of the estimation. R. V. S.

Crystalline Form of Nitrogen Sulphide. G. F. HERBERT SMITH (*Min. Mag.*, 1911, **16**, 97—99).—Crystals of nitrogen sulphide, N_4S_4, prepared by F. P. Burt and F. L. Usher (Abstr., 1911, ii, 389) gave constants [$a:b:c=0·8879:1:0·8480$; $\beta=89°37'$] in close agreement with those obtained by E. Artini (Abstr., 1906, ii, 533). The crystals are, however, of a different habit, having the appearance of cubes with truncated edges and corners. The refractive indices (about 2·046 and 1·908) are near to those of rhombic sulphur. L. J. S.

Oxidation of Arsenious and Antimonious Oxides. J. BISHOP TINGLE (*J. Amer. Chem. Soc.*, 1911, **33**, 1762—1763).—When arsenious oxide (0·5 gram) is boiled for twenty-six hours with 95% alcohol (3 c.c.) and water (5 c.c.), it is completely converted into arsenic acid. Antimonious oxide behaves in a similar manner. E. G.

Quantity of Carbon Dioxide in the Atmosphere at Monte Video. JOHANNES SCHRÖDER (*Chem. Zeit.*, 1911, **35**, 1211).—Ten thousand parts by volume of the air were found to contain from 2·70 to 3·30 volumes of carbon dioxide, the average quantity being 2·98 volumes. The largest quantities of carbon dioxide were found during June and July, 1908, and the smallest in February, 1909. The quantity tended to increase when the wind blew from the interior, and diminished during the sea breezes. W. P. S.

History of Colloidal Silicic Acid. PAUL WALDEN (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 145—146. Compare Abstr., 1910, ii, 500).—A historical reference to the earliest observations on the solubility of silicic acid, and the behaviour of its solutions towards acids. Quotations are given from papers by Pott (1746), Baumé (1773), and reference made to the experiments of Meyer (1775–1785) and Bergman (from 1779 onwards). H. M. D.

Diffusion of Neon through Hot Quartz. Owen W. Richardson and R. C. Ditto (*Phil. Mag.*, 1911, [vi], 22, 704—706).—A new silica tube, which had never contained any foreign substance, was exhausted and heated in the air for about an hour at 1000°. The gas contained in the tube was then drawn off and examined. It gave a faint blue argon spectrum, and showed the yellow helium line. After three hours' heating, the helium spectrum was fully developed, and the neon line $\lambda = 5852$ was well marked. After being heated all night, the helium and neon spectra were both quite strong, but no sensible increase in the intensity of the argon spectrum could be detected.

From these experiments the author draws the conclusion that neon diffuses through quartz at about 1000°, but its coefficient of diffusion is smaller than that of helium. The first argon spectrum, which did not change in intensity with the time of heating, is attributed to traces of air absorbed by the walls of the tube before the heating commenced. H. M. D.

Volatilisation of Electrodes in a Tube of Neon. Georges Claude (*Compt. rend.*, 1911, **153**, 713—715. Compare this vol., ii, 602).—An account of experiments to explain the appearance of helium in luminescent tubes of neon apparently free from this gas. The tube employed was cross-shaped, and had four copper electrodes. The current was passed between two opposite electrodes until a sufficient amount of copper had volatilised, and then between the remaining pair.

It was found that the first deposit gave 1 c.c. per gram of gas rich in helium on treatment with nitric acid, whilst the second yielded a gas in which neon was the predominant constituent. It follows, therefore, that the results described in a previous communication cannot be ascribed to a transformation of neon into helium, but were probably due to a selective action of copper for helium, whereby a concentration of this gas was effected to a sufficient extent to enable it to be recognised spectroscopically. Ramsay and Collie have conducted experiments leading to the same conclusion (private communication). W. O. W.

Rare Gases of Coal Mine Natural Gases. Charles Moureu and Adolphe Lepape (*Compt. rend.*, 1911, **153**, 847—849).—Analyses of five natural gases from mines are given. The amount of helium and neon varies between 0·0003 and 0·05%, and that of argon (with traces of krypton and xenon) from 0·003 to 0·04% by volume. The relative proportions of the inert gases are about the same as in other natural gaseous mixtures. W. O. W.

Solidification of Aqueous Solutions of Metallic Chlorides. Alexander W. Speransky and A. Pavlinova (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1006—1022).—The authors have investigated the compositions of the crystals obtained on freezing solutions of sodium, potassium, calcium, and magnesium chlorides of varying concentration and containing different proportions of sodium hydroxide or hydrochloric acid (compare Roozeboom, "Die heterogenen Gleichgewichte," 2, 222; Balló, Abstr., 1910, i, 355).

With NaCl–HCl solutions, it is found that, in the more concentrated solutions, the ratio between the amounts of chlorine in the form of sodium chloride and hydrogen chloride respectively is constant both for the solid separating and for the mother liquor. With dilute solutions, however, the value of this ratio is much greater for the ice than for the mother liquor. Similar relations are observed with NaCl–NaOH, KCl–HCl, and $CaCl_2$–HCl solutions.

With $MgCl_2$–HCl solutions, even when concentrated, the presence of magnesium chloride in the ice is observed.

It was found, however, that the concentration has no immediate influence, the principal part being played by the consistency of the separated ice, which is in hard masses from concentrated solutions and in a friable condition from dilute solutions when slowly cooled. That this is the case was shown by cooling two solutions of similar composition in such manners that they gave the two kinds of ice.

These phenomena are regarded as being due to adsorption effects.

T. H. P.

Preparation of Lithium Persulphate. C. NICOLESCU OTIN (*Zeitsch. Elektrochem.*, 1911, **17**, 919).—The attempt was made to prepare lithium persulphate by electrolysis of a solution of lithium sulphate in sulphuric acid at −20°, but although the persulphate was obtained in solution, it could not be separated in the solid form. An alternative method was therefore used. Persulphuric acid was prepared by electrolysis of sulphuric acid in the usual way, the sulphuric acid removed as the barium salt, lithium carbonate added to the persulphuric acid thus obtained, and the filtered solution evaporated in a vacuum. The pink, crystalline product contained about 82% of lithium persulphate, the remainder being lithium sulphate. The pure persulphate was not obtained.

G. S.

Preparation of Ammonium Salts from Nitrogen Compounds of Aluminium. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 235868).—When aluminium nitride is heated with sulphuric acid (or aluminium sulphate) and water, the following reactions take place:

$$2AlN + H_2SO_4 + 6H_2O = 2Al(OH)_3 + (NH_4)_2SO_4$$
$$6AlN + Al_2(SO_4)_3 + 24H_2O = 8Al(OH)_3 + 3(NH_4)_2SO_4.$$

The products can be employed as manure, and the reaction has been extended to the production of ammonium acetate and nitrate by employing acetic acid or nitrous gases respectively in this operation.

F. M. G. M.

The Ternary System Zinc–Lead–Tin. MARIO LEVI-MALVANO and O. CECCARELLI (*Gazzetta,* 1911, **41**, ii, 269—282).—From the thermal study of numerous mixtures of zinc, lead, and tin, the authors have constructed the thermal diagram of this ternary system. The general form of the gap of miscibility resembles those given by Wright and Thomson (Abstr., 1891, 267). The ternary eutectic separates at 177°, and corresponds with a mixture of 5% of zinc, 24% of lead, and

71% of tin. The alloys were also studied microscopically, and photographs are given of the appearances presented. R. V. S.

Alloys of Zinc, Lead, and Tin. MARIO LEVI-MALVANO and O. CECCARELLI (*Gazzetta,* 1911, **41**, ii, 314—318).—In view of the importance of alloys of these metals for industrial purposes, the authors have determined the hardness (with Brinell's apparatus, using a pressure of 500 kilograms) of the ninety-seven alloys prepared in the course of the work described in the preceding abstract. The results are recorded in a diagram, so that the connexion between hardness and composition can be seen, and it is pointed out that three alloys, which, according to Hiorns, are employed for anti-friction purposes, are all in the area of alloys from which zinc crystallises first, but are very near the zinc–lead eutectic, and microscopically consist of long crystals of zinc disseminated in a mass of the binary eutectic containing a little of the tertiary eutectic. R. V. S.

The Alloys of Tellurium with Zinc. MATSUSUKE KOBAYASHI (*Mem. Coll. Sci. Eng. Kyōtō,* 1911, **3**, 217—221).—Tellurium and zinc form a single compound, TeZn, which melts at 1238·5°, and has D^{13} 5·54. The two eutectic points practically coincide with the pure components. The freezing-point curve falls steadily from the compound to tellurium, but alloys richer in zinc lose zinc so rapidly by volatilisation that it is not possible to determine the course of the curve, although the zinc eutectic arrest is well marked. In microscopical examination the compound appears in needles.
C. H. D.

The Ternary System Copper–Silver–Gold. ERNST JÄNECKE (*Metallurgie,* 1911, **8**, 597—606).—The freezing point of gold is rapidly lowered by the addition of silver, and does not, as stated by Roberts-Austen and Rose (*Proc. Roy. Soc.*, 1903, **71**, 161), remain practically constant up to 50% Ag. The curve is a smooth one, slightly convex upwards, and the interval of crystallisation is never more than 13°. The majority of the ternary alloys form homogeneous, solid solutions, the range within which duplex structures are observed being defined by the eutectic line, which runs from the eutectic point of the copper–silver alloys at 60·2 atomic % Ag and ends at a point corresponding with 42·5 atomic % Cu, 35·5% Ag, and 24·0% Au, at a temperature of 800°. The curve separating homogeneous and heterogeneous alloys passes through this point and through the limiting concentrations of the two copper–silver solid solutions. These results are confirmed by microscopical examination. C. H. D.

The Corrosion of Metals. PERCY LONGMUIR (*J. Iron Steel Inst.*, 1911, **83**, 147—169).—A deposit obtained from the atmospheric corrosion of brass contained 22·75% ZnO, 15·93% CuO, 7% CO_2, and 28·65% SO_3, whilst another sample, due to corrosion by fumes from illuminating gas, contained 36·18% SO_3. Samples of iron rust, formed by purely atmospheric corrosion, contained from 0·686% to 3·124% SO_3. Rust from steel rails, especially when laid in tunnels, also showed a

high proportion of sulphur. Corrosion by sulphuric acid produces brittleness in iron or steel.
C. H. D.

Cerium–Tin Alloys. Rudolf Vogel (*Zeitsch. anorg. Chem.*, 1911, **72**, 319—328).—Metallic cerium reacts with most gases, and is not readily melted. If introduced into a carbon tube and heated, carbide and nitride are formed, and the metal does not yield a regulus. By throwing a piece of cerium (93·48% Ce) into a carbon tube previously heated to 1200° without any protecting gas, fusion readily takes place and a homogeneous mass is obtained, giving an indistinct freezing point of 830° (623°, Muthmann and Weiss). The alloys with tin are prepared in the same manner. The freezing-point curve rises with increasing amount of tin, reaching a maximum at 1400° and 30% Sn, corresponding with the compound Ce_2Sn. There is a second maximum at 1165° and 56% Sn, corresponding with the compound Ce_2Sn_3, and a third at 1135° and 64% Sn, due to the compound $CeSn_2$. Microscopical examination is rendered difficult by the rapid tarnishing of the sections, even when polished and examined under petroleum, but it is possible to recognise the compounds as homogeneous and to detect the eutectic structure in other alloys of the series. All the alloys containing less than 80% Sn are pyrophoric, especially those containing the compound Ce_2Sn, mere scratching with a hard object producing a shower of sparks. This compound has also the maximum hardness, of about 6, is very unstable in air, and reacts very vigorously with water.
C. H. D.

The Ferromagnetic Compounds of Manganese with Phosphorus, Arsenic, Antimony, and Bismuth. Siegfried Hilpert and Theodor Dieckmann (*Ber.*, 1911, **44**, 2831—2835).—*Manganese phosphide*, MnP, was prepared from manganese and phosphorus in a manner similar to that used for the arsenide (this vol., ii, 985). It forms an inodorous, black powder, which burns on heating in the air, giving magnetic, black oxidation products. It is insoluble in hydrochloric acid, which acid may therefore be used to purify it; it is readily soluble in nitric acid.

Manganese antimonide, MnSb, was obtained by heating a manganese amalgam, prepared by electrolysis, with the requisite amount of antimony in an atmosphere of hydrogen, the mercury being finally distilled off. It is a grey substance, which burns in the air, giving non-magnetic products; it is soluble in hot hydrochloric acid, and readily soluble in nitric acid. *Manganese bismuthide*, MnBi, was prepared similarly to the antimonide, and has similar chemical properties; it is silver-white in colour.

The following are the temperatures at which the magnetic properties of these compounds are lost and regained, the first temperature denoting loss of magnetic properties on heating, and the second, gain of the same on cooling; they indicate that hysteresis occurs: MnP, 18—26°; MnAs, 40—45°; MnSb, 320—330°; MnBi, 360—380°. The higher the atomic weight of the element combined with manganese, the higher is the temperature at which the magnetic properties are lost.
T. S. P.

The Thermal Formation of Potassium Manganate from Manganese Dioxide and Potassium Hydroxide. F. BAHR and OTTO SACKUR (*Zeitsch. anorg. Chem.*, 1911, **73**, 101—124. Compare Sackur, Abstr., 1910, ii, 214, 215; this vol., ii, 400; Askenasy and Klonowski, Abstr., 1910, ii, 297).—The dissociation pressure of mixtures prepared by adding manganese dioxide to molten potassium hydroxide and pulverising the product have been measured. The dissociation pressure of manganese dioxide at 572° is 816 mm. From the curves thus obtained, an isothermal dissociation curve is drawn for the temperature 661°, and the results show that the final product of dissociation is potassium manganite, K_2MnO_3, which has no dissociation pressure, even at 1000°. Potassium manganate and manganite, however, form a solid solution, which is saturated when the atomic proportion of available oxygen to manganese is 1 : 1·6, corresponding with the composition $3K_2MnO_4,2K_2MnO_3$. The formation of products further saturated than this is attributed to supersaturation. This degree of oxygen corresponds with Sackur's compound $Mn_5O_{13},8K_2O$. C. H. D.

Cementation of Iron by Solid Carbon. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1911, **153**, 671—673. Compare Abstr. 1910, ii, 215).—Iron was heated in contact with graphite at 950° under very low pressures in an atmosphere of hydrogen, nitrogen, and carbon monoxide containing about one-third of the latter. When the pressure did not exceed 0·3 mm., no cementation occurred. Cementation, however, was very distinct if the pressure was allowed to rise to 0·4—1·5 mm.; after thirteen hours' heating under these conditions the iron was found to contain 0·5% of carbon and to show the perlite structure. These experiments explain the contradictory results of previous observers, who have not taken sufficiently into account the effect of small quantities of carbon monoxide. W. O. W.

Iron-Silicon-Carbon Alloys. W. GONTERMANN (*J. Iron Steel Inst.*, 1911, **83**, 421—475).—The previous work on this system (Abstr., 1908, ii, 851) has been extended. Increasing the percentage of silicon in cast iron accelerates the formation of graphite, but above 4—5% Si the temperature of reaction is so far lowered that the separation of graphite under ordinary conditions of cooling is diminished, becoming zero with more than 20% Si. C. H. D.

The Growth of Cast Irons after Repeated Heatings. HAROLD C. H. CARPENTER (*J. Iron Steel Inst.*, 1911, **83**, 196—248).—The increase in external volume which takes place when cast iron is repeatedly heated in air is mainly due to disintegration caused by the oxidation of silico-ferrite. The distribution of the graphite affects the growth, by determining the access of oxidising gases. The presence of phosphide retards the oxidation. The higher the percentage of silicon in the iron, the greater the growth. When heated in a quartz tube in a vacuum, growth occurs owing to the escape of dissolved gases, and to a smaller extent, to the liberation of temper-carbon from carbide. An iron containing 3·98% of carbon and 1·07% of silicon shows a growth of 11% under these conditions, and becomes porous and coarsely crystalline. Increasing the silicon diminishes the growth in a vacuum, which becomes zero with 4% Si or more.

An alloy containing 2·66% C, 0·587% Si, and 1·64% Mn does not show growth after 150 heats. Its initial freezing point is 1346°.

C. H. D.

The Influence of Vanadium on the Physical Properties of Cast Iron. WILLIAM H. HATFIELD (*J. Iron Steel Inst.*, 1911, **83**, 318—331).—The addition of vanadium to cast iron favours the retention of the carbon in the combined condition, the greater part of the vanadium entering into the carbide and increasing its stability. With 0·65% of vanadium, the carbide remains undecomposed after one hour at 1040°. C. H. D.

Heat-treated 3% Nickel Steels. ANDREW McWILLIAM and ERNEST J. BARNES (*J. Iron Steel Inst.*, 1911, **83**, 269—293).—The pearlite point for steels containing 3% of nickel lies between 0·74 and 0·91% C. The point Ar_2 can be recognised as distinct from Ar_3 in such steels containing 0·12, 0·28, and 0·30% of carbon. C. H. D.

Influence of 0·2% Vanadium on Steels of Varying Carbon Content. ANDREW McWILLIAM and ERNEST J. BARNES (*J. Iron Steel Inst.*, 1911, **83**, 294—317).—The pearlite point for steels containing 0·2% of vanadium lies between 0·71 and 0·98% C. The point A_2 is markedly irreversible, even in steels containing as little as 0·2% V. A part of the vanadium is in solid solution in the ferrite.

C. H. D.

The Chemical and Mechanical Relations of Iron, Chromium, and Carbon. JOHN O. ARNOLD and ARTHUR A. READ (*J. Iron Steel Inst.*, 1911, **83**, 249—268).—A series of alloys, containing about 0·85% of carbon and variable quantities of chromium, have been examined. The ductility is increased by the addition of 5% of chromium, and diminished by further additions up to 24%. The carbides have been isolated by electrolysis in hydrochloric acid, D 1·02. Practically the whole of the carbon in the annealed steels is obtained as carbides, the proportion of chromium in the carbide increasing at first with the proportion of chromium in the steel, afterwards becoming constant. The constant product has the composition $2Fe_3C,3Cr_4C$, and is probably a double compound, crystallising in slate-coloured needles. Alloys containing less than 5% of chromium are pearlitic, whilst richer alloys consist of ferrite containing chromium, with distinct particles of a double carbide. C. H. D.

The Influence of Impurities on the Corrosion of Iron. JOHN W. COBB (*J. Iron Steel Inst.*, 1911, **83**, 170—195).—When the local corrosion of iron is studied by means of the ferroxyl reagent (Abstr., 1909, ii, 485) it is found that solution of the iron is greatly accelerated by contact with ferrous silicate, black oxide scale, ferrous sulphide, or iron phosphide or carbide. Graphite acts in the same manner.

Manganese sulphide is practically a non-conductor, and is without effect, and the behaviour of manganese silicate is similar. Manganese coupled with iron dissolves, the iron becoming the cathode. When two varieties of iron, such as Swedish steel and pure Swedish iron, are connected, any difference of potential between the two is found to be unimportant in comparison with the local currents, and corrosion takes place irregularly on both electrodes. When examined microscopically with the ferroxyl reagent, corrosion of ordinary iron is frequently found to begin at points where no recognisable impurity can be detected. These tests also show that manganese sulphide, unlike the silicate, does initiate local corrosion when present in microscopic particles. C. H. D.

I. Cause of the De-rusting of Iron in Ferroconcrete. II. Two Chemical Processes Occurring in a Railway Tunnel. PAUL ROHLAND (*Zeitsch. angew. Chem.*, 1911, **24**, 2011—2012).—I. A reply to Donath (this vol., ii, 897). The author rejects the explanation suggested by Michaelis, that the ferric oxide (rust) reacts with the lime of the concrete, forming a calcium ferrite, since he has not been able to detect any reaction between calcium hydroxide and ferric oxide, even after days.

II. In a railway tunnel at Hönebach it has been found that when lining it with cement or concrete the latter must be protected as long as possible from the action of sulphurous acid formed during the combustion of the coal burned on trains passing through. During the setting of the cement, calcium hydroxide is formed by hydrolysis, and this would combine with the sulphurous acid, ultimately forming calcium sulphate and bringing about the destruction of the cement.

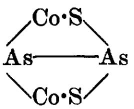
The second chemical process referred to is the action of sulphurous acid on the old lime-mortar of the tunnel, whereby a plastic mass was formed, consisting of calcium sulphate and calcium hydrogen sulphate, the latter in the colloidal condition. T. S. P.

Ore Deposition in Relation to Iron Sulphides. EUGENE T. ALLEN (*J. Washington Acad. Sci.*, 1911, **1**, 170—177).—Iron-pyrites and marcasite are produced artificially by the action of hydrogen sulphide on ferric sulphate solution, the latter being first reduced to ferrous sulphate with the separation of free sulphur ($FeSO_4 + H_2S + S = FeS_2 + H_2SO_4$). This reaction takes place at the ordinary temperature, and the dark precipitate is minutely crystalline; at a higher temperature (about 200°), in a sealed tube, distinct crystals are produced. Determinations of the relative amounts of iron-pyrites and marcasite present in these products were made by the method of H. N. Stokes (Abstr, 1902, ii, 87); the results prove that higher temperatures and low degree of acidity favour the production of iron-pyrites. At 100° in a solution containing 1% free sulphuric acid only marcasite is formed. Iron-pyrites only is formed in neutral or alkaline solutions by the action of sodium polysulphide on a ferrous salt, or by the action of hydrogen sulphide on pyrrhotite and free sulphur. Marcasite when heated at 450° changes into iron-pyrites with development of heat; but this change is not reversible, and iron-pyrites cannot be changed directly into marcasite. Pyrrhotite is formed by the decomposition of iron-pyrites in hydrogen sulphide above 575°, more sulphur being lost at higher temperatures. The variable composition of pyrrhotite is explained by the solid solution of sulphur in ferrous sulphide, the formula being $(FeS)S_x$.

The bearing of these experiments and temperature limits is discussed in connexion with the modes of occurrence in nature of these minerals, their probable modes of origin, and the conditions necessary for their formation. They are in harmony with the fact that marcasite is formed near the surface from acid solutions, whilst iron-pyrites is formed in deeper veins from hot alkaline solutions; pyrrhotite, on the other hand, often occurs in igneous and contact-metamorphic rocks.

L. J. S.

Experiments with Cobaltite. A. Beutell (*Centr. Min.*, 1911, 663—673).—Experiments were made on the same lines as those previously made with mispickel and glaucodote (this vol., ii, 485, 728), the mineral being heated in a cathode vacuum before and after roasting. Cobaltite was found to be more stable than glaucodote under these conditions, and the annexed constitutional formula is suggested.



The crystallised cobaltite from Håkansboda, Sweden, used in the experiments contained:

S.	As.	Fe.	Co.	Ni.	Total.
21·48	42·88	2·92	32·36	0·32	99·96

L. J. S.

Equilibrium between Chloropentamminocobalt Chloride and Aquopentamminocobalt Chloride in Aqueous Solution. Robert Pers (*Compt. rend.*, 1911, **153**, 673—675).—The equilibrium between purpureo- and roseo-cobalt chloride in aqueous solution has been studied by boiling a solution of the former, and estimating the amount of the latter by precipitation as oxalate and the amount of precipitable chloride by means of silver nitrate. The equilibrium curves are reproduced, and show that two reactions occur simultaneously, one corresponding with the equation:

$$(CoCl\cdot5NH_3)Cl_2+H_2O \rightleftharpoons (H_2O\cdot Co\cdot5NH_3)Cl_3,$$

the other involving decomposition of both products with formation of cobalt chloride. If no decomposition occurred, equilibrium would be attained when the mixture contained 42% of purpureocobalt chloride.

W. O. W.

The Exfoliation of Electrolytic Nickel. Karl Engemann (*Zeitsch. Elektrochem.*, 1911, **17**, 910—917).—Nickel electrolytically deposited from an acidified solution of pure nickel chloride or sulphate is obtained as a homogeneous coherent layer, whilst from ammoniacal solution the metal is obtained in a form which peels off in sheets, even when no iron is present. When a solution of a nickel salt containing iron is electrolysed, the iron deposits more easily than the nickel, so that the first layers are richer in iron than those deposited later, and, owing to this inequality in composition, the metal tends to split off in thin sheets. The influence of various factors on the composition of the layers has been investigated. With increase of temperature, the proportion of iron in the different layers becomes more nearly equal, and the ratio of the total iron in the alloy to that in the solution diminishes.

The hardness of electrolytic nickel is very little influenced by the nature of the salt, whether sulphate or chloride; it increases with increasing acidity of the solution, and is diminished by the addition of sodium salts to the nickel solution.

The elasticity of the metal obtained from sulphate solutions is greater than that obtained from chloride solutions. The addition of sodium salts to the electrolyte also increases the elasticity. G. S.

Alloys of Nickel and Zinc. ÉMILE VIGOUROUX and A. BOURBON (*Bull. Soc. chim.*, 1911, [iv], 9, 873—879).—Tafel has shown (Abstr., 1908, ii, 105), that nickel combines with zinc to form an alloy $NiZn_3$, and this has been confirmed by Voss (Abstr., 1908, ii, 194). The authors find that two alloys exist, $NiZn_4$ and Ni_3Zn.

The ingots obtained were homogeneous when the amount of nickel was below 19%, at this stage they became brittle, and when the amount of nickel was largely increased, they became cavernous, sonorous, and more and more malleable. They were not magnetic up to 70·9% of nickel, but became magnetic at 72·8% of this metal. When pulverised and subjected to the action of hydrochloric or acetic acid, the residues from mixtures containing up to 18·3% of nickel became progressively richer in this element and developed magnetic properties. The residues from mixtures containing over 18·3% nickel showed little variation in composition as the attack progressed. Alloys containing less than 18% of nickel on treatment with nitric acid (1%) gave invariably a residue containing 18·6% of nickel, corresponding with the alloy $NiZn_4$, which was isolated in this way as a crystalline, non-magnetic powder of density 7·71 and m. p. 850° (approx.). This was rapidly attacked by hydrochloric acid (1%), leaving a magnetic deposit which was sometimes pyrophoric; the solution generally contained zinc only. Dilute sulphuric acid attacked the alloy slowly, forming a solution of the two sulphates, and depositing a magnetic powder. Nitric acid of more than 1% strength dissolved the alloy completely. Nickel chloride solution dissolved the alloy on warming, giving rise to zinc hydroxide and a magnetic deposit.

Determination of the *E.M.F.*'s developed by the use of poles formed of mixtures of the two metals against poles of zinc showed "breaks" at 18·33% and 72·92% of nickel, corresponding with the compounds $NiZn_4$ and Ni_3Zn respectively. T. A. H.

The Reactions in a System of Nickel or Platinum, Mercury, and Sodium Chloride. CHARLES A. PETERS (*Amer. J. Sci.*, 1911, [iv], 32, 386—387).—When a solution of sodium chloride is left over mercury with a nickel wire connecting both liquids, crystalline nickelous hydroxide is formed very slowly, sodium hydroxide being produced at the same time. When platinum is substituted for nickel, mercurous chloride is formed, sodium hydroxide being likewise produced. T. S. P.

Chromic Sulphates and Ions. Albert Colson (*Bull. Soc. chim.*, 1911, [iv], 9, 862—868. Compare Abstr., 1907, ii, 267, 780, 877).—The author has shown previously (*loc. cit.*) that solutions of the chromic sulphates give anomalous conductivity and cryoscopic measurements after heating and after dilution. To explain this he recalled Recoura's suggestion that the violet sulphate undergoes polymerisation and then hydrolysis, thus: $2Cr_2(SO_4)_3 + H_2O = [Cr_4O(SO_4)_4]SO_4 + H_2SO_4$, and on thermochemical evidence supposed that this kind of reaction occurred with the isomeric chromic sulphates. This view has been called in question by Urbain as the result of his own work and that of Denham (Abstr., 1908, ii, 389). These authors suppose that when the violet sulphate is boiled, the polymeride,

$$[Cr_4(SO_4)_4]2SO_4,$$

is formed, and is more or less hydrolysed without thermal change. This explanation is improbable from what is known of polymerides of this composition (compare Recoura, Abstr., 1896, ii, 27; Colson, Abstr., 1907, ii, 177). T. A. H.

Uranyl Salts. III. Alexis M. Vasilieff (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1183—1184. Compare Abstr., 1910, ii, 1072).—The author has determined the values of n_D^{17} and D_{17}^{17} of a series of eighteen aqueous solutions containing from 54·77% to 2·80% of anhydrous uranyl nitrate. The solution saturated at this temperature has very approximately the composition, $UO_2(NO_3)_2,18H_2O$, and has n_D^{17} 1·41155 and D_{17}^{17} 1·7536. T. H. P.

Alloys of Tin and Antimony. N. S. Konstaninoff and Wladimir A. Smirnoff (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1201—1220).—Investigations by the thermal method and by means of the electrical conductivity and its temperature-coefficient shows that, after equilibrium is reached, the system Sn–Sb consists of (1) solid solution of tin and antimony, the limiting concentration being 10 atom. % Sb; (2) the definite compound, SnSb, capable of dissolving up to 56% Sb; (3) the definite compound, Sn_3Sb_2, capable of dissolving up to 44% Sb; and (4) solid solution of antimony in tin with a limiting concentration of 10 atom. % Sn. T. H. P.

Titanium. IV. Arthur Stähler and Fritz Bachran (*Ber.*, 1911, 44, 2906—2915).—An improved apparatus is described for the preparation of titanium trichloride, the glass cooler and quartz tube of the previous apparatus (Abstr., 1909, ii, 894) being replaced respectively by a copper cooler and a silundum tube; the latter is heated directly by passage of the electric current.

When titanium trichloride is heated at 660—700° in an atmosphere of hydrogen, the following reaction takes place: $2TiCl_3 \rightleftarrows TiCl_2 + TiCl_4$. The tetrachloride is volatile, the dichloride remaining as a deep black powder; it was not quite pure, being contaminated with some metallic titanium. It begins to sublime at 300° in a vacuum.

The only satisfactory test for bivalent titanium is the formation of a violet colour (due to $TiCl_3$) when mixed with an hydrochloric acid solution of titanium tetrachloride.

Titanium can be obtained by heating titanium dichloride at 1100° in a current of hydrogen, the reaction being $2TiCl_2 \rightleftarrows TiCl_4 + Ti$. A dark grey, spongy mass is obtained, which in the most favourable case contains 94·4% of titanium; the yield is not improved by heating the titanium dichloride in a vacuum.

The statement of Pfordten (Abstr., 1887, **14**, 337) that titanium dichloride and titanium thiochloride (TiSCl) can be obtained by leading dry hydrogen sulphide into anhydrous titanium tetrachloride could not be verified. Derivatives of quadrivalent titanium are formed, possibly of the composition $TiSCl_2$. At 800—850°, hydrogen sulphide and titanium tetrachloride interact with the formation of titanium disulphide. The compound $TiSCl_2$ could not be reduced to the monosulphide, TiS.

Titanium tetrachloride is reduced to the trichloride by heating with finely powdered aluminium, antimony, arsenic, or tin, in a sealed tube at 400°. Lower oxidation products of titanium could not be obtained by electrolysis of solutions of titanium tetrachloride in anhydrous hydrogen cyanide.

On mixing solutions of titanium trichloride and of sodium, potassium, or ammonium formates in the presence of air, olive-green, microscopic needles of the double formates separate. They cannot be purified by recrystallisation from water, owing to hydrolysis, but must be washed successively with cold water, alcohol, and ether, air being excluded. The dry salts are relatively stable in the air. On being heated in the absence of air, some formaldehyde is produced. *Titanium ammonium formate*,

$$Ti(CHO_2)_3,3Ti(CHO_2)_2OH,2NH_4CHO_2,H_2O.$$

Titanium potassium formate, $Ti(CHO_2)_3,3Ti(CHO_2)_2OH,2KCHO_2$. A *barium* salt was also obtained in the impure condition. These salts are analogous to the acetates (Stähler and Wirthwein, Abstr., 1905, ii, 595); they may be used as mordants, owing to their ready hydrolysis in solution.

Titanium trichloride reacts with a gold solution in a similar way to stannous chloride, producing colloidal gold which is analogous to purple of Cassius. One part of gold in 20 million parts of water can be detected by this reaction. T. S. P.

The Melting Point and Frequency of Atomic Vibration of Germanium. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1911, **72**, 313—318).—Experiments with two specimens of metallic germanium by the method formerly employed to determine the melting point of certain sulphides (Abstr., 1908, ii, 845), show that germanium melts in an atmosphere of hydrogen at 958° ±5°, but if saturated with oxide, at 916° ±5°. It is not appreciably volatile in nitrogen at 1250°, but in the presence of some oxide, vapour is observed from 750° onwards. The oxide, GeO_2, is not volatile at 1025°. The lower oxide, GeO, is volatile. The reaction, $GeO_2 + Ge = 2GeO$, does not take place under the conditions examined.

The frequency of atomic vibration, calculated from the atomic volume, atomic weight, and melting point is 3·7. C. H. D.

Attempts to Prepare Bismuth Hydride. LUDWIG VANINO and EMILIE ZUMBUSCH (*Arch. Pharm.*, 1911, **249**, 483—493).—The following attempts to prepare bismuth hydride gave negative results. Hydrogen was passed over alloys of lead, tin, and bismuth, or of one of these three metals with cadmium, heated to their melting points. Aluminium, zinc, iron, cadmium, or lead was added to an acid or neutral solution of a bismuth compound. Bismuth–magnesium or bismuth–zinc alloy was placed in dilute acid. Calcium hydride mixed with bismuth compounds was moistened with water or aqueous solutions of bismuth chloride.

Hydrogen was passed over mixtures of bismuth or bismuth–oxide with platinum black, nickel–asbestos, or reduced nickel. Palladium saturated with hydrogen was placed in a solution of bismuth sulphate, or an electric current was passed through a cell containing bismuth sulphate in solution, and having an anode of palladium saturated with hydrogen and a cathode of platinum or a cathode of bismuth and anode of platinum.

Aluminium, activated by Wislicenus' method (Abstr., 1896, i, 671), was allowed to remain in bismuth–mannitol solution or with a mixture of bismuth and bismuth oxide, or in solutions of bismuth salts in alcohol.

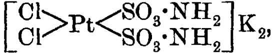
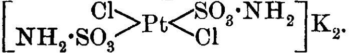
Hypophosphorous acid added to bismuth sulphate or to bismuth nitrate in solution gave only a precipitate of metallic bismuth. The presence of bismuth hindered the preparation of copper hydride by this method. T. A. H.

Colloidal Gold. ALEXANDER GUTBIER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 175—189. Compare Abstr., 1902, ii, 610).—The influence of temperature on the nature of the colloidal gold solutions obtained by reduction of gold chloride by hydrazine has been examined in great detail. When small quantities of aqueous hydrazine are added to dilute gold solutions, blue hydrosols are produced at the ordinary temperature, whereas at 80°, 90°, and 100° the colour is red, or more usually reddish-violet. The same result is obtained when the procedure is reversed by adding small quantities of the gold chloride solution to very dilute hydrazine, except that in this case violet hydrosols are occasionally formed even at the ordinary temperature. The addition of electrolytes or of gum arabic as protective colloid is without influence on the nature of the products.

The colloidal solutions prepared at 100° are very sensitive towards electrolytes. The addition of a few drops of $0{\cdot}1N$-solutions at the ordinary temperature gives rise quickly to a blue solution of colloidal gold. H. M. D.

Dichloro-disulphaminoplato-salts. The Stereoisomerism of Platinum and the Transformation of Sulphamic Acid. HEINRICH KIRMREUTHER (*Ber.*, 1911, **44**, 3115—3121).—By the action of potassium platinochloride on sulphamic acid, two *potassium dichlorodisulphaminoplatinites* have been obtained, the α-salt, $[Cl_2Pt(NH_2\cdot SO_3)_2]K_2,2H_2O$, being yellow and readily soluble, whilst the β-salt, $[Cl_2Pt(NH_2\cdot SO_3)_2]K_2$, is almost colourless and more difficultly soluble. Both salts contain only the potassiums in an ionogenic condition and both are neutral, so that they cannot be structural isomerides in accordance with the formulæ:

$$[Cl_2Pt(\cdot SO_3\cdot NH_2)_2]K_2$$

and $[Cl_2Pt(\cdot NH\cdot SO_3H)_2]K_2$. Both salts dissolve in potassium hydroxide, giving an intense golden-yellow solution containing a tetrapotassium salt; they must, therefore, be derived from the second of the above formulæ, that is, they are platosimines. Acids re-precipitate the salts from the solution in potassium hydroxide. The author considers them to be stereoisomerides, similar to the dichloroplatosamines, and from analogy to already known isomerides of platinum, the α-salt is characterised as the *cis*-form,  $\left[\begin{matrix}Cl\\Cl\end{matrix}>Pt<\begin{matrix}SO_3\cdot NH_2\\SO_3\cdot NH_2\end{matrix}\right]K_2$, and the β-salt as the *trans*-form,  $\left[\begin{matrix}Cl\\NH_2\cdot SO_3\end{matrix}>Pt<\begin{matrix}SO_3\cdot NH_2\\Cl\end{matrix}\right]K_2$.

Potassium cis-*dichlorodisulphaminoplatinite* is obtained by the interaction of potassium platinochloride (1 mol.) and sulphamic acid (2 mols.) in cold aqueous solution. After keeping for twenty-four hours the solution deposits tabular, golden-yellow crystals, which are weakly pleochroitic; they belong probably to the rhombic system, and are soluble to the extent of 1 part in 38 parts of water at 21°. $1H_2O$ is lost at 90° and $2H_2O$ at 130°. Barium chloride and hydrochloric acid give no precipitate, even on warming, proving that the sulphamic acid residue is in the inner complex sphere. Pyridine replaces the sulphamic acid from the residue, giving *cis*-dichloro-dipyridine-platinum.

Potassium trans-*dichlorodisulphaminoplatinite* is obtained when more than 2 mols. of sulphamic acid react with 1 mol. of potassium platinochloride, the reaction being best carried out on the water-bath. After heating for two to three hours, the solution, on cooling, deposits a mass of almost colourless, felted needles, which dissolve in water to the extent of 1 part in 342 parts at 21°. The reactions of this salt are similar to those of the *cis*-isomeride, except that pyridine gives *trans*-dichloro-dipyridine platinum.

Tetrapotassium trans-*dichlorodisulphiminoplatinite*,

$$[Cl_2Pt(NH\cdot SO_3)_2]K_4,$$

is obtained by dissolving the above salt in potassium hydroxide and precipitating the solution with alcohol. It forms intense yellow, radiating clusters of prisms, and gives a strongly alkaline solution.

Potassium trans-*dibromodisulphaminoplatinite*,

$$[Br_2Pt(SO_3NH_2)_2]K_2,$$

and *potassium* trans-*di-iodo-disulphaminoplatinite*,

$$[I_2Pt(SO_3NH_2)_2]K_2,$$

were obtained from the dichloro-compound by interaction with potassium bromide and iodide respectively. The former gives bright orange-yellow prisms, whilst the latter forms reddish-brown prisms.

T. S. P.

Mineralogical Chemistry.

Atacamite. HENRI UNGEMACH (*Bull. Soc. franç. Min.*, 1911, **34**, 148—216).—A monograph of the species. In the new orientation of the crystals (the axes *b* and *c* being interchanged) the elements are $a:b:c = 0{\cdot}87808:1:1{\cdot}32710$. Many new crystal-forms are given. Crystals from Antofagasta, Chili, have D 3·769, 3·778, 3·780; from Boleo, Lower California, Mexico, 3·774, 3·776. Previous analyses are tabulated, and the following new ones are given. The rhombohedral form assigned to paratacamite (G. F. H. Smith, Abstr., 1906, ii, 455) is explained by twinning on *e*(011) of atacamite according to the new law of W. E. Ford (*Amer. J. Sci.*, 1910, **30**, 16).

	Cl.	Cu.	CuO.	H_2O.
Antofagasta	16·48	14·75	55·81	13·09
Boleo	16·22	14·53	55·33	13·15

L. J. S.

Schwartzembergite. G. F. HERBERT SMITH and GEORGE T. PRIOR (*Min. Mag.*, 1911, **16**, 77—83).—Crystals of schwartzembergite from San Rafael mine, Sierra Gorda, Chili, are tetragonal (not rhombohedral as previously stated) with $a:c = 1:0{\cdot}430$, and have the form of flat square pyramids with rounded faces. They are optically anomalous, showing a division into sectors with optic axial angles 2V about 16° and 28°; refractive index about 2·35. The colour is honey-yellow to brownish or reddish, and the powder is straw-yellow. Analysis gave:

Pb.	Cu.	CaO.	Cl.	I.	SO_3.	O and loss.	Sp. gr.
75·07	trace	0·67	7·96	8·64	0·47	[7·19]	7·39

The calcium sulphate is present as gypsum. Calculating these results as an oxychloroiodide of lead (as done for previous analyses) there is still a deficit of nearly 4%. When the mineral is heated with hydrochloric acid, abundant chlorine is evolved, and in the cold nitric acid solution the iodine is present as iodate, and not as iodide. The formula is, therefore, written as $3(PbCl_2,2PbO),PbI_2O_6$, representing a molecular compound of lead iodate with a lead oxychloride having the composition of mendipite. L. J. S.

Micro-structure of Magnetite. OTTO MÜGGE (*Jahrb. Min. Beil.-Bd.*, 1911, **32**, 491—534).—Etching experiments were made on crystals and plates of magnetite and of some other minerals of the spinel group, and a detailed description illustrated by many photomicrographs is given of the resulting etched surfaces. When a crystal of magnetite is placed in freshly fused potassium hydrogen sulphate it is only very slightly attacked, but at a higher temperature, when the free sulphuric acid has been largely expelled, there is an energetic action. An octahedral face of an etched crystal shows a shimmer in three positions. This is shown to be due to a regular orientation of minute crystals of hæmatite on the magnetite, the basal plane of the former being parallel to the octahedral face of the latter. A similar result is obtained when magnetite crystals are heated in the air; and the martite pseudomorphs are shown to possess a similar structure. Hæmatite when heated in nitrogen at about 1500°, or in the presence of a reducing agent at the lower temperature of 700°, loses part of its oxygen, and magnetite is developed on its surface in regular orientation. L. J. S.

A Ferriferous Dolomite from the Simplon Tunnel. GABRIELLE LINCIO (*Atti R. Accad. Sci. Torino*, 1911, **46**, 969—988).—The mineral was found about 4590 metres from the Italian end of the tunnel, and was deposited in association with calcite and other minerals. It has D 3·003 at 14—15°, and on analysis gave the following numbers:

CaO.	MgO.	FeO.	CO_2.	Total.
29·61	12·94	12·99	44·72	100·26

corresponding with the formula: $3CaCO_3,2MgCO_3,FeCO_3$. The mineral is crystalline, and contains included many minute gaseous bubbles. R. V. S.

The Distribution of Borates in Potash Deposits. WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1911, **72**, 302—312).—The distribution of borates has been studied in the same specimens from the Stassfurt and Vienenburg deposits as have been already used for the estimation of nitrogen and of copper (Abstr., 1909, ii, 571, 1011) together with specimens from other German deposits. Special samples have also been analysed, taken from the immediate neighbourhood of the concretions of boracite, and at definite distances from them. The proportions found vary from 0·4% in some of the salt clays to 0·01% in carnallite and kieserite, whilst the polyhalite region is free from borates. Most of the boric acid is found in the residue insoluble in water. Where lenses of rock salt are enclosed in carnallite, the veins contained in these lenses are much richer in borates than those of the typical older salts. No such regularity is found in the distribution of borates as in that of ammonia and bromine. The proportion of borates is slightly lowered in the immediate neighbourhood of boracite concretions.

The turmeric test is sensitive to 0·00005 milligram B_2O_3 in 1 c.c. The quantitative estimation is best performed by Wherry's method (Abstr., 1909, ii, 92). C. H. D.

The Alunite-Beudantite Group. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1911, [iv], **32**, 359—364).—The minerals of this group (compare G. T. Prior, Abstr., 1903, ii, 377) are all rhombohedral, but they often exhibit optical anomalies. They fall into the following three subgroups of sulphates, phosphates, and sulphato-phosphates, of which alunite, hamlinite, and beudantite respectively may be taken as the types. The general formula is written $[R'''(OH)_2]_6R''[M]_2[M_2]$.

Various incompletely-described minerals, which may possibly belong to this group, are discussed. It is suggested that goyazite is identical with hamlinite; and utahite, carphosiderite and its aluminous variety apatelite, raimondite, pastreite, and cyprusite are all united under the name carphosiderite, with the new formula $3Fe_2O_3,4SO_3,7H_2O$ (identical with that in the above table). The formula of pharmacosiderite, when written in the form $2(H,K)_2O,3Fe_2O_3,2As_2O_5,7H_2O+4H_2O$, suggests that this mineral may also belong to the hamlinite sub-group.

Sulphates.	Alunite	$[Al(OH)_2]_6$	K_2	$[SO_4]_2$	$[SO_4]_2$
	Natroalunite	$[Al(OH)_2]_6$	Na_2	$[SO_4]_2$	$[SO_4]_2$
	Jarosite	$[Fe(OH)_2]_6$	K_2	$[SO_4]_2$	$[SO_4]_2$
	Natrojarosite	$[Fe(OH)_2]_6$	Na_2	$[SO_4]_2$	$[SO_4]_2$
	Plumbojarosite ...	$[Fe(OH)_2]_6$	Pb	$[SO_4]_2$	$[SO_4]_2$
	Carphosiderite ...	$[Fe(OH)_2]_6$	H_2	$[SO_4]_2$	$[SO_4]_2$
Phosphates	Hamlinite	$[Al(OH)_2]_6$	Sr	$[HPO_4]_2$	$[Sr(PO_4)_2]$
	Plumbogummite..	$[Al(OH)_2]_6$	Pb	$[HPO_4]_2$	$[Pb(PO_4)_2]$
	Gorceixite	$[Al(OH)_2]_6$	Ba	$[HPO_4]_2$	$[Ba(PO_4)_2]$
	Florencite	$[Al(OH)_2]_6$	$Ce_{\frac{2}{3}}$	$[Ce_{\frac{1}{3}}PO_4]_2$	$[Ce_{\frac{2}{3}}(PO_4)_2]$
Sulphato-phosphates.	Beudantite	$[Fe(OH)_2]_6$	Pb	$[SO_4]_2$	$[Pb(AsO_4)_2]$
	Corkite	$[Fe(OH)_2]_6$	Pb	$[SO_4]_2$	$[Pb(PO_4)_2]$
	Svanbergite	$[Al(OH)_2]_6$	Sr	$[SO_4]_2$	$[Sr(PO_4)_2]$
	Hinsdalite	$[Al(OH)_2]_6$	Pb	$[SO_4]_2$	$[Pb(PO_4)_2]$
	Harttite	$[Al(OH)_2]_6$	Sr	$[SO_4]_2$	$[SO_4]_2$
		$2[Al(OH)_2]_6$	Sr	$[HPO_4]_2$	$[Sr(PO_4)_2]$

L. J. S.

Composition of French Phosphorite Minerals. Waldemar T. Schaller (*J. Washington Acad. Sci.*, 1911, 1, 151).

—Lacroix has regarded the French phosphorites as mixtures of collophanite, dahllite (=podolite), and francolite (=staffelite), and he has ascribed certain formulæ to these species (Abstr., 1910, ii, 622, 720). A study of the published analyses leads to the following formulæ as more probable:

Dahllite............	$9CaO,3P_2O_5,CaO,CO_2,H_2O$
Francolite.........	$9CaO,3P_2O_5,CaF_2,CO_2,H_2O$
Collophanite......	$9CaO,3P_2O_5,CaO,CO_2,H_2O+nH_2O$

L. J. S.

Herderite Crystals from Auburn, Maine. William E. Ford (*Amer. J. Sci.*, 1911, [iv], 32, 283—286).

—A crystallographic description is given of herderite crystals from Mt. Apatite, Auburn, Maine, which are of interest, in that some of them are untwinned and distinctly monoclinic, whilst others show the union of two individuals twinned on the basal plane, so producing the pseudo-orthorhombic forms characteristic of this mineral. The measured angles approach more closely those of Penfield (1894) for the hydro-herderite, $Ca[Gl(OH)]PO_4$, from Paris, Maine, than those of Dana (1884) for the hydro-fluor-herderite, $Ca[Gl(F,OH)]PO_4$, from Stoneham, Maine. A partial analysis of the crystals gave, however, $F=6{\cdot}04\%$, $H_2O=3{\cdot}62\%$, proving the material to be hydro-fluor-herderite. The suggestion of Penfield that the angles of the crystals vary with the composition is therefore not supported. Penfield's angles are adopted for both varieties as being the most trustworthy. L. J. S.

Hinsdalite, a New Mineral. Esper S. Larsen, jun., and Waldemar T. Schaller (*Amer. J. Sci.*, 1911, [iv], 32, 251—255).

—This new mineral occurs in considerable abundance at the Golden

Fleece Mine, near Lake City, Hinsdale Co., Colorado, where, together with quartz, it forms the gangue of a vein intersecting volcanic rocks. Associated minerals in the vein are barytes, iron-pyrites, galena, tetrahedrite, and rhodochrosite. The hinsdalite is granular and coarsely crystalline, with a dark grey colour and a vitreous to greasy lustre. Crystals are nearly colourless with a greenish cast; they have the form of cube-like rhombohedra ($rr' = 91°18'$) or of six-sided plates. There is a perfect cleavage parallel to the base; H. = $4\frac{1}{2}$; sp. gr. 3·65. The crystals are zoned and exhibit optical anomalies; an optically (+) uniaxial centre is surrounded by sectors with axial angles $2E = 32°$. Refractive indices, $\alpha = 1·670$, $\beta = 1·671$, $\gamma = 1·689$. Analysis gave:

PbO.	SrO.	CaO.	Al_2O_3.	SO_3.	P_2O_5.	H_2O.	Total.
31·75	3·11	trace	26·47	14·13	14·50	10·25	100·21

corresponding with $2PbO,3Al_2O_3,2SO_3,P_2O_5,6H_2O$, mixed with 17·44% of the svanbergite molecule. The mineral is infusible and is practically insoluble in acids; its water is lost between 400° and 600°. Hinsdalite therefore falls into the following isomorphous group:

		Rhombohedral ($a : c$).
Svanbergite............	$2SrO,3Al_2O_3,2SO_3,P_2O_5,6H_2O$	1 : 1·2063
Hinsdalite	$2PbO,3Al_2O_3,2SO_3,P_2O_5,6H_2O$	1 : 1·2677
Corkite	$2PbO,3Fe_2O_3,2SO_3,P_2O_5,6H_2O$	1 : 1·1842
Beudantite	$2PbO,3Fe_2O_3,2SO_3,As_2O_5,6H_2O$	1 : 1·1842

L. J. S.

Crystallised Variscite from Utah. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1911, 1, 150—151).—The bright green crystals from Lucin, Utah, are orthorhombic with a tabular habit or a form similar to those of the analogous minerals, scorodite and strengite (= phosphosiderite). They are only slightly pleochroic, and have a mean refractive index of 1·560 and birefringence 0·032. All the water is lost at 160°, and the crystals become lavender-coloured with strong pleochroism, mean refractive index 1·448, and birefringence 0·003. The dehydrated material is readily soluble in acids, whilst the green crystals are sparingly soluble. Analysis agrees with the usual formula $Al_2O_3,P_2O_5,4H_2O$:

P_2O_5.	V_2O_3.	Cr_2O_3.	Fe_2O_3.	Al_2O_3.	H_2O.	Total.	Sp. gr.
44·73	0·32	0·18	0·06	32·40	22·68	100·37	2·54

L. J. S.

Fermorite and Tilasite from the Manganese-ore Deposits of India. G. F. HERBERT SMITH and GEORGE T. PRIOR (*Min. Mag.*, 1911, **16**, 84—96).—The new mineral fermorite forms veins of pale pinkish-white or white material in the manganese-ore (a mixture of braunite, hollandite, and pyrolusite) at Sitapar, Central Provinces. It is translucent with a greasy lustre, and is optically uniaxial and negative. One specimen showed a prism of 60°, proving the mineral to be hexagonal, and, as seen from analysis I, isomorphous with apatite. Formula: $3[(Ca,Sr)_3(P,As)_2O_8],Ca(OH,F)_2$.

	As_2O_5.	P_2O_5.	FeO.	CaO.	SrO.	MgO.	F.	H_2O.	Insol.	Total less O for F.	Sp. gr.
I.	25·23	20·11	—	44·34	9·93	—	0·83	trace	0·08	100·17	3·518
II.	50·35	0·43	0·55	25·68	0·66	18·34	7·18	0·73	0·05	100·35	3·77

Tilasite occurs as pale green, translucent to opaque crystals, somewhat resembling apatite in appearance, in a quartz-barytes vein traversing the manganese-ore, and in a quartz-spessartite-braunite rock; both occurrences are at Kajlidongri, Jhabua State. The crystals are monoclinic [$a:b:c=0{\cdot}7503:1:0{\cdot}8391$; $\beta=59°0\frac{1}{2}'$], and are of interest in belonging to the clinohedral class, there being a plane of symmetry, but no axis of symmetry. The optic axial plane is perpendicular to the plane of symmetry; $2V=82°44'$; $\alpha=1{\cdot}640$, $\beta=1{\cdot}660$, $\gamma=1{\cdot}675$(Na). Analysis II gives the formula: $(MgF)CaAsO_4$. The identity of the mineral with tilasite or fluor-adelite from Sweden (Sjögren, 1895) is discussed. L. J. S.

Analyses of Stibiotantalite. WILLIAM E. FORD (*Amer. J. Sci.*, 1911, [iv], **32**, 287—288).—In the analyses of stibiotantalite from San Diego Co., California (Penfield and Ford, Abstr., 1906, ii, 681), the relative amounts of tantalum and columbium were estimated indirectly from the specific gravity of the mixed oxides on the assumption that the composition and sp. gr. vary proportionally. It has been shown, however, by Foote and Langley (Abstr., 1911, ii, 71) that the curve obtained by plotting the sp. gr. against the composition is not quite a straight line; the oxides apparently form a solid solution, and do not exist together simply as a mechanical mixture. From the table of Foote and Langley a correction of about 2% is to be made in the old analyses, which are re-calculated under I and II. Under III are given the results of a new analysis by Foote and Langley:

	Ta_2O_5.	Cb_2O_5.	Sb_2O_3.	Bi_2O_3.	Total.	Sp. gr.
I.	13·00	37·30	49·28	0·53	100·11	5·98
II.	33·86	21·47	44·26	0·33	99·92	6·72
III.	41·92	16·19	40·95	0·60	99·66	6·80

L. J. S.

Trans-Baikal Minerals. S. D. KUSNETZOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1911, 897—901).—Descriptions are given of the following minerals.

Powellite, in crusts of white plates. Composition:

MoO_3.	CaO.	Fe_2O_3,Al_2O_3.	SiO_2.	Total.
70·05	25·10	3·45	1·80	100·50

The original powellite from Idaho contained 10·28% WoO_3.

Bismuthospherite.—Two specimens: (*α*) greenish-brown, D 7·00, and (*β*) apple-green, D 6·86, gave on analysis, after allowing for insoluble residue:

Bi_2O_3.	CO_2.	H_2O.	Total.
90·13—90·19	9·23—9·11	0·64—0·70	100

Pure bismuthospherite, Bi_2CO_5, contains Bi_2O_3, 91·3, and CO_2, 8·7%.
T. H. P.

A New Variety of Chrysocolla from Chile. HARRY F. KELLER (*Proc. Amer. Phil. Soc.*, 1909, **48**, 65—66).—Chrysocolla shows wide variations in composition, and the colour ranges from bright green to blue. Analyses of green material agree with the formula

$$CuSiO_3,2H_2O.$$

The following analyses are given of turquoise-blue material occurring as enamel-like crusts in a honey-combed, siliceous matrix from Huiquintipa, prov. Tarapacá, Chile. It is brittle; $H. = 3\frac{1}{2}$; and is readily decomposed by acids without gelatinisation. The powder is pale green. It blackens when heated; two-thirds (13·41%) of the water is lost below 125°, and the remainder only at a red-heat. The formula is therefore written as a hydrated acid metasilicate,

$$CuH_2(SiO_3)_2,H_2O:$$

	SiO_2.	CuO.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total	Sp. gr.
I.	46·14	28·85	0·58	1·38	1·64	0·83	20·15	99·54	2·532
II.	45·89	28·69	0·47	1·33	1·67	1·01	20·32	99·38	—

L. J. S.

Beryl and Rhodizite from the Pegmatites of Madagascar.

Louis Duparc, M. Wunder, and R. Sabot (*Bull. Soc. franç. Min.*, 1911, **34**, 131—139).—A crystal of beryl from Maharitra, of tabular habit and rich in faces, differs from those previously described from this locality (Abstr., 1910, ii, 312; 1911, ii, 736) in being much thinner and in its pale bluish-green (instead of rose-red) colour. D 2·8474; refractive indices (Na light), ω 1·5974, ϵ 1·5890. Analysis I.—These results confirm the presence in the Madagascar pegmatites of two types of beryl: one the ordinary aquamarine with prismatic habit and few crystal-faces, low density and refractive indices, poor in alkalis, and without cæsium and rubidium; the other of tabular habit parallel to the base and rich in faces, with higher density and refractive indices, and rich in alkalis, particularly cæsium and rubidium:

	SiO_2.	Al_2O_3.	GlO.	MgO.	K_2O.	Na_2O.	Li_2O.	Cs_2O.	Rb_2O.	Loss on ignition.	Total.
I.	61·67	17·41	11·76	trace	0·68	2·05	1·99	0·87	1·34	2·20	99·97
II.	3·18	27·40	14·93	0·11	1·41	1·78	0·68	3·47	2·29	1·42	*

* B_2O_3, by difference, 43·33.

Rhodizite occurs in association with rubellite at Ampakite in the Sahatany valley. The two crystals described have the form of the rhombic-dodecahedron with small tetrahedral faces; they are, however, pseudo-cubic and birefringent; refractive index (Na) 1·6935 (and 1·6952); D 3·344. The crystals are translucent with a vitreous lustre, and yellow with a tinge of green. Analysis II, corresponding with $B_{14}Al_6Gl_7(Li,K,Cs,Rb,Na,H)_4O_{39}$, differs appreciably from Pisani's analysis (Abstr., 1910, ii, 57) of rhodizite from Madagascar.

L. J. S.

Samarskite, etc., from Madras.

George Howlett Tipper (*Rec. Geol. Surv. India*, 1911, **41**, 210—213).—Angular masses of samarskite, up to 200 lb. in weight, occur in a garnet-bearing pegmatite in the Sankara mica mine in Nellore district, Madras. On the conchoidal fracture it is black with a brilliant lustre; D 5·4—5·7. It is a columbate and tantalate of cerium and yttrium earths, with iron, calcium, and very variable amounts of uranium. Associated with it are long, black crystals resembling allanite, but differing from this in containing 17·8% Cb_2O_5 and 5·39% U_3O_8; it contains also 19·8% cerium earths; D 3·05. Another associated mineral is a hydrated zircon resembling cyrtolite, but containing some uranium. This occurs as sheaf-like groups of pale greyish-brown crystals; D 4·09. The following analysis corresponds with the formula $2ZrSiO_4,H_2O$. The powdered mineral is attacked by hot concentrated hydrochloric acid, and, after one hour, 15% is dissolved, all the iron and part of the zirconia going into solution:

ZrO_2.	SiO_2.	Fe_2O_3.	Ce_2O_3, etc.	MnO.	U_3O_8.	H_2O.	Total.
62·3	26·06	5·41	trace	trace	2·42	3·3	99·49

L. J. S.

Meteoric Iron from Currant Creek, Colorado. William P. Headden (*Proc. Colorado Sci. Soc.*, 1908, **9**, 79—80).—This mass of 596 lbs. was found about 1906 at Currant Creek, twenty-two miles south-west of Cripple Creek. It shows no Widmanstätten figures on a polished and etched surface. Analysis gave:

Fe.	Ni.	Co.	Mn.	Cr.	Cu, P, CaO, MgO.	Sp. gr.
89·793	9·999	0·554	0·054	0·048	traces	7·9394

L. J. S.

Chemical and Petrological Examination of the El Nakhla Meteorite. Stanislas Meunier (*Compt. rend.*, 1911, **153**, 785—787).—This meteorite, which fell recently near Alexandria, shows a remarkably crystalline structure, and consists principally of fragments of hypersthene (83·34%) united by a cement soluble in hydrochloric acid. The hypersthene shows the macled structure, and contains inclusions of ilmenite. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O and Na_2O.	MnO.	Total.
47·40	0·69	20·80	15·20	14·61	0·05	0·85	99·60

W. O. W.

The Gas of the Boriferous "Soffioni" of Larderello. C. Porlezza and G. Norzi (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 338—342).—A new analysis of the gas from this source has given results very similar to those of Nasini, Anderlini, and Salvadori (Abstr., 1898, ii, 527). The principal differences occur in the case of the rare gases, for which more accurate methods are now available. The gas has the following composition:

CO_2.	H_2S.	CH_4.	H_2.	O_2.	N_2.	A.	He.	Total.
92·2000	2·0000	1·7800	2·4500	0·1800	1·3500	0·0245	0·0155	100·0000

The quantity of radium emanation in the gas amounts to $4·813 \times 10^{-7}$ c.mm. R. V. S.

Physiological Chemistry.

The Nitrous Oxide Method of Estimating the Quantity of Blood in the Body. I. MARKOFF, FRANZ MÜLLER, and NATHAN ZUNTZ (*Zeitsch. Balneol., Klimatol. Kurort-Hygiene*, 1911, **4**, Nos. 14, 15. Reprint, 16 pp.).—By allowing a person or animal to breathe a measured quantity of nitrous oxide and subsequently examining a sample of the blood, and estimating the tension of the gas in it, the total volume of the blood can be calculated. The difficulty of estimating the gas can be largely overcome by the use of the gas interferometer. The influence of bath-treatment, climate, work, etc., on the blood volume is to be investigated by this method.

W. D. H.

Action of Extracts of Invertebrate Tissues on Blood-pressure. JEAN GAUTRELET (*Bull. stat. biol. d'Arcachon*, 1910, **13**, 53—63).—The hepato-pancreas of the crab, and of *Maia*, contains one or more substances slightly soluble in alcohol which lower the blood-pressure of the dog when intravenously injected. Aqueous or alcoholic extracts of the genital glands are inactive. Among molluscs, extracts of the genital glands and of the liver in *Sepia*, *Octopus*, and *Aplysia* (liver only) depress blood-pressure and diminish cardiac action. The same is true for echinoderms. In cases where depression of blood-pressure occurs, previous administration of atropine does not influence the result.

W. D. H.

The Size, and the Growth of the Blood in Tame Rats. R. A. CHISOLM (*Quart. J. exp. Physiol.*, 1911, **4**, 207—230).—The average oxygen capacity per kilo. of rats weighing from 50 to 150 grams each is 10 c.c., and the blood volume 63 c.c. The average hæmoglobin percentage is 86, and the number of red corpuscles 9 million per cubic millimetre. A fall in hæmoglobin, oxygen capacity, and blood volume occurs temporarily during the suckling period, and a fall in blood volume takes place in later life as the rate of growth diminishes. The oxygen capacity is less variable than the other factors mentioned. The volume of the blood is less variable than the weight of kidneys, liver, and spleen considered as percentages of the body-weight.

The volume of the blood in rats may be calculated by the formula $a\ 0{\cdot}9/10{\cdot}1$, and the total oxygen capacity by the formula $a\ 0{\cdot}95/8$, where a is the body-weight.

W. D. H.

The Influence of Under-feeding on the Blood. ARTHUR E. BOYCOTT and R. A. CHISOLM (*J. Path. Bact.*, 1911. **16**, 263—268).—Under-feeding with a diet deficient in protein does not necessarily cause any wasting of the blood in rats. It is suggested that this result throws some light on the duration of life of the red corpuscles.

W. D. H.

The Influence on the Blood of the Rat of the Presence of a Transplanted Sarcoma. R. A. Chisolm (*J. Path. Bact.*, 1911, **16**, 152—166).—Transplanted sarcomata in rats usually produce a diminution in oxygen capacity and in hæmoglobin percentage, which is parallel to the decrease in red corpuscles. The volume of the blood is increased. The anæmia is usually accompanied by wasting of the tissues. The blood histologically shows signs of regeneration, but the mechanism of the blood destruction is unknown. In small tumours occasionally the oxygen capacity and the blood volume increase to meet the needs of the tumour. W. D. H.

The Fat-splitting Properties of the Blood and Serum of the Dog under Different Conditions. Emil Abderhalden and Peter Rona (*Zeitsch. physiol. Chem.*, 1911, **75**, 30—37).—The introduction of foreign blood into the circulation raises the fat-splitting power of the dog's blood, and especially of the serum. W. D. H.

The Individual Differences of the Red Blood-corpuscles on Hæmolysis. Stephan Rusznyâk (*Biochem. Zeitsch.*, 1911, **36**, 394—396).—The author denies the correctness of the conclusion of Dienes (this vol., ii, 740), that the corpuscles show individual differences on hæmolysis, on the ground that Dienes has assumed that the dried matter of the blood-corpuscles contains 50% hæmoglobin, whereas Abderhalden has shown that they contain 77%. If Dienes' results be calculated on the latter assumption, his conclusions cannot be substantiated. S. B. S.

The Action of Selenium Salts on Red Blood-corpuscles. Charles O. Jones (*Bio.-Chem. J.*, 1911, **6**, 106—109).—Sodium selenite does not produce hæmolysis outside the body, but does so after hypodermic injection. The cause of this is obscure. Sodium selenite is reduced to selenium in the portal circulation, chiefly in the spleen and liver. Only a proportion of the red corpuscles are hæmolysed, suggesting that these from the portal system were mixed in the general circulation with those which are unaffected. Glycogen and sugar disappear in a remarkable manner after the injection, but whether this is a factor in hæmolysis is very questionable. W. D. H.

The Rate of Regeneration of Hæmoglobin after Hæmorrhage. Arthur E. Boycott (*J. Path. Bact.*, 1911, **16**, 269—275).—Rats regenerate hæmoglobin after hæmorrhage more quickly than do rabbits, roughly in the proportion of three or four to one. Young rats and rabbits regenerate more quickly than adults. W. D. H.

The Enzymes of Leucocytes. M. Tschernoruzki (*Zeitsch. physiol. Chem.*, 1911, **75**, 216—231).—The polynuclear leucocytes of the dog carry the following enzymes: protease, amylase, diastase, catalase, nuclease, and peroxydase, but not lipase. W. D. H.

Biotoxin. Francesco Marino-Zuco, R. Onorato, and L. Giuganino (*Gazzetta*, 1911, **41**, ii, 358—367. Compare Abstr., 1910, ii, 223, and this vol., i, 1049).—When its excretion by way of the kidneys is interfered with, biotoxin accumulates in the blood, but its quantity does not increase indefinitely, so that a part of the toxin must be eliminated in some way. The suppression of the renal secretion was effected in dogs in three ways; (1) by extirpation of the kidneys; (2) by cutting the ureters; (3) by producing an artificial nephritis. R. V. S.

The Acidity of the Gastric Juice of Scyllium Stellare. (Fräulein) H. A. van Herwerden and Wilhelm E. Ringer (*Zeitsch. physiol. Chem.*, 1911, **75**, 290—307).—Fräulein van Herwerden in her first paper showed that the Sjoqvist method was inapplicable to the investigation of the gastric juice of the dog-fish; the acidity is quite considerable, and she believed it might possibly be due to organic acid. A method was devised for testing this question with artificial juice, and found trustworthy. Applying it to the dog-fish juice, the conclusion is now reached that the major part of the acidity is due to hydrochloric acid; this was confirmed by actual analyses.
W. D. H.

Digestion of Casein. Louis Gaucher (*Compt. rend.*, 1911, **153**, 891—892. Compare Abstr., 1909, ii, 249, 236).—The experiments on dogs described in the earlier communications have been repeated on a boy, in whom, owing to the necessity of an operation, a fistula had been established at the opening of the jejunum. The curdling of milk in the stomach is not necessary to digestion, since a considerable amount passes into the intestine without having coagulated. The larger clots are broken up into much smaller fragments by the movements of the stomach; if the organ is incapable of effecting this, digestion may be hindered. No peptonisation occurs until the milk has passed the duodenum. W. O. W.

Studies in Nutrition. I. The Utilisation of the Proteins of Wheat. Lafayette B. Mendel and Morris S. Fine (*J. Biol. Chem.*, 1911, **10**, 303—325).—It has been held in the past that vegetable proteins are not utilised as thoroughly in the body as those of animal origin. The indigestibility of such proteins is largely due to unfavourable concomitant conditions, of which the most important is admixture with cellulose. In the present experiments such conditions were eliminated as far as possible, and it was found in men and dogs that glidin (a commercial product, which is mainly gliadin, and is free from starch), gluten (also commercial), and the two characteristic proteins of wheat, gliadin and glutenin, are as thoroughly utilised as are the nitrogenous components of fresh meat. W. D. H.

Studies in Nutrition. II. The Utilisation of the Proteins of Barley. Lafayette B. Mendel and Morris S. Fine (*J. Biol. Chem.*, 1911, **10**, 339—343).—Under favourable conditions, barley protein, like that of the closely related cereal, wheat, would be almost perfectly digested. W. D. H.

The Resorption of Gelatin from the Small Intestine. Felix Reach (*Biochem. Zeitsch.*, 1911, **36**, 498).—The author recalls his own experiments (Abstr., 1901, ii, 667), in which the time of action was five and a-half hours, whereas in Minami's experiments (this vol., ii, 810) the time of action was only one hour. S. B. S.

Physiology of Digestion. IV. The Total Chlorine of the Animal Body on a Diet Rich in Chlorine. RUDOLF ROSEMANN (*Pflüger's Archiv*, 1911, **142**, 447—458. Compare Abstr., 1910, ii, 1082).—The percentage of chlorine in the body of the normal dog is 0·112. On food poor in chlorine this falls. The present research deals with the effect of a diet rich in chlorine, and consists of experiments on two dogs. In the first, the feeding was continued for three weeks. The chlorine rose to 0·136%, but that of the skin was not greater than that of the body as a whole. In the second, the feeding was kept up for two months. The percentage in the whole body rose to 0·163%, and of the skin to 0·342%, which confirms the statements previously made concerning the skin as a chlorine depôt. The percentage in the blood was also high (0·308%). W. D. H.

Physiology of Digestion. V. The Total Chlorine of the Human Fœtus. RUDOLF ROSEMANN (*Pflüger's Archiv*, 1911, **142**, 459—460).—That the fœtus has a high percentage of chlorine is confirmed by the analyses recorded of a human fœtus 18 centimetres long; it contained 0·252% of chlorine. W. D. H.

Chemistry of the Hen's Egg. KENJI KOJO (*Zeitsch. physiol. Chem.*, 1911, **75**, 1—12).—The following analytical figures are given:

	White.	Yolk.
Water	87·71	49·73
Total solids.........	12·29	50·27
Ash	0·4	1·44
Organic solids	11·89	48·83
Total nitrogen......	1·75	2·49
Dextrose	0·55	0·27

W. D. H.

Biology of the Egg, a Chemico-Anatomical Co-ordination. VINCENZO DIAMARE (*Anat. Anzeiger*, 1911, **40**, 205—207).—The eggs of birds and reptiles contain dextrose, which is apparently formed from the living material present. The bulk of the paper is polemical against Salkowski, who, it is complained, has misrepresented the author's views on the part played by sugar in development.
W. D. H.

The Catalase of Sea-Urchin Eggs Before and After Fertilisation, with Especial Reference to the Relation of Catalase to Oxidation in General. SAMUEL AMBERG and M. C. WINTERNITZ (*J. Biol. Chem.*, 1911, **10**, 295—302).—The fertilisation of sea-urchin's eggs leads to an increase of four to six times its cell oxidation, but this is not accompanied by an increase in its catalytic activity.
W. D. H.

Are the Oxidative Processes Independent Variables in Vital Processes? JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, **36**, 345—356).—The experiments were carried out with the eggs of sea-urchin (*Arbacia*), and the temperature-coefficients of oxidation and rate of development were determined. The latter was estimated by determining the time elapsing between fertilisation with the spermatozoa and the first bifurcation of the eggs. The temperature-coefficients for both processes between 15° and 30° were found to be nearly identical (= about 2). The temperature-coefficient for the development rate increased with decreasing temperature, whereas that of the oxidation process remained nearly constant. The amount of sodium cyanide necessary to just inhibit development did not decrease the oxidative process by quite one-quarter of the total. This fact is in harmony with the discovery that the rate of oxidative processes is increased by about one-quarter by fertilisation. From these facts it can be understood why the temperature-coefficients of oxidation and development rate are no longer identical at lower temperatures. At temperatures above 32°, at which bifurcation is impossible, the oxidative processes also rapidly diminish. The results, without confirming the hypothesis that the oxidative processes are independent variables in the development of the egg, do not contradict it. S. B. S.

Chemical and Physiological Examination of the Liver of Oxen. A. Daniel-Brunet and C. Rolland (*Compt. rend.*, 1911, **153**, 900—902).—The bile of oxen gave the following analytical results, stated to be more complete than any hitherto published. The weights are in grams per kilogram of fresh material. The amount of bile from one animal varied from 395 to 630 c.c. It had D^{17} 1·024—1·027, and gave an extract, dried in a vacuum, of 90·3—90·5; dried at 100°, 88·5—92·5; at 110°, 86·80 to 89·60. Ash, 12·5—14·30; chlorides (as NaCl), 2·38—2·68; P_2O_5, 1·31—1·58; Fe, 0·016—0·018. Nitrogen, 2·3—2·5; fat, 27·80—28·80; bile salts (sodium glycocholate and taurocholate), 15·30—15·80; nucleoprotein, 1·15—2·25; lipoids, 1·100—2·130. The latter contained cholesterol 0·410—0·813, with lecithin and neutral soaps 0·690—1·317. The livers of the same animals gave water, 689—755·20; ash free from carbon, 16·20—20·49; glycogen, 28·80—83·40; carbamide, 0·615—0·683; P_2O_5, 2·90—3·48; chlorides (as NaCl), 1·95—2·86. The figures represent parts per 1000 of fresh substance. W. O. W.

The Relationship between Nuclear Material and Development. Ernst Masing *Zeitsch. physiol. Chem.*, 1911, **75**, 135—140).—The numbers given in connexion with the liver of rabbit embryos show that nucleic acid is more abundant relatively in early than in later stages. W. D. H.

Bio-chemical Relations of Various Lipoid Substances in the Liver. Frederick P. Wilson (*Bio.-Chem. J.*, 1911, **6**, 100—105).—The acetone-insoluble fraction of the ether extract of the liver yields the most suitable antigen in the Wassermann reaction. Extracts made with cold and hot alcohol yield substances which differ from each other and from those in the ether extract in physical and bio-chemical properties, but these differences are apparently not dependent on the saponification or iodine values. W. D. H.

Deamidisation. GERTRUDE D. BOSTOCK (*Bio.-Chem. J.*, 1911, **6**, 48—68).—Emulsions of liver and intestinal mucosa liberate ammonia from asparagine to a less extent than from glycine and leucine, and more than from alanine. This confirms Lang's statement, but no inhibition of the deamidising enzyme was found on adding an antiseptic. In the body the nitrogen of glycine appears quantitatively as urea in the urine within eight hours, whilst only 63% of asparagine nitrogen so appears in the same time, whereas *in vitro*, ammonia is more readily liberated from asparagine than from glycine, that is, the amide nitrogen attached to the carboxyl group is more readily liberated than the amide group in the α-position. W. D. H.

The Possible Vicarious Relationship between the Pituitary and Thyroid Glands. SUTHERLAND SIMPSON and ANDREW HUNTER (*Quart. J. exp. Physiol.*, 1911, **4**, 257—272).—Complete removal of the thyroid in lambs from seven to eight months old and in adult sheep does not lead to the appearance of iodine in the pituitary even after so long an interval as five to six months. On the assumption that the active substance secreted by the thyroid is the one which contains iodine, no support is lent to the view, originally advanced by Rogowitsch, that there is a vicarious relationship between the two organs. In thyroidectomised animals the increase noted in the size of the pituitary body was not so great as has been reported by other observers.
W. D. H.

The Thyroid and Enzymatic Processes. A. J. JUSCHTSCHENKO (*Zeitsch. physiol. Chem.*, 1911, **75**, 141—168).—Removal of the thyroid in dogs and rabbits lessens the amount of catalase in all the organs investigated, including the blood; the amount of nuclease is also lessened. Administration of thyroid extract increases the catalase, the nuclease, the inorganic phosphates of the blood, the antitryptic and hæmolytic power of the serum, and the appearance in the blood of materials which, together with the antigen from the thyroid, lead to a union with complement. W. D. H.

Proteolysis in the Thymus of the Calf. NILS J. RODIN (*Zeitsch. physiol. Chem.*, 1911, **75**, 197—206).—Proteolytic changes occur more readily in the autolysing thymus if the reaction is acid than if it is alkaline or neutral. This apparently is not due, as in the spleen (Hedin), to the effect of acid in destroying an inhibitory substance. The proteolytic enzyme was obtained by perfusing the organ with 0·2% acetic acid; it is feebly antagonised by ox-serum; if the enzyme is prepared by a neutral (calcium carbonate) infusion, no such inhibition is noticed. Kaolin added in quantity sufficient to completely precipitate proteins leaves the enzyme prepared by either method largely in solution. W. D. H.

Fatty Streaks in the Tunica Intima of Arteries. OSKAR KLOTZ and M. F. MANNING (*J. Path. Bact.*, 1911, **16**, 211—220).—In this degenerative condition, which may occur in quite young people, the fat is deposited in the cells of the sub-endothelial layer, and the endothelium may be but loosely attached; the elastic fibres also appear as though they were undergoing a fatty change, and the process may go on and involve the middle coat of the artery. The fat stained as neutral fat does; it was all dissolved out by alcohol and ether; sometimes the fat globules are anisotropic, and are therefore probably lipoid. The cause of this change, which primarily attacks the internal coat, is probably direct irritation by toxins produced by infection.

W. D. H.

Gas Production in Teleostean Fishes. W. N. F. WOODLAND (*Anat. Anzieger*, 1911, **40**, 225—242).—The structure of the swim bladder, and the very remarkable arrangements for its blood supply are described in full. In the process of oxygen secretion into the bladder, there is no hæmolysis of corpuscles, but the gas comes from what is in solution in the plasma. The use of a second rete mirabile of capillaries on the course of the returning venous blood is at present unknown. W. D. H.

Stability of the Photogenic Material of the Lampyridæ and its Probable Chemical Nature. F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1911, **33**, 1791—1797. Compare Kastle and McDermott, Abstr., 1910, ii, 1088; McDermott, this vol., i, 396).—A further study of the photogenic compound of *Photinus pyralis* and other *Lampyridae* has shown that it is more stable towards atmospheric oxygen than is usually supposed, especially when it has been dried out of contact with the air. There can be little doubt that the luminous activity is the result of the oxidation of the photogenic compound, which is probably a lipoid (phosphatide) containing an unsaturated aliphatic radicle and an albuminous complex.

A bibliography of the subject is appended. E. G.

Proteolytic Enzymes of Invertebrates. J. SELLIER (*Bull. stat. biol. d'Arcachon*, 1910, **13**, 67—205).—In the majority of cases, the juices are neutral or slightly acid; the acidity is insufficient for true peptic action, and in certain cases is due to amino-acids. The hepatopancreas of *Helix* and *Aplysia* has no proteolytic action. The digestive juices of crustacea, cephalopods, and worms are ereptic, readily liberating amino acids from proteins and proteoses. The juices of gasteropod molluscs are inactive. Frequently rennetic action occurs, which runs parallel with proteolytic power. In many cases the liver appears to be an organ of absorption. W. D. H.

The Surface-tension of Lymph. I. and II. GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1911, **36**, 411—420, 421—434).—(I) The blood of animals four to five hours after ingestion of food, and of fasting animals showed no marked differences in either the sp. gr. or surface-tension. On the other hand, the lymph, the surface tension of which was not affected much by the ingestion of carbohydrates, showed a marked diminution after ingestion of proteins and fats (as compared with the lymph of fasting animals). The sp. gr. also is lowered, whilst the percentage of total solids increases. The fats cause a greater lowering of surface-tension than proteins. The significance of these facts as they bear on the method of resorption of food-stuffs is discussed. The surface-tension of lymph falls markedly in the first hour after food ingestion, and does not commence to rise again even after ten hours.

(II) By the same method it was found that alcohol is rapidly absorbed both from the stomach and small intestine, and enters the general circulation through the lymph and blood capillaries. Bile salts introduced into the stomach affect the surface-tension neither of the blood nor lymph. From the small intestine, on the other hand, they are absorbed and pass without change into the blood stream and lymph. Sodium soaps are absorbed in a similar way, whereas peptone does not appear (except perhaps in very small quantities) to pass the small intestine unchanged. The rate of absorption of these various substances was also investigated, and it appears that alcohol enters the circulation most rapidly. S. B. S.

Physico-chemical Investigations on Animal Liquids. VI. Chemical Reaction of Lymph. G. Quagliariello (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 273—279).—The author has determined the reaction of dog's lymph: (1) by measuring the *E.M.F.* of a couple formed of the lymph and $0{\cdot}01N$-hydrochloric acid, the two liquids being united with potassium chloride solution (compare this vol., ii, 962); (2) by observing how much alkali must be added to the lymph to give an alkalinity corresponding with $C_{H^{\cdot}} = 1 \times 10^{-9}$, or of acid to reach an acidity corresponding with $C_{OH'} = 2 \times 10^{-4}$. The second estimation is carried out with the aid of two mixtures of phosphates and phosphoric acid which have that degree of alkalinity and acidity respectively; the same amount of indicator is added to the standard solution as to the lymph, and acid or alkali is added to the latter until it acquires the same colour as the standard solution (compare Walpole, Abstr., 1910, ii, 541, 995). The dissociation constant of lymph considered as a base is from $0{\cdot}3$ to 2×10^{-12}, whilst the dissociation constant when it is considered as an acid is $0{\cdot}6$ to $1{\cdot}9 \times 10^{-14}$.

R. V. S.

Physico-chemical Investigations on Animal Liquids. VII. Chemical Reaction of Bile. G. Quagliariello (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 302—305. Compare preceding abstract). —The measurement of the concentrations of $H^{\cdot}$ and OH' in the bile of various animals by the electric method shows that its reaction may be practically neutral or faintly alkaline or acid, the variations being possibly due to the condition of the animal. Measured by the titration method already described, the neutralising power of the bile appears to be well marked, although less than that of lymph or blood-serum; the variations are considerable. Of three cases quoted, one is neutral, one alkaline, and one acid. R. V. S.

The Behaviour of Sterile and Boiled Milk Towards Rennet and Acid. Alois Kreidl and Emil Lenk (*Biochem. Zeitsch.*, 1911, 36, 357—362).—Both boiled and sterile milk clot on treatment with rennet, if either the latter or the vessels in which the experiments are carried out are not sterilised. Sterile milk (acidity 20—22) will not clot if treated with sterile rennet in sterile vessels. Touching the mixture with a non-sterile finger, or the addition of a few drops of ordinary milk, is sufficient to cause it to clot. The lactic acid bacillus develops best in slightly acidified milk (0·2—0·6 c.c. *N*/10-acid in 10 c.c. of milk). The addition of acid to the extent even of 2 c.c. to 10 c.c. of sterile milk in sterile vessels causes no precipitation, and no additional formation of acid at incubator temperature. S. B. S.

The Influence of the Cooling of Milk on the So-called Schardinger Reaction. Robert Burri and H. Schmid (*Biochem. Zeitsch*, 1911, **36**, 376—388).—In fresh milk, with few bacteria, the Schardinger methylene-blue–formaldehyde reaction is not an unalterable constant, but depends on the temperature at which the milk has been preserved. The reaction time is reduced by cooling the milk to 10° or lower. The same result is obtained whether the milk be cooled only to 10° or frozen. The authors have studied the conditions under which the changes produced by cooling may be made reversible. They assume that by the cooling of milk the fat is converted into two separable phases, the first being a change from the liquid to the solid condition, and the second being a change in the solid phase, whereby crystallisation processes play the main part. S. B. S.

The Ammonia of the Urine and its Relationship to Gastric Secretion. S. A. Gammeltoft (*Zeitsch. physiol. Chem.*, 1911, **75**, 57—70).—The investigations on human beings described in this paper confirm Loeb's statement, that ammonia excretion falls after a meal. This indicates that ammonia production is regulated with the object of maintaining a constant concentration of hydrogen ions in the tissues. When after a meal hydrochloric acid is absorbed, it is neutralised by ammonia. W. D. H.

Creatinine Excretion in Man Under the Influence of Muscular Tonus. Cornelis A. Pekelbaring (*Zeitsch. physiol. Chem.*, 1911, **75**, 207—215 *).—The present observations on man confirm the results previously arrived at from experiments on other vertebrates, that in muscular tonus the chemical change is different from that associated with contraction. In the former case, creatine is formed as a product of nitrogenous metabolism, whereas in contraction it is non-nitrogenous substances which are utilised.

W. D. H.

Protein Metabolism of the Fœtus. The Distribution of Nitrogen in the Maternal Urine and in the Fœtal Fluids Throughout Pregnancy. Dorothy E. Lindsay (*Bio.-Chem. J.*, 1911, **6**, 79—99).—The urine of the cow contains a large amount of allantoin and of hippuric acid; bullock's urine contains much less hippuric acid and amino-acids, whilst allantoin is almost entirely absent. Throughout the first half of pregnancy, the non-protein nitrogen increases in the fœtal-fluids, but the amount of nitrogen per unit of weight of the fœtus decreases regularly. The fœtal fluids contain urea, allantoin, monoamino-acids, creatinine, and creatine together with small amounts of polypeptides, diamino-acids, and contain other nitrogenous compounds (which are absent in adult urine) of undetermined nature. Throughout pregnancy the main variation in the fœtal fluids consists in a decrease in the proportion of urea and a corresponding increase in allantoin and amino-acids. The early allantoic fluid, that is, the urine of the early fœtus, shows as compared with the urine of the adult a low urea content, a high proportion of allantoin and amino-acids, and of undetermined nitrogen. The fœtal metabolism differs from that of the adult in the less complete katabolism of protein, and a greater activity of nuclear metabolism, as indicated by the amount of allantoin. The materials used in the research were obtained from sheep, oxen, and cows. W. D. H.

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* *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 310—314.

The Urine of Women Under Normal Conditions, with Special Reference to the Presence of Creatine. R. A. Krause (*Quart. J. exp. Physiol.*, 1911, **4**, 293—304).—In women creatine is not an abnormal urinary constituent; it is always present immediately after menstruation, and often in the inter-menstrual period; it is present throughout pregnancy, and after parturition is temporarily increased. After menstruation and during pregnancy, ammonia and undetermined nitrogen increase, whilst urea diminishes in the urine. The existence of a correlation between creatinuria and the female sexual cycle also occurs in the bitch. W. D. H.

The Maximum Production of Hippuric Acid in Animals, with Consideration of the Origin of Glycine in the Animal Body. A. I. Ringer (*J. Biol. Chem.*, 1911, **10**, 327—338).—Goats and rabbits have the power of eliminating hippuric acid containing more glycine than is preformed in the proteins they metabolise. As much as 38·4% of the total nitrogen of the goat is eliminated as glycine in hippuric acid. The ingestion of the benzoates increases the nitrogen eliminated, but not the urea; the increase is greater than is accounted for in hippuric acid. It is suggested that the large amount of glycine originates from the "extra destroyed" protein, and not from the protein which would have been metabolised if no benzoate had been given. The diet has no influence on the amount of hippuric acid eliminated. No synthetic production of glycine from glycollic acid could be determined. A suckling calf, fifteen days old, which had never received the glycine complex in its food, was in full possession of the power to synthesise hippuric acid and eliminate it in large quantities. W. D. H.

Are Starch Granules Excreted by the Kidneys? J. Voigt (*Biochem. Zeitsch.*, 1911, **36**, 397—400).—The author fed a normal individual on rice starch contained in a gel made from gelatin, and the urine voided during the twenty-four hours after the starch diet was examined. The various precautions taken to avoid any accidental contamination with starch granules are described in detail. He failed to find any trace of starch in the urine, a result which was not in accordance with those of Rahel Hirsch and of Verźar (this vol., ii, 744). S. B. S.

Pancreatic Diabetes in Cold-blooded Animals. VINCENZO DIAMARE (*Arch. ital. biol.*, 55. Reprint, 11 pp.).—In frogs, removal of the pancreas produces intense glycosuria, which is usually fatal within a fortnight. Mere separation of the pancreas from the intestine, provided its blood vessels are intact, does not lead to this result. Frogs can also be rendered glycosuric by hypodermic injections of dextrose; the pancreas is not thereby altered histologically. Removal of both liver and pancreas does not produce glycosuria, but the animals do not usually survive this severe operation long.

In the dog-fish (*Scyllium catulus*), extirpation of the pancreas produces hyperglycæmia, but no glycosuria. The kidney of this animal is not permeable to dextrose, and none passes into the urine even when large amounts are introduced directly into the circulation.

W. D. H.

Action of Barium and Calcium on the Heart. Extra Systolic Ventricular Tachycardia Experimentally Produced by Stimulation of the Accelerator Nerves. C. J. ROTHBERGER and HEINRICH WINTERBERG (*Pflüger's Archiv*, 1911, **142**, 461—522).—One result of stimulation of the accelerator nerves of the heart in the dog is that extra beats of the ventricles are occasionally seen. After the injection of barium or calcium salts this always occurs, these salts increasing the irritability of the neuro-muscular mechanism of the heart. This occurs more readily on the left than on the right side. Strontium and magnesium salts are inactive in this direction. W. D. H.

The Increase of Cardiac Activity Produced by Calcium. C. J. ROTHBERGER and HEINRICH WINTERBERG (*Pflüger's Archiv*, 1911, **142**, 523—530).—Injection of small quantities of calcium chloride markedly increases the output of the cat's heart as measured by a stromuhr, without increasing its rate; the rate may be slightly lessened. W. D. H.

Action of Barium Ions on the Heart. N. WERSCHININ (*Arch. exp. Path. Pharm.*, 1911, **66**, 191—204).—Barium ions, like substances of the digitalis group, have a systolic and diastolic action on the frog's heart when applied endo- or exo-cardially. There is, however, a quantitative difference due to the small power the barium ions have in penetrating the outer surface of the heart; the inner surface is more permeable. The effect is easily removed by washing out with pure Ringer's solution. W. D. H.

Biology of the Metal Thorium. ARNOLD ROSSEL (*Arch. Sci. Phys. Nat.*, 1911, [iv], **32**, 347—348).—Bolton has observed that if thorium is kept in sterilised water, bacteria, which can be developed by culture on gelatin, are formed on the surface of the metal. This result was not obtained with any of the ordinary metals. The author has completed this observation as follows: Thorium was mixed with sterilised sea-sand in proportions varying from 0 to 50%. These mixtures were then placed in sea-water in separate flasks, and into each there were put twelve to fifteen examples of a simple vertebrate animal (the fish *Lanceolatus*). After five months all the fish were dead in the flask with no thorium, and there was a thick growth of algæ. In the flask containing 50% thorium all the fish were alive, and there were practically no algæ. In the intermediate flasks there was a gradation in the state of the contents. This seems to show that metal thorium is capable of destroying certain injurious germs without endangering life. W. G.

Biological Action of Thorium. Werner von Bolton (*Zeitsch. Elektrochem.*, 1911, **17**, 816—817).—Ordinary distilled water kept in closed sterilised vessels containing metallic thorium for six months contains micro-organisms capable of growing on nutrient media. No signs of life are found after one year. Comparative experiments with other metals showed no signs of life at all.

Amphioxus kept in well aerated sea-water containing sea-sand, or mixtures of sand and thorium, died in five weeks with sand alone; with 10% of thorium, 10% of the fish were alive after three months; with 25% of thorium, 30% of the fish survived this time, whereas with 50% of thorium, 90% of the fish were still alive after seven months. Thorium oxide had a very much weaker effect.

The effect on the growth of plants of mixing from 10 to 50% of thorium with soil is also studied. Seeds germinate some days later, and the young plants die when half developed in the soil containing the metal. T. E.

Investigations with Mesothorium on Animal Germ Cells; an Experimental Proof of the Idioplasmic Nature of the Nuclear Material. Oscar Hertwig (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, **39**, 844—873).—Previous work by the author has shown that exposure of the male and female germ cells to the influence of radium emanations does not kill the cells, but when impregnation occurs, development is slowed, and gives rise to imperfect and distorted larvæ. This effect is more marked the longer the exposure. Histological and other evidence is adduced to show that the emanations produce their effect by injuring the nuclei. The theory that the harm is produced by toxic products liberated by the cleavage of lecithin is discussed, but not agreed with. The present research continues and amplifies these conclusions by further experiments on the generative cells of frogs. The material used was mesothorium, the radioactivity in the specimens used being eight times greater than that of the radium bromide used in the previous experiments. The effects are much more pronounced. Exposure to the rays from fifteen to thirty seconds produces a marked effect, an effect the sensitiveness of which is compared to that of light on a photographic plate. The experiments confirm the doctrine that the nucleus has an idioplasmic nature, that is, contains the hereditary elements; objections to this view are discussed at length. W. D. H.

The Action of Cholesterol and its Derivatives with Lecithin as Syphilitic Antigen and as Hæmolysin with Cobra Venom. Carl H. Browning and John Cruickshank (*J. Path. Bact.*, 1911, **16**, 225—246).—A full account of a research of which a preliminary notice has already appeared (this vol., ii, 1014). W. D. H.

Pharmacological Properties of Certain Acid Oxidation Products of Cholesterol. FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1911, **66**, 221—237).—The acids with formulæ $C_{27}H_{44}O_4$, $C_{27}H_{40}O_5$, and $C_{27}H_{40}O_8$ (compare Windaus, Abstr., 1908, i, 264) are strongly toxic, and are physiologically related to the pharmacological group of the bile acids and saponins. They are absorbed with difficulty, produce local necrosis of tissues, paralysis of skeletal and cardiac muscle, slowing of the heart, and intense hæmolysis. In such properties they also closely resemble certain snake venoms, especially viper-venom. They may perhaps be intermediate products in the formation of bile acids from cholesterol, and formed in small amount may normally be important in the maintenance of muscular tonus.

W. D. H.

[Physiological Action of Iodo-fatty Acid Derivatives.] EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1911, **75**, 38—56).—See this vol., i, 954.

Influence of Chemical Constitution on the Toxicity of Nitriles and Amides. ALEXANDRE DESGREZ (*Compt. rend.*, 1911, **153**, 895—898. Compare this vol., ii, 756).—Comparison of the toxic power of a number of saturated nitriles and the corresponding unsaturated compounds towards rabbits and guinea pigs has shown that double or triple linkings increase the toxicity. A similar generalisation holds good for amides, and hence it is unnecessary to suppose that the great toxicity of unsaturated nitriles, such as the cyanoacetylenes previously studied, is due to fixation of water followed by liberation of hydrogen cyanide. The difference is less marked between saturated and unsaturated compounds in the aromatic series than in the aliphatic. Generally speaking, toxicity increases with the molecular weight, but the aromatic compounds are more poisonous than aliphatic substances of about the same molecular weight.

W. O. W.

The Action of Nucleic Acid on the Fermentative Processes in the Animal Body. M. TSCHERNORUZKI (*Biochem. Zeitsch.*, 1911, **36**, 363—375).—The sodium salt of yeast-nucleic acid (Merck's preparation) was administered in various ways (subcutaneously, *per os*, and intravenously) to a number of puppies from the same litter. One other animal received no treatment, and was kept as a control. The nucleate, even in large doses (1·5 grams to a kilo. of body-weight), exerted no injurious effect. At the end of a given period, after repeated administrations, the animals were killed, and the organs were removed from the body and dried at low temperatures. The amounts of the various ferments in the different organs were then estimated by the usual methods, and the results obtained in the treated animals compared with those from the control animal. The chief changes were observed in the brains, lungs, muscles, and thymus. In the case of the brain, the amylase was found to be 400 times greater than the normal, the diastase 4·4 times greater, and the protease 10 times. In the lungs, the diastase was 250 times greater than normal, and

6·4 times greater in the muscles. The results for other ferments and organs were not sufficiently definite for generalisation.

S. B. S.

Pharmacological Properties of Adaline (α-Bromo-α-ethylbutyrylcarbamide). Eduardo Filippi (*Arch. Farm. sper. Sci.*, 1911, 12. Reprint 10 pp. Compare Impens, *Med. Klin. Woch.*, 1910, No. 47).—Adaline is a sedative producing light, but lasting, sleep; it exerts no cardiac action, and its toxicity (for rabbits) is very small. Pancreatic extract dissolves the substance somewhat readily. The urine of animals (rabbits, dog) to which the substance has been administered contains some of it unaltered, but the urine also yields an *acid*, which forms acicular crystals, m. p. 87—89°, and contains bromine. Ionic bromine appears in the urine only in cases of severe poisoning.

R. V. S.

Pharmacology of the Bronchial Musculature. Hans Januschke and Leo Pollak (*Arch. exp. Path. Pharm.*, 1911, 66, 205—220).—Intravenous injection of adrenaline increases the respiratory excursions of the lungs, especially when muscarine asthma has been induced. The latter is due to cramp of the bronchial muscles, and this is antagonised by adrenaline. Bronchial spasm produced by injection of peptone (but not that produced by β-iminazolylethylamine [4-β-aminoethylglyoxaline] or ergotoxin) is also inhibited by adrenaline.

W. D. H.

Physiological Action of β-Aminoethylindole. Patrick P. Laidlaw (*Bio.-Chem. J.*, 1911, 6, 141—150).—β-Aminoethylindole is formed from tryptophan by bacterial action. It exerts a transient stimulant effect on the central nervous system, and has also a direct stimulant action on plain muscle, especially of the iris, uterus, and arterioles.

W. D. H.

Pharmacology of Veronal. I. Symptoms and Doses. Carl Roemer (*Arch. exp. Path. Pharm.*, 1911, 66, 241—260)—A general account of the effects of veronal in frogs, rabbits, and cats, especially when used in fatal doses. The minimal fatal dose for the frog is 1·5 grams, for the rabbit 0·4 gram, and for the cat 0·3 to 0·35 gram per kilo. of body-weight.

W. D. H.

Pharmacology of Veronal. II. Influence on Temperature, Breathing, and Circulation. Carl Jacobj and Carl Roemer (*Arch. exp. Path. Pharm.*, 1911, 66, 261—295).—Veronal lowers the body-temperature, somewhat slows the rate of breathing while increasing its depth, and lowers blood pressure by dilating peripheral vessels. The effect on the vessels appears to be mainly due to a local action of the drug. Larger doses are needed to affect the isolated frog's heart.

W. D. H.

Pharmacology of Veronal. III. Action of Veronal in Reference to its Specific Paralytic Action on the Vessel Walls. Carl Jacobj (*Arch. exp. Path. Pharm.*, 1911, 66, 296—312). —This is largely a commentary on the preceding papers, written mainly from the therapeutic point of view. The use of the drug is contra-indicated in cases where dilatation of the vessels should be avoided, for instance, in diseases of the kidney associated with venous congestion. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Action of Certain Bacteria on Proteins. FRANCIS A. BAINBRIDGE (*J. Hygiene*, 1911, **11**, 341—355).—When solutions of pure egg-albumin, serum-protein, or alkali-albumin are inoculated with the organisms, *B. coli*, *B. enteritidis*, *B. typhosus*, *B. proteus*, *B. pyocyaneus*, *Staphylococcus p. aureus*, and *Gonococcus*, the bacteria diminish in number when the seeding is large, but multiply to some extent when the seeding is small. The latter effect is probably due to non-protein nitrogenous substances, and not to the fact that bacteria use the protein as food. If any protein is used, it must be the smallest traces. The organisms examined (with the exception of *B. proteus*) do not break down appreciable quantities of egg- and serum-protein, even in the presence of sufficient non-protein nitrogenous food to ensure vigorous growth. W. D. H.

The Decomposing Power of Water Bacteria. WILHELM SPÄT (*Arch. Hygiene*, 1911, **74**, 237—288).—The amount of ammonia formed when 0·2 c.c. of a sample of water is added to 100 c.c. of 2% peptone solution, and incubation allowed to proceed at 37° for twenty-four hours, may serve as a criterion of the purity of the sample employed. The amount of decomposition does not bear any direct relation to the absolute number of bacteria, since those normally present in water are able to ammonify peptone only to a slight extent; this also applies to *Bacterium coli* and to pathogenic organisms generally. Contamination of the water by surface drainage introduces physiologically active soil bacteria, and is reflected in a greatly increased decomposing power of the sample in the majority of the cases investigated. Storage does not affect the decomposing power of the water, so that ice-cooling during transit of the sample is unnecessary. H. B. H.

The Action on Nitrates and Nitrites of Dysentery Organisms. W. J. LOGIE (*J. Hygiene*, 1911, **11**, 361—372. Compare Abstr., 1910, ii, 988).—The organisms examined were killed (1) by temperatures which should not have destroyed the reducing enzyme; (2) by sodium fluoride and four other antiseptics, derivatives of phenol mentioned below, and (3) by acetone. In each case there was total destruction of the reducing power. Filtrates of fluid cultures have also failed to reduce nitrates to nitrites. The reduction cannot, therefore, be due to a soluble extra-cellular enzyme. The high antiseptic value of tetrachloro-*o*-diphenol, tetrabromo-*o*-cresol, *p*-chloro-*m*-cresol, and hexabromodihydroxydiphenylcarbinol is established for dysentery organisms. W. D. H.

Sugar Tests and Pathogenicity in the Differentiation of Streptococci. J. M. BEATTIE and A. G. YATES (*J. Path. Bact.*, 1911, **16**, 247—256).—A full account of a research of which a preliminary notice has already appeared (this vol., ii, 1019). W. D. H.

The Mechanism of Alcoholic Fermentation. A. VON LEBEDEFF (*Ber.*, 1911, **44**, 2932—2942; *Bull. Soc. chim.*, [iv], **9**, 953—957). —A detailed description of the experimental evidence on which is founded the theory of alcoholic fermentation already given (Abstr., 1911, ii, 816). W. J. Y.

Alcoholic Fermentation. HARTWIG FRANZEN and O. STEPPUHN (*Ber.*, 1911, **44**, 2915—2919).—The action of yeast on formic acid was determined by growing pure cultures in sterile beer-wort containing 0·01 molar sodium formate, and estimating the formic acid present at daily intervals. In most cases it was found that considerable quantities of formic acid disappeared. In several cases, however, a formation of this substance occurred during the early stages of the growth, which was followed by a gradual decrease as time went on. It was further found that when no formate was originally present in the wort, formic acid was first formed and then gradually fermented. This formic acid cannot all be derived from the alcoholic fermentation of amino-acids, since the quantity found was greatly in excess of that corresponding with the amyl alcohol and succinic acid produced in the fermentations.

The conclusion is drawn that it is formed as an intermediate product in the alcoholic fermentation of the sugar of the wort, the quantity found representing the balance between the amount formed and that fermented.

These experiments thus lend support to the theory of alcoholic fermentation of Wohl as elaborated by Schade, according to which lactic acid is formed from the sugar, and is then converted into acetaldehyde and formic acid, which react together to form carbon dioxide and alcohol. W. J. Y.

The Formation of Plasma Protein by Yeasts and Moulds. FELIX EHRLICH (*Biochem. Zeitsch.*, 1911, **36**, 477—497).—It has been shown by the author and his co-workers that when yeasts, etc., act on amino-acids, alcohols, such as amyl alcohol, tyrosol, etc., are produced (according to the amino-acid used in the experiment), and that the amount of destruction of the amino-acid is proportional to the amount of alcoholic fermentation. The conclusion is drawn from the results, that the alcohols, such as amyl alcohol or tyrosol, which are derived from the amino-acids are merely waste products, and form no direct part in the protein synthesis of the yeast, which merely uses the ammonia set free. The latter substance acts on the degradation products of the dextrose only, to form the amino-acids which are concerned in the synthesis of the plasma protein. Experiments were therefore carried out to determine whether yeast would grow in the presence of sugar degradation products only, with tyrosine as the source of nitrogen. This substance yields as reaction product either tyrosol or *p*-hydroxyphenyl-lactic acid, according to the mould used in the experiment. Both these substances can be readily isolated, and the ratio between the amounts isolated and the protein nitrogen formed in the yeast growth was estimated. Tartaric, lactic, and formic acids (as sodium salts), glycerol, methyl and ethyl alcohols were the degradation products of sugar employed. In the case of yeast the results were negative, but this was not so in the case of certain "wild" yeasts and moulds which were employed, namely, *Willia anomala*, Hansen, and *Oidium lactis*. The former yielded tyrosol, whereas the latter yielded *p*-hydroxyphenyl-lactic acid. Positive results were obtained with ethyl alcohol and glycerol, and, to a small extent, with methyl alcohol, and the amount of nitrogen in the culture was, in the case of the *Willia anomala*, more or less proportional to the amount of tyrosol recovered. In the case of the *Oidium lactis* positive results were also obtained with sodium lactate. Preliminary experiments carried out in a similar way with pyruvic acid also yielded positive results with *Willia anomala* and a brewer's yeast, although the latter only developed slowly in the artificial culture medium. S. B. S.

The Anti-bactericidal Action of the Bile Salts. S. LYLE CUMMINS (*J. Hygiene*, 1911, 11, 373—380).—Sodium taurocholate and glycocholate possess anti-bactericidal qualities; glycine, taurine, and cholic acid have not. This explains why the addition of bile salts to culture media, such as serum, increases the growth of the typhoid bacillus. The action depends on interference with the complement, and not on inhibition of the action of the amboceptor. The action of bile may explain the survival of the bacilli in typhoid carriers.

W. D. H.

Increasing the Activity of Higher and Lower Plants by Small Amounts of Poisons. EDWIN BROUN FRED (*Centr. Bakt. Par.*, 1911, ii, 185—245).—Ether, carbon disulphide, potassium dichromate, and copper sulphate promote the growth of lower organisms when sufficiently dilute solutions are employed. The organisms included *Azotobacter*, dinitrifying, ammonia, and putrefactive bacteria, and yeasts. In presence of ether, the fixation of nitrogen by *Azotobacter* in mixed cultures is increased; with pure cultures, fixation of nitrogen is increased by ether and carbon disulphide, but not to the same extent as with mixed cultures. The growth of denitrifying organisms is slightly increased by antiseptics.

Application of ether to soil at first retards nitrification; subsequently nitrification is considerably increased. Experiments with plants showed that ether and carbon disulphide increase the growth.

The conclusion is drawn that the beneficial effect of these substances is due to their stimulating action on the plants and on soil organisms.

N. H. J. M.

Action of Ether and Carbon Disulphide on Higher and Lower Plants. ALFRED KOCH (*Centr. Bakt. Par.*, 1911, ii, 31, 175—185).—The results of pot experiments in which buckwheat, followed by mustard, were grown in soil to which ether was applied, and in the same soil without ether, showed that the yield of buckwheat and the nitrogen assimilated were doubled under the influence of ether, whilst the second crop (mustard) was somewhat less than in the check pots.

Small amounts of ether have a retarding action on nitrification, followed by a slight increase. The conclusion is drawn that the increased yields obtained after the application of ether or carbon disulphide cannot be due to increased nitrification or diminished dinitrification, but to stimulation of the higher plants.

The results of fermentation experiments showed that small amounts of ether increase the activity of yeast. Carbon disulphide gave negative results (compare Goemer, *Koch's Jahresber*, 2, 169).

N. H. J. M.

The Wandering of Betaine in Certain Vegetative Processes in Plants. VLADIMIR STANĚK (*Zeitsch. physiol. Chem.*, 1911, 75, 262—271).—The dry residue of young leaves contains more betaine and more total nitrogen than old leaves. In the ripening of plant organs, betaine diffuses simultaneously with other nitrogenous substances. It is probably not a katabolic product, and trimethylamine is never found.

Betaine is formed during germination of the seed, and it is difficult to say whether it originates from reserve materials or in assimilated nitrogenous substances. During sprouting the betaine collects in the leaves, but it plays no part in the action of light on etiolised leaves, nor in the assimilation of carbon. W. D. H.

Enzymic Degradation of Arginine in Plants. ALEXANDER KIESEL (*Zeitsch. physiol. Chem.*, 1911, 75, 169—196).—Arginine may be decomposed by ferments into ornithine and carbamide, or oxidised to give γ-guanidinobutyric acid, or with the loss of carbon dioxide to agmatine, $NH_2·C(NH)·NH·[CH_2]_4·NH_2$. Each of these products may conceivably undergo further decomposition.

An attempt has been made to establish the manner of the decomposition of arginine in plants; it is proved that the change, although not quantitative, consists for the great part in the conversion into ornithine and urea. The formation of neither agmatine nor guanidine could be detected. The absence of guanidine is not due to any possibility of its removal by secondary changes; this point is still being investigated in the case of agmatine. Agmatine could not be obtained on hydrolysis of wheat embryos or by the autolysis of yeast.

The fact that ornithine has not yet been found in plants is not due to its removal by further change, but probably to the inadequate methods of isolation and identification when it is present in an impure condition. The formation of putrescine as a decomposition product of ornithine could not be detected. Plants contain a ferment (urease) which decomposes carbamide as rapidly as it is formed, so that carbamide can only be found in those plants which lack this enzyme. Wheat embryos contain a very active urease. Urease is very specific in its action, and does not act synthetically. E. F. A.

Formation of Anthocyanic Pigments. RAOUL COMBES (*Compt. rend.*, 1911, **153**, 886—889).—A preliminary note recording the isolation from autumnal leaves of *Ampelopsis hederacea* of a pigment crystallising in clusters of purple needles. The substance is very soluble in alcohol, sparingly so in water, ether, and benzene, and forms a green compound with lead acetate. Green leaves of the same plant yielded a substance crystallising in brown needles, and forming a yellow compound with lead acetate. The red colour of the autumn leaves is probably due to the first-mentioned pigment, which is related to the second in the manner suggested in an earlier paper (Abstr., 1909, ii, 426). W. O. W.

Manganese in Digitalis purpurea. JAMES BURMANN (*Bull. Soc. chim.*, 1911, [iv], **9**, 957—959).—*Digitalis ambigua* and *D. lutea* are indigenous to Switzerland, whilst *D. purpurea* can only be grown in gardens and does not reproduce itself. This seems to be due to the fact that the two former do not require manganese, whilst the third species does. Digitalis leaves grown on soil derived from ferruginous grit in Alsace gave 5·08% of ash, containiug 9·02% manganese and 0·80% iron, whilst the grit itself contained 0·43% manganese and 4·82% iron. The presence of manganese in the ash serves to distinguish *D. purpurea* from *D. ambigua* and *D. lutea.* T. A. H.

Green and Yellow Dyes of Florideæ. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1911, **75**, 272. Compare Kylin, this vol., ii, 1024).—Kylin was unable to isolate chlorophyllanic acid and *allo*-chlorophyllanic acid from his material; these substances are best identified by conversion into phyllocyanin and phylloxanthin.

E. F. A.

Hydnocarpus Fats. K. LENDRICH, E. KOCH, and L SCHWARZ (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 441—458. Compare Power and Gornall, Proc., 1904, **20**, 137; Trans., 1904, **85**, 838, 851; Power and Barrowcliff, Trans., 1905, **87**, 884, 896).—Margarine made with a so-called "cardamom oil" from India having caused several cases of illness, the margarine and the "cardamom oil" have been examined chemically and physiologically with the view of identifying the botanical source of the oil and to ascertaining the cause of its toxicity. The oil is probably derived from the seeds of either *Hydnocarpus Wightiana* or *H. venenata,* and owes its physiological action to the presence of chaulmoogric and hydnocarpic acids (compare Litterscheid, *Chem. Zeit.*, 1911, **35**, 9; Reinsch, *Chem. Zeit.*, 1911, **35**, 77; Thoms and Müller, *Zeitsch. Nahr. Genussm.*, 1911, **21**, 226; Plücker, *ibid.*, 1911, **21**, 257).

The "cardamom" oil had D 0·9549—0·9560, m. p. 23·3—23·8°, acid number 9·3—20·5, saponification number 202·6—205·8, iodine number 92·4—96·9, $[\alpha]_D^{20}$ +54·67° in 50% or +55·02° in 10% benzene solution. *Hydnocarpus Wightiana* fat had acid number 12·0, saponification number 203·9, iodine number 100·7, $[\alpha]_D^{20}$ +55·6°. *H. venenata* fat had acid number 44·0, saponification number 202·4, iodine number 97·0, $[\alpha]_D^{20}$ +55·9°. *H. inebrians* fat had saponification number 213·3, iodine number 80·9, $[\alpha]_D^{20}$ +42·3°. *H. anthelmintica* fat had acid number 12·0, saponification number 209·8, iodine number 84·5, $[\alpha]_D^{20}$ +51·5°. *Taraktogenos Kurzii* fat had saponification number 219·7, iodine number 89·1, $[\alpha]_D^{20}$ +47·7° (compare Power and collaborators, *loc. cit.*). The "cardamom" oil furnished chaulmoogric and hydnocarpic acids identical with those isolated by Power, Gornall, and Barrowcliff from the fats of *Taraktogenos Kurzii* and *Hydnocarpus anthelmintica* (Trans., 1904, **85**, 838; 1905, **87**, 884), but, unlike these fats, yielded no palmitic acid, in which respect it resembles the *H. Wightiana* fat examined by Power and Barrowcliff (*loc. cit.*, p. 884). The "cardamom" oil produced nausea and sickness in dogs, as did also the chaulmoogric, hydnocarpic and liquid fatty acids isolated from it. The oxidised or brominated total fatty acids of the oil, however, proved to be physiologically inactive. All the *Hydnocarpus* fats and the *Taraktogenos Kurzii* fats also produced sickness in dogs. The toxic symptoms observed in all cases were vomiting and irritation of the mucous membrane of the stomach, with in some cases clonic convulsions of the whole body. This physiological action appears to be correlated with the presence of an ethylene linking in the optically active acids of this group of fats, since the oxidised or brominated acids are inactive.

Hydnocarpus alpina fat had acid number 5·6, saponification number 209·06, iodine number 84·5, $[\alpha]_D^{20}$ +49·0°, and is probably quite similar to the other fats of this genus examined (compare Grimme, *Chem. Rev. Fett. u. Harz.*, 1911, **18**, Part 7). T. A. H.

Shea Butter. ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1911, [iv], **9**, 959—963. Compare Southcombe, Abstr., 1909, ii, 604).—Shea butter (Fr. karité butter) yields 96% of total fatty acids, m. p. 51°, containing 33% of oleic acid and 67% of saturated acids composed of arachidic, stearic, and palmitic acids. There is no material difference in the yield or characters of the fats derived from sun- or kiln-dried kernels (compare *Bull. Imp. Inst.*, 1908, **6**, 369).

T. A. H.

Experimental Chlorosis of Maize. PIERRE MAZÉ (*Compt. rend.*, 1911, **153**, 902—905).—Maize grown in nutrient solutions free from iron or sulphur develops a very thin, almost transparent parenchyma, and the leaves do not become green. Deprivation of chlorine, magnesium, or silicon does not have this effect. That iron and sulphur are assimilated and fixed by the cells is shown by the fact that leaves etiolated in iron- or sulphur-free solutions are turned green by drops of ammonium sulphate or ferric nitrate respectively, but only in the immediate neighbourhood of the drops. W. O. W.

The Carbohydrates of the Foliage Leaf of the Snowdrop (Galanthus nivalis) and their Bearing on the First Sugar of Photosynthesis. JOHN PARKIN (*Bio.-Chem. J.*, 1911, **6**, 1—47).—The total carbohydrates in the leaf amount to 20—30% of the dry weight. Starch and maltose are absent; sucrose, dextrose, and lævulose are present. The variations described in the relative amount of the three sugars occur in relation to time of day and season of the year, but the main fluctuation is in the sucrose. If the leaves are largely depleted of their sugars by darkness, the hexoses are not increased by exposure to sunlight, the augmentation being almost solely in the sucrose. The last-named sugar is regarded as the first sugar to appear, the others being derived from it by inversion; the lævulose is always in excess of the dextrose, because the latter is more immediately utilised by the leaf. This view that the first sugar to arise in photosynthesis is sucrose was first advanced by Brown and Morris, but raises a difficulty, which is discussed in full, if the current formaldehyde theory is correct. W. D. H.

The Cyanogen Compounds of Tobacco Smoke. JULIUS TÓTH (*Chem. Zeit.*, 1911, **35**, 1262. Compare this vol., ii, 143).—In reply to private enquiries, the author states that having reconsidered the process given for the estimation of cyanogen compounds in tobacco smoke (Abstr., 1910, ii, 443) he comes to the following conclusions: (1) The assumption that the conversion of cyanogen into ferrocyanide by means of potassium hydroxide and ferrous sulphate is a complete one is quite correct. (2) In consequence, it is quite certain that tobacco smoke contains more cyanogen compounds than hitherto supposed. L. DE K.

Effect of Chemical Reagents on the Respiration and Growth of Wheat Seedlings. H. S. REED (*Bied. Zentr.*, 1911, **40**, 716; from *Bot. Gaz.*, 1910, **49**, 81; *Bot. Zentr.*, 1911, 204).—Small amounts of calcium and sodium phosphate increase, whilst potassium salts diminish, respiration; sodium nitrate generally increases respiration, but its effect varies.

Respiration is diminished by inorganic acids, whilst the effect of organic acids is variable. Pyrogallol and tannic acid increase respiration considerably. N. H. J. M.

The Disease Causing Bitterness in Wines in Connexion with the Acrylic Fermentation of Glycerol. E. VOISENET (*Compt. rend.*, 1911, **153**, 898—900. Compare Abstr., 1909, ii, 738, 909).—The presence of acraldehyde in wines which have developed bitterness has been demonstrated previously, and its formation attributed to the dehydration of glycerol by a specific ferment. The bitter taste of such wines appears to be due to condensation products of acraldehyde. These substances are of a resinous character, and are produced when a dilute solution of acraldehyde is warmed with potassium hydrogen tartrate; the ferment producing the aldehyde is also capable of effecting resinification. These observations render unnecessary Wortmann's theory that bitterness is caused by the action of oxydases on tannin and colouring matters.

W. O. W.

Effect of Soluble Salts on the Adsorption of Phosphates by Soils. Harrison E. Patten (*J. Physical Chem.*, 1911, 15, 639—658. Compare Abstr., 1908, ii, 126).—The rate of extraction of phosphoric acid from superphosphated soils is increased by the presence of dissolved salts in the percolating water. The soils examined were quartz flour (83% silt, 17% clay), "Podunk" fine sandy loam, and "Elkton" clay. To each kilo. of soil was added 0·61 gram of calcium monophosphate, $CaH_4(PO_4)_2$, this being equivalent to 350 lb. per acre (depth not stated).

In the case of quartz flour the amount of phosphoric acid dissolved out by distilled water was large at first (93 parts per million), but rapidly diminished to a constant low value of about 6 parts. On substituting 0·05% sodium nitrate solution for the distilled water without interrupting the continuity of the percolation, the concentration of phosphoric acid immediately rose to 44 parts per million and remained constant. The rates of percolation of distilled water and sodium nitrate solution were approximately equal.

With the "Podunk" loam and "Elkton" clay such marked increases in the phosphoric acid concentration were not generally observed, since the rate of percolation of the salt solution was almost invariably higher than that of distilled water. Potassium carbonate solution produced a deflocculation of the loam, which became clogged and stopped the passage of the liquid.

The author draws the conclusion that higher concentrations of phosphate may be obtained when weak solutions of the salts ordinarily used as soil amendments (potassium chloride, sulphate nitrate and carbonate, and sodium nitrate) are passed through the soil than can be obtained by the use of distilled water alone. The effect is mainly produced by the mutual interference of the adsorptions of added salt and superphosphate by the soil particles.

R. J. C.

[Amount of Nitrogen as Ammonia and as Nitrates in Rain-water Collected at Uithuizermeeden.] J. Hudig and H. Welt (*Verslag. landbouwkund. onderzoek. Rijkslandbouwproefstat*, 1911, No. 10, 188—118).—Nitrogen in the forms of ammonia and nitrates was estimated in the rain-water collected at Uithuizermeeden, Groningen, from September, 1901, to August, 1910. The average amounts of rain and of nitrogen in the two forms were as follows:

	Nitrogen per million		Nitrogen per acre (lb.)		
Rainfall, inches.	as ammonia.	as nitrates.	as ammonia.	as nitrates.	Total.
26·20	0·724	0·237	4·301	1·407	5·708

N. H. J. M.

Analytical Chemistry.

The Sodium Phosphate Standards of Acidity. EDMUND B. R. PRIDEAUX (*Bio.-Chem. J.*, 1911, 6, 122—126).—The H˙ ion concentrations obtained by mixing sodium hydroxide and phosphoric acid in varying proportions are represented graphically. Most of the results have already been published (compare Trans., 1911, 99, 1224). The effect of errors in determining the concentrations of the reagents, and the influence of carbon dioxide have been measured. The reproducibility of the monohydrogen phosphate (Na_2HPO_4) standard from crystalline salt was found to be accurate, provided the salt is recrystallised under definite conditions. G. S.

Rapid Electroanalysis with Stirring by Bubbling a Gas Through the Solution. FRANZ FISCHER, CARL THIELE, and EMIL STECHER (*Zeitsch. Elektrochem.*, 1911, 17, 905—906).—Instead of using a mechanical stirrer, the same object is advantageously effected by bubbling hydrogen through the electrolyte. The electrolytic cell consists essentially of a wide cylindrical glass tube, in which the cathode is supported at some distance from the bottom. The hydrogen is introduced by means of a long glass tube ending in a bulb provided with a number of small holes; the tube is so placed that the bulb is near the bottom of the cell. The cell is loosely closed by means of a funnel placed in the neck. As the electrolysis is conveniently carried out at 60°, the vapour from the solution condenses on the inner wall of the cell, and washes down any electrolyte which may be carried up on the walls by the stream of gas. It is shown that the method gives accurate results. G. S.

Rapid Electroanalysis under Reduced Pressure. FRANZ FISCHER, CARL THIELE, and EMIL STECHER (*Zeitsch. Elektrochem.*, 1911, 17, 906—908. Compare preceding abstract).—The stirring of the electrolyte may also be effected by carrying out the experiment under reduced pressure, the volume of the gas given off during the electrolysis being thereby greatly increased. The apparatus, which is described and figured, is similar to that discussed in the former paper, except that the cell is closed by a rubber cork through which the connexions pass, as well as a glass tube connected to an ordinary filter pump. G. S.

Physico-chemical Volumetric Analysis. III. Precipitation Followed by Alteration in Potential. PAUL DUTOIT and GOTTFRIED VON WEISSE (*J. Chim. phys.*, 1911, 9, 578—607. Compare Abstr., 1910, ii, 342).—The contact potential of a metallic electrode undergoes a sudden change at the moment the last traces of the most electropositive metal in the solution are removed by precipitation. In order to render this phenomenon available in volumetric analysis, a very small current is passed through the solution, using platinum electrodes, and the potential between the rapidly rotating cathode and an auxiliary calomel electrode is continuously noted during the introduction of the precipitant from a burette.

When the burette readings are plotted against the voltage, the end point of the titration corresponds with a double inflexion in the curve. This inflexion point, even if well marked, may differ from the theoretical end point by as much as 10%.

Foreign substances in some cases, not only affect the absolute value of the voltages obtained, but may also displace the inflexion point. If the polarisation current is long continued, or of too high a density, an amount of metal is apparently electro-deposited out of all proportion to the electro-chemical equivalent. The errors are such as would arise through the absorption of the solution by the precipitate.

Precipitates arranged in order of increasing absorbing power are silver bromide, copper sulphide, zinc sulphide, silver chloride, silver iodide, silver ferrocyanide, copper ferrocyanide. The precipitation of the last-mentioned substance is the most susceptible to experimental conditions.

In each case the most favourable concentrations of solution and precipitant, and the minimum current density with which a good inflexion point is obtainable, must be predetermined, and the titration must be carried out as quickly as possible. R. J. C.

Physico-chemical Volumetric Analysis. V. Estimation and Separation of the Halogens. PAUL DUTOIT and GOTTFRIED VON WEISSE (*J. Chim. phys.*, 1911, **9**, 630—640. Compare Behrend, Abstr., 1893, ii, 387).—The use of the electrometric method instead of an indicator in the estimation of halogens has the advantage that very dilute solutions can be titrated accurately. Using silver nitrate as precipitant, 15 mg. of chloride can be estimated in a litre, and with bromide and iodide yet smaller quantities.

The alteration of potential on removing silver iodide is greater than occurs with the more soluble bromide or chloride. Iodide may be estimated in presence of an enormous excess of chloride or bromide provided that the solution is vigorously stirred to prevent premature precipitation of chloride or bromide. Chloride cannot be distinguished from bromide, as there is no marked potential change at the end of the precipitation of the bromide.

The method has been applied to the estimation of traces of chloride in potassium chlorate, and the estimation of iodine in urine. In the latter case very small quantities of iodide cannot be detected, being masked by the colloidal substances present. R. J. C.

Use of Carbon Disulphide for the Direct Estimation of [Free] Sulphur in Minerals. NATHAN LÉVY-W. (*Bull. Assoc. chim. Sucr. dist.*, 1911, **29**, [iv], 218—220).—The author uses carbon disulphide for the assay of sulphur deposits containing mineral matter (sand). The difficulty is, however, to evaporate the solvent completely without violent spirting towards the end of the operation; spontaneous evaporation is very tedious, and has other drawbacks. The author now operates as follows: The carbon disulphide containing the sulphur from one gram of the sample is filtered into a long tube containing a little water, and, of course, collects at the bottom. The tube is now placed, in an inclined position, in a water-bath, and the carbon disulphide is completely distilled off. The vapours pass through a long, doubly bent tube, which dips into a vessel containing water, where the carbon disulphide is recovered. A small bulb with which the tube is furnished prevents regurgitation.

The sulphur is now transferred to a weighed filter, which is then washed, dried, and re-weighed. L. DE K.

The Volumetric Estimation of Sulphur in Iron and Steel. T. GIFFORD ELLIOT (*J. Iron Steel Inst.*, 1911, 83, 412—420).—Many specimens of iron and steel do not evolve the whole of their sulphur when treated with concentrated hydrochloric acid after annealing in hydrogen. Better results are obtained by the following method, which is applicable to all varieties of iron and steel, except those containing titanium. Five grams of the drillings are mixed with 0·25 gram of dry, powdered potassium ferrocyanide, wrapped in a 11 cm. filter paper if a grey iron, or in two such papers if a white iron or steel, and annealed for twenty minutes at 750—850° in a porcelain crucible. The mass, enclosed in the charred paper, is broken up and introduced into the evolution flask, covered with 50 c.c. of hydrochloric acid, D 1·19, and heated. The absorbing solution is made by dissolving 20 grams of cadmium chloride in water with a few drops of hydrochloric acid, adding ammonia until the precipitate completely dissolves, and acidifying with acetic acid, then adding a further 20 c.c. of acetic acid, and making up to 2 litres. Sixty c.c. of this solution are used for each estimation. When no more gas is evolved, an excess of iodine solution is added to the absorbing vessel, followed by hydrochloric acid until the cadmium sulphide is dissolved. The iodine is then titrated with sodium thiosulphate. C. H. D.

Detection of Nitrogen in Organic Substances. A. HALENKE and M. KLING (*Chem. Zeit.*, 1911, 35, 1180).—The substance to be tested is mixed with potassium hydroxide and placed in a test-tube. To the mouth of the tube is attached a Fresenius filter-tube, the bulb of which is filled with glass beads, placed over a pad of glass wool. A strip of moist red litmus paper is suspended from a hook in the upper part of the filter-tube, and the whole is connected with a vacuum pump. The test-tube is then heated slowly until the potassium hydroxide fuses. Any potassium hydroxide sprayed up is retained by the beads; therefore, if the evolved vapours turn the paper blue, ammonia must be present. L. DE K.

Decomposition of Uric Acid by means of Dilute Sodium Hydroxide Solutions. CLARENCE E. MAY (*J. Amer. Chem. Soc.*, 1911, 33, 1783—1787).—In view of Steel's modification of Folin's method for the estimation of ammonia in urine (this vol., ii, 68), in which a large excess of sodium chloride is employed in order to prevent the decomposition of carbamide and uric acid, a study has been made of the action of dilute sodium hydroxide on solutions of uric acid. The results show that a small, but constant, quantity of ammonia is produced, but that the presence of sodium chloride has very little effect. It is possible that other nitrogenous constituents of urine may be protected by sodium chloride, but the use of such large amounts as recommended by Steel (*loc. cit.*) does not seem to be justified.

E. G.

Estimation of Nitric Acid in Milk by means of Diphenylamine-Sulphuric Acid. J. TILLMANS and A. SPLITTGERBER (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 401—404).—In estimating nitric acid (nitrates) in milk by the process described previously (this vol., ii, 151), it is recommended that the milk be treated with its own volume of a mixture consisting of equal parts of 5% mercuric chloride solution and 2% hydrochloric acid. After filtration, 1 c.c. of the serum is mixed with 4 c.c. of the diphenylamine-sulphuric acid reagent, and the coloration produced compared with those obtained with solutions containing known quantities of nitric acid. As milk contains certain substances which prevent the full development of the coloration due to the nitric acid present, these standard solutions should be prepared by placing quantities of 0·45, 0·85, 1·2, 1·5, and 2·0 c.c. of a 0·01871% potassium nitrate solution in separate 100 c.c. flasks, adding 2 c.c. of saturated sodium chloride to each, and diluting to 100 c.c.; these solutions will then contain quantities corresponding with 1, 2, 3, 4, and 5 mg. of nitric acid (N_2O_5) respectively per litre of milk.

W. P. S.

The Accuracy of Nitrate Estimations. SIEGFRIED SEYDEL and L. WICHERS (*Zeitsch. angew. Chem.*, 1911, **43**, 2046—2054).—A criticism of the various methods for the estimation of nitric nitrogen now in vogue, particularly in their application to soil analysis.

Reduction in alkaline solution by means of zinc and iron gives good results if the amount of nitric nitrogen actually present does not exceed 30 mg. Densch's objection that ammonia is split off from nitrogenous organic matters present, and so affects the result, was found to be groundless. With great care, and making a check experiment side by side, Schloesing's process (measuring as nitric oxide) also gives good results in presence of organic matters (urea excepted). The results obtained by the "nitron" process are a little too low, but this method may be used even in the presence of urea and asparagine. Ulsch's process (reduction with iron in acid solution) is, according to Densch, liable to give excessive results in the presence of much organic matters; the author's confirm that statement.

Densch's indirect process cannot be recommended. L. DE K.

Analysis of Nitrates. ANTONIO QUARTAROLI (*Gazzetta*, 1911, **41**, ii, 53—59).—See this vol., ii, 1085.

Estimation of Phosphorus in Pig Iron and Cast Iron without Separation of Silicon. EUGEN R. E. MÜLLER (*Chem. Zeit.*, 1911, **35**, 1201—1202).—Four grams of the sample are placed in an Erlenmeyer flask, and boiled with 60 c.c. of nitric acid (D 1·2). When all dissolved, the liquid (which should not occupy less than 30 c.c.) is transferred to a 100 c.c. flask and made up to the mark. Twenty-five c.c. are then taken and boiled in a beaker with 2 c.c. of potassium permanganate (40 grams per litre) for two minutes, and, after cooling the beaker for ten minutes in a stream of cold water, the excess of the permanganate, together with any manganese peroxide formed, is decomposed by careful addition of sodium peroxide in small portions at the time.

The clear solution is now again heated to boiling, and then mixed with its own volume of molybdenum solution. A pure yellow precipitate is obtained, fit for direct weighing, after drying at 150°. Contrivances for cooling and filtering are described and figured in the original.

L. DE K.

Mechanicalising Analysis as an Aid to Accuracy and Speed. CHARLES H. RIDSDALE and N. D. RIDSDALE (*J. Iron Steel Inst.*, 1911, **83**, 332—374).—The rapid methods of estimating phosphorus and manganese in steel, iron, or slag have been modified by employing the oxidising and other reagents in the form of compressed solid tablets or "analoids," thus saving weighing and ensuring the uniformity of the conditions of oxidation and precipitation. C. H. D.

Estimation of Hypophosphites. ERWIN RUPP and KROLL (*Arch. Pharm.*, 1911, **249**, 493—497).—Rupp and Finck have described (Abstr., 1903, ii, 330) a process for the estimation of hypophosphites, which depends on their oxidation to phosphites and eventually to phosphates by the action of iodine. The first step in this reaction is slow, and the whole estimation occupies about twenty hours.

The authors now find that the oxidation may be accomplished much more speedily by using the standard bromine solution devised by Beckurts and Koppeschaar, which is formed by adding dilute sulphuric acid to a solution of potassium bromate and bromide of known strength. The amount of bromine solution used must be about twice that required to oxidise the hypophosphite to phosphate, and the reaction requires one hour for completion. The excess of bromine is determined by adding standard potassium iodide solution, and titrating the liberated iodine with standard thiosulphate.

T. A. H.

Method for the Detection and Estimation of Arsenic in Organic Compounds. GIUSEPPE BRESSANIN (*Boll. Chim. Farm.*, 1911, **50**, 727—730).—The arsenic in sodium cacodylate, sodium methylarsinate (arrhenal), sodium *p*-aminophenylarsinate (atoxyl), and dihydroxydiaminoarsenobenzene dihydrochloride (salvarsan) can be estimated by the author's method for arsenic in inorganic compounds, which depends on the insolubility of arsenic iodide in sulphuric acid or hydrochloric acid. In these cases, however, the substances must first be heated for about two hours with concentrated sulphuric acid in order to remove the arsenic from organic combination.

An account is also given of the behaviour of "salvarsan" towards a number of reagents. R. V. S.

Detection, Separation, and Estimation of Arsenic and Antimony. GIUSEPPE BRESSANIN (*Boll. Chim. Farm.*, 1911, **50**, 691—694).—The method of estimating arsenic given by Blattner and Brasseur (Abstr., 1904, ii, 291) gives good results when applied to sulphuric acid of 45° Baumé, and also with mixtures of sulphuric and hydrochloric acids, provided that the amount of the latter is not more than one-third of that of the former; if this proportion is exceeded, loss occurs owing to partial solution of the arsenic tri-iodide by the hydrochloric acid, washing off the precipitate with the latter acid causing further loss. Instead of 5 c.c. of 30% potassium iodide solution, only 2·5 c.c., or even less, should be used for the precipitation. Hence for estimating arsenic in hydrochloric acid, 1 part of this is mixed with 2 parts of pure sulphuric acid of 45° Baumé. With sulphuric acid free from tin and lead, the precipitation is effected without addition of hydrochloric acid, whilst with commercial sulphuric acid (45° Baumé) one-third of its volume of hydrochloric acid is added; if nitrous compounds are present, these must be decomposed by adding a sufficient quantity of urea crystals. For washing the precipitate, a mixture of 2 parts of sulphuric acid (45° Baumé) and 1 part of hydrochloric acid is employed. The above procedure gives results which are much nearer to the truth than Blattner and Brasseur's method, and are not vitiated if the sulphuric acid has a density as high as 50° Baumé.

The estimation of antimony in sulphuric acid can be carried out in a similar manner, but the antimony iodide is soluble in hydrochloric acid. The most suitable density of the sulphuric acid for the complete precipitation of antimony iodide is 50° Baumé, and the precipitate is freed from the iodine which separates by three washings with sulphuric acid (50°Bé.). The antimony iodide is dissolved in 10% Rochelle salt solution prior to titration.

Arsenic and antimony may be estimated simultaneously by dissolving the substance in, and making up to a known volume with, sulphuric acid of 50° Baumé. In an aliquot part of the solution, the two iodides are precipitated, and the precipitate dissolved and titrated with iodine solution as above. Another aliquot portion is mixed with one-third of its volume of hydrochloric acid, this solution yielding only arsenic tri-iodide on precipitation.

The same method is applicable to the estimation of arsenic or antimony in arsenates or antimonates. T. H. P.

Spectrophotometric Estimation of Xenon. Constancy of the Xenon-Argon and Xenon-Krypton Ratios in Natural Gaseous Mixtures. CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1911, **153**, 740—743. Compare Abstr., 1909, ii, 363; 1910, ii, 136; this vol., ii, 392, 439, 808).—The amount of xenon in mixtures of the gas with argon can be determined by a method identical in principle with that already described for krypton, the line λ 4671·42 being employed for the purpose. In this way it is possible to estimate 0·0005 cm. of the gas in 4 c.c. of a mixture. The ratio of xenon to krypton was found to be fairly constant in seventeen natural gases from thermal springs and in one from a volcano. Taking this in conjunction with the results already recorded for argon, it is shown that the constant proportions in which these gases occur resemble that of the components of a definite compound, a conclusion in harmony with the nebular hypothesis of the origin of the solar system. W. O. W.

Potassium: its Titrimetric Estimation in Small Amounts. LEON T. BOWSER (*J. Amer. Chem. Soc.*, 1911, **33**, 1752—1757).—The author has recently described a method for the detection of small quantities of potassium as the cobaltinitrite (this vol., ii, 1031). A process for the estimation of potassium has now been devised in which the metal is precipitated as dipotassium sodium cobaltinitrite, and the latter is collected and titrated with dilute potassium permanganate.

The solution in which potassium is to be estimated is evaporated nearly to dryness, and, when cold, is treated with 2·5 c.c. of sodium cobaltinitrite solution and 10 c.c. of a mixture of equal volumes of glacial acetic acid and 95% alcohol. The precipitate is collected on an asbestos filter, and washed with 20% acetic acid. The asbestos pad and precipitate are transferred to a beaker, and an excess of 0·005*N*-potassium permanganate solution is added from a burette. The mixture is boiled, acidified with sulphuric acid, and, after continuing the boiling for a moment, the excess of potassium permanganate is titrated back by means of 0·005*N*-oxalic acid. After making the necessary deduction indicated by a blank experiment, the number of c.c. of permanganate used when multiplied by 0·00004282 gives grams of K_2O, or by 0·00003554 gives grams of K.

The estimation is not affected by the presence of moderate quantities of sodium, calcium, or magnesium. The method is recommended as being simple and trustworthy for small amounts of potassium (about 50 parts per million), but cannot be used for the estimation of large quantities. E. G.

Estimation of Potassium in Urine. HARRY H. GREEN (*Bio.-Chem. J.*, 1911, **6**, 69—75).—The volumetric method of estimating .potassium as the cobaltinitrite, described by Drushel (Abstr., 1908, ii, 66), has been modified for the estimation of potassium in urine (compare also Drushel, Abstr., 1909, ii, 94). Twenty-five c.c. of urine are evaporated to dryness and ignited; the ash is moistened with nitric acid, and again ignited until free from organic matter and ammonium salts. It is then dissolved in water containing a little hydrochloric acid, neutralised with sodium hydroxide containing a little sodium acetate, the solution evaporated to 5—10 c.c., 1 c.c. of glacial acetic acid and 10 c.c. of the cobalt reagent, prepared as described by Adie and Wood (Trans., 1900, **77**, 1076) added, and then evaporated to crystallisation. The cobaltinitrite, $K_2NaCo(NO_2)_6,H_2O$, is freed from the brown matrix by treatment with about 50 c.c. of 10% acetic acid, washed with dilute acetic acid, dried, and then oxidised with potassium permanganate as described by Drushel (*loc. cit.*). Potassium can be estimated with equal accuracy as chloride, sulphate, nitrate, and acetate by this method, provided no free acid other than acetic is present during evaporation with the sodium cobaltinitrite reagent.

Salts of other metals have very little effect on the accuracy of the method. G. S.

The Electrolysis of Sodium Chloride with the Mercury Cathode. CHARLES A. PETERS (*Amer. J. Sci.*, 1911, [iv], 32, 365—385).—The author shows that in the electrolysis of sodium chloride in the Hildebrand apparatus for the electrolytic determination of anions (Abstr., 1907, ii, 574), the anode being of silver or of silver-plated platinum, and the cathode of mercury, silver is always transferred from the anode to the cathode. Under certain conditions, which must be determined by experiment for each apparatus and strength of solution used, the amount of silver thus transferred may be neglected for analytical purposes.

It is recommended that the anode covered with silver chloride be first heated below the fusing point of the chloride to decompose all the silver oxide, and that then the heat be increased so as to fuse the chloride, five or ten minutes at 400—500° being sufficient.

Sodium hydroxide is always present in the inner cell after the beginning of the electrolysis, a low current with corresponding increase in time of electrolysis producing more alkali than a high current and short time of electrolysis.

The best method for removing the fused chloride from an anode is to heat it for about twenty minutes at 500° in a current of hydrogen. T. S. P.

Use of the Edison Accumulator in Electro-analysis. OTTO BRUNCK (*Zeitsch. angew. Chem.*, 1911, 24, 1993—1997).—The author uses the Edison accumulator for the estimation and separation of metals which can be deposited from sulphuric acid solution with less than 1·36 volts; such metals are silver, mercury, palladium, platinum, rhodium, iridium, etc. The accumulator is connectly directly with the electrolytic apparatus, a rheostat in the circuit not being necessary (compare Foerster., Abstr., 1906, ii, 805), unless the current density exceeds 0·2 ampere per sq. dcm. A gauze cathode of 50 sq. cm. area is used.

Silver is best deposited from a sulphuric acid solution at a temperature of 80—90°, at which temperature the solubility of silver sulphate is sufficient to retain it in solution; any nitric acid present is previously expelled by evaporation with sulphuric acid. The results are quantitative in the presence of copper, arsenic, antimony, or lead. In the presence of antimony some tartaric acid must be added before the electrolysis is proceeded with, and it is not necessary to filter off any lead sulphate before depositing the silver.

The author has also used a Leclanché dry cell in place of the Edison accumulator, care being taken not to let the current density exceed 0·2 ampere per sq. dcm.; it could be used for two years without renewal, since during any electrolysis with graded potential the current gradually falls to zero. T. S. P.

Estimation of Calcium in the Presence of Magnesium and Phosphates. Estimation of Calcium in Urine. FRANCIS H. MCCRUDDEN (*J. Biol. Chem.*, 1911, 10, 187—199).—The method described previously by the author (Abstr., 1910, ii, 243) may be rendered more rapid as follows: the neutralised urine is acidified with hydrochloric acid, oxalic acid and sodium acetate are added, and the mixture is shaken for ten minutes or placed aside overnight. The calcium oxalate is then collected, washed, and ignited, or titrated with permanganate solution. W. P. S.

Physico-chemical Volumetric Analysis. IV. Estimation of Copper and Silver. PAUL DUTOIT and GOTTFRIED VON WEISSE (*J. Chim. phys.*, 1911, **9**, 608—629).—The precipitation of copper or silver by a soluble sulphide gives a more sharply defined potential change than when other precipitants, such as sodium hydroxide, potassium ferrocyanide, or sodium thiosulphate, are employed.

Potassium sulphide containing excess of potassium hydroxide, prepared in the laboratory, was used in most of the experiments, but was found to undergo slow conversion into thiosulphate with loss of precipitating power. Crystalline sodium sulphide was afterwards found to be more stable.

The precipitation of silver by alkali sulphide proceeds normally, but copper always requires 2—3% more sulphide than theory demands. The sulphide must, therefore, be standardised against solutions of the same metal at about the same concentration as it is to be employed with. The potassium sulphide must not be weaker than $N/50$, since more dilute solutions undergo decomposition to thiosulphate at a rapid rate. Hence in the titration of small quantities of copper or silver a microburette is used.

The solutions are neutralised and acidified with acetic acid before titration. Mineral acids in the solution give rise to serious errors. The current density of the polarising current must not exceed 10^{-4} amperes. With very dilute solutions, a correction may be applied for electro-deposited metal.

Copper and silver may be titrated accurately in solutions containing 20 mg. per litre, and even traces of the order 0·1 mg. per litre can be estimated, although no visible precipitate or coloration is present.

The estimation of copper is unaffected by relatively enormous proportions of neutral salts, so that the method may be found applicable in the examination of preserved foods. R. J. C.

Quantitative Estimation of Copper in Commercial Sulphate by means of Alkali Hypophosphites. ALFREDO CAVAZZI (*Gazzetta*, 1911, **41**, ii, 374—378).—The author calls attention to his publications on this subject (*Rend. R. Accad. Sci. Bologna*, 1900—1902). The solution of 2 grams of copper sulphate in about 25 c.c. of water is acidified with 12 drops of 5% sulphuric acid, 10 c.c of 40% sodium hypophosphite are added, and the mixture is heated on the water-bath for twenty minutes. A 10% solution of sodium carbonate is then added, until no more carbon dioxide is evolved, care being taken that the hot liquid remains clear, and the heating is continued for ten minutes. While still hot, the liquid is again neutralised, the copper is collected, and weighed after ignition in a current of hydrogen. The process is rapid and accurate, and is only interfered with (and then but slightly) by the presence of arsenic, which is infrequent.

R. V. S.

Precipitation of Zinc, Manganese, Cobalt, Nickel, Copper, and Cadmium from their Ammoniacal Solution with Sodium Carbonate and Phenyltrimethylammonium Carbonate. ERIK SCHIRM (*Chem. Zeit.*, 1911, **35**, 1177, 1193—1194).—The solutions of the above metals to which has been added excess of ammonia (or, in some cases, ammonium carbonate) do not deposit the hydroxides (or carbonates) completely on boiling, but do so when a solution of sodium carbonate is added. On account of its complete volatility on ignition, phenyltrimethylammonium carbonate may be used in preference to the sodium salt.

The carbonates separated are completely free from sulphates. The sulphuric acid can, therefore, be entirely recovered from the filtrate. When dealing with manganese salts, a little hydrazine hydrochloride should be added to prevent turbidity when adding ammonia.

L. DE K.

Iron Metabolism. I. The Estimation of Small Amounts of Iron. FRIEDRICH JAHN (*Zeitsch. physiol. Chem.*, 1911, **75**, 308—338).—The author has endeavoured to find a suitable method of estimating small quantities of iron in organic substances. Neumann's so-called wet incineration method (Abstr., 1903, ii, 243; 1905, ii, 68) should be used, any iron in the acids used being estimated and allowed for. He finds that estimation by means of potassium permanganate, hydriodic acid, or stannous chloride does not lead to exact results, and prefers the method of reducing the iron by means of a slight excess of standard titanous chloride solution, and subsequent determination of this excess by means of standard iron solution, potassium thiocyanate being used as indicator.

The effect of varying the volume of solution, and the amounts of potassium thiocyanate, iron, sulphuric and hydrochloric acids has been studied.

H. W.

Quantitative Separation of Iron and Manganese. JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1911, [iv], **9**, 880—881).—The process depends on the fact that from a solution containing ferric and manganous salts, pyridine precipitates the iron as ferric hydroxide, leaving manganese dissolved. By this means, 0·0005 gram of manganese may be estimated in presence of 1 gram of iron.

In the case of manganese minerals, 1 gram is dissolved in warm hydrochloric acid, and the silica rendered insoluble by evaporation to dryness twice. The filtrate is nearly neutralised by sodium hydroxide, diluted to 100 c.c., pyridine added in excess, and the whole boiled during ten minutes. If manganese is present in large amount, the precipitated ferric hydroxide should be collected, washed, and re-treated.

In minerals containing metals of Group I, the latter should be removed by hydrogen sulphide, and the filtrate boiled and oxidised before adding the pyridine. Zinc is also precipitated by pyridine, although incompletely, and if this metal is present, the ferric hydroxide should be redissolved and reprecipitated by ammonia in presence of ammonium chloride. T. A. H.

Estimation of Nickel [in German Silver]. FRED IBBOTSON (*Chem. News*, 1911, **104**, 224)—0·5 Gram of the alloy is dissolved in 10 c.c. of nitric acid (D 1·2), and diluted to 400 c.c. 0·3 Gram of tartaric acid is added, and then ammonia in excess. After heating to 50°, an excess of solution of dimethylglyoxime is added.

The precipitate containing the nickel is collected on a filter, and washed with a hot solution of ammonium nitrate until the washings are colourless. As it always retains copper, it must be re-dissolved in hot dilute nitric acid (1 : 1) and re-precipitated as directed.

The precipitate whilst still wet is enclosed completely in two filters, transferred to a crucible, and heated cautiously at the mouth of the muffle or over a small flame until the outer papers are thoroughly charred. The temperature is then gradually increased to a bright red heat. L. DE K.

Precipitation of Nickel Compounds and Preparation of Spongy Nickel. WILSON H. LOW (*Analyst*, 1911, **36**, 539—540).—Nickel is not precipitated completely from its solutions either by ammonia or hydrazine on boiling, but if a solution of a nickel salt containing ammonium chloride is boiled with excess of hydrazine, the nickel is completely precipitated. When the precipitate is ignited in a current of hydrogen, spongy nickel is obtained, which, of course, is free from fixed alkali. L. DE K.

Estimation of Tungsten in Wolframite in the Presence of Molybdenite. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 2142—2143).—One gram of the finely powdered ore is gently roasted in a platinum crucible until the odour of sulphur dioxide has gone off. The mass is then extracted three or four times with warm dilute ammonia, which dissolves the molybdenum trioxide formed. The filter, after being washed with solution of ammonium nitrate, is replaced in the crucible, and the whole is again ignited; the residue is then submitted to the ordinary fusion with sodium hydroxide, which should be done in a nickel crucible. L. DE K.

Use of Hæmatin in Qualitative Analysis and in the Volumetric Estimation of Bismuth. ETTORE VASSALLO (*Gazzetta*, 1911, **41**, ii, 204—212. Compare Moffatt and Spiro, Abstr., 1907, ii, 653).—Solutions of hæmatin, obtained by extracting logwood with alcohol, give colorations with most metals and metalloids, but only a few of these persist in faintly acid solutions. Bismuth gives an intense violet coloration, even in fairly acid solution; arsenic, antimony, and tin also give a violet coloration. Solutions of molybdenum give an intense blue coloration, which is stable towards fairly concentrated acid. Schemes of analysis are given for recognising tin and bismuth in alloys and mixtures by the use of hæmatin test-papers. The sensibility, in presence of suitable concentrations of acid, exceeds one part in fifty thousand.

The volumetric estimation of bismuth is effected by adding a standard solution of disodium phosphate to the bismuth solution, and testing the liquid for bismuth by means of the logwood test-papers at intervals. The results quoted show a positive error ranging from 0·9 to 0·1%, the variation being associated with different conditions of dilution and temperature. The best results are obtained when the solution is kept cold and also neutral. R. V. S.

Colorimetric Detection of Alcohol in Presence of Acetone. Colour Reactions of Certain Groups of Organic Compounds in Presence of Mineral Acids and Potassium Dichromate. HENRI AGULHON (*Bull. Soc. chim.*, 1911, [iv], **9**, 881—885. Compare Nicloux, Abstr., 1898, ii, 543).—The author finds that the reduction of potassium dichromate in presence of sulphuric acid by organic substances becomes more specific in character when nitric acid, phosphoric acid, or potassium hydrogen sulphate is substituted for sulphuric acid.

Potassium dichromate, 0·5 gram, dissolved in 100 c.c. of nitric acid (36°Bé) gives at once a bluish-violet coloration in the cold with substances containing a $-CHO$ or $-OH$ group, and with certain other compounds, such as ether, ethyl acetate, formic acid, and unsaturated fatty acids. The aliphatic ketones give a coloration, but as a rule only after some hours. Acetophenone and the quinones behave like acetone, but *cyclo*hexanone and its homologues give the coloration immediately. Certain phenols give the same colour reactions as they do with potassium dichromate alone. The reaction is less specific on warming, and under these conditions a green coloration is developed.

With phosphoric acid (60°Bé) the range of applicability is the same as with nitric acid, but the reagent is then less delicate.

With potassium hydrogen sulphate in water no coloration is produced in the cold, but a green tint is produced on warming. This is given by alcohols, aldehydes, *cyclo*hexanone, and its homologues, ether, ethyl acetate, etc., but not with aliphatic ketones, acetophenone, or unsaturated fatty acids. In this form the reagent may be used to distinguish ricinoleic acid, which contains an $-OH$ group, from oleic and other like acids which do not. T. A. H.

Analysis of Lactic Acid. A. A. BESSON (*Chem. Zeit.*, 1911, **35**, 1209—1210).—It is shown that the total acidity of lactic acid containing lactic anhydride may be accurately estimated by neutralising the free acid, adding an excess of *N*/1-alkali, leaving the mixture at the ordinary temperature for ten minutes, neutralising the excess of alkali, adding a slight excess of *N*/1-acid, boiling, and titrating the acid. W. P. S.

Estimation of β-Hydroxybutyric Acid in Urine. ROBERT A. COOKE and E. E. GORSLIN (*J. Biol. Chem.*, 1911, **10**, 291—294).—Results of experiments carried out by the authors show that the method described by Shaffer (Abstr., 1908, ii, 992) is trustworthy, provided that the urine is treated with an excess of basic lead acetate and ammonia before the distillation part of the process is commenced. This treatment is especially necessary in the case of urines containing large quantities of dextrose. The excess of lead should be removed before the distillation, in order to prevent "bumping."

W. P. S.

Polarimetric Method for the Estimation of Malic Acid and its Application to Cane and Maple Products (Sugars).

Peter A. Yoder (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 329—350).—The method depends on the increase in the rotatory power of malic acid when the acid is treated with uranium salts. A solution of malic acid containing 1 gram per 100 c.c., when converted into the uranium compound by the addition of uranium acetate in the proportion of at least 1·25 atoms of uranium to 1 molecule of malic acid, has a rotatory power of −29·7° Ventzke at 20°C. for white light, or −28·9° for sodium light. The presence of organic acids, with the exception of optically active hydroxydicarboxylic acids, does not, within certain limits, have any great influence, and sugars, such as sucrose, dextrose, and lævulose, have no effect; mineral acids, however, seriously affect the rotatory power of the malic acid–uranium compound. The rotatory power decreases by 0·03° Ventzke for each 1° rise in temperature. In the case of a 1% solution of tartaric acid, the uranium compound has a rotatory value of +26·1° Ventzke. For the estimation of malic acid in sugar-cane and maple products, 50 grams of the syrup, or a mixture of 33·33 grams of sugar with 16·66 c.c. of water, are neutralised, diluted with water to a weight of 65 grams, and treated with 10 c.c. of lead acetate solution, D 1·25. After the addition of 150 c.c. of 95% alcohol, the mixture is set aside for three hours, then filtered, and the precipitate washed with 75% alcohol. The precipitate is treated with hydrogen sulphide, the lead sulphide is removed by filtration, the filtrate is evaporated to a volume of about 30 c.c., and then diluted to 50 c.c. The rotatory power of 20 c.c. of this solution is determined before and after the addition of uranium acetate, the mixture being neutralised in the latter case, and allowance made for the alteration in volume. The percentage quantity of malic acid, x, present, is calculated from the formulæ: for white light,

$$x = \frac{(P_1 - P) \times [1 + 0{\cdot}001(t - 20)]}{-29{\cdot}6 \times 0{\cdot}5L},$$

or, for sodium light, $x = \frac{(P_1 - P) \times [1 + 0{\cdot}001(t - 20)]}{-28{\cdot}8 \times 0{\cdot}5L}$, where P and P_1 are the rotatory powers before and after treatment with uranium acetate respectively, and L the length of the polarimeter tube in dcm. Barium acetate may be employed in place of lead acetate in the process. Sugar-cane syrup was found to contain 0·02% of malic acid, and maple syrup from 0·26 to 0·51%. If the total acidity, n, expressed in c.c. of $N/1$-alkali be known, malic and tartaric acids may be estimated in mixtures of the same; let the increase in the rotatory power at 27·5° in a 20 cm. tube be m° Ventzke, x the percentage of malic acid, and y

the percentage of tartaric acid, then $n=\frac{x}{0{\cdot}06703}+\frac{y}{0{\cdot}07503}$ and $m=25{\cdot}16y-29{\cdot}27x$, or, $x=0{\cdot}03287n-0{\cdot}01741m$ and $y=0{\cdot}03824n+0{\cdot}01949m$.

W. P. S.

Detection of Benzoic Acid in Foods. EDUARD POLENSKE (*Arbeit. Kaiserl. Gesundheitsamte*, 1911, **38**, 149—154; Reprint).—I. *Estimation of the Total Benzoic Acid in Cranberries, etc.*—The cranberries are heated with alcohol for one hour, the mixture is then treated with an excess of sodium hydroxide, filtered, the filtrate is evaporated to remove alcohol, and the residue is extracted with a mixture of ether and light petroleum, after being acidified with sulphuric acid. The ethereal extract is then shaken with dilute sodium hydroxide solution, and the alkaline aqueous extract containing the benzoic acid is treated with potassium permanganate as described by Heide and Jakob (Abstr., 1910, ii, 359). The benzoic acid is next extracted with ether, the ethereal solution is evaporated, the residue is re-dissolved in a small volume of ether, transferred to a test-tube, and after the ether has been evaporated, the benzoic acid is sublimed on to the upper sides of the tube. The lower portion of the tube is then cut off, and the benzoic acid is dissolved in alcohol and titrated. The amount of benzoic acid found in various samples of cranberries varied from 0·089 to 0·206% (compare Abstr., 1910, ii, 440).

II. *Detection of Benzoic Acid in Wine.*—The method of separating benzoic acid from wine described by Heide and Jakob (*loc. cit.*) was found to be trustworthy; it is recommended, however, that the wine be filtered, after being evaporated in the presence of alkali and then acidified, previous to the extraction with ether. The benzoic acid obtained may be identified by fusing it for not longer than three minutes with potassium hydroxide, and testing the resulting salicylic acid with ferric chloride.

W. P. S.

Detection of Benzoic Acid in Margarine, Butter, and Other Fats. WALTHER FRIESE (*Pharm. Zentr.-h.*, 1911, **52**, 1201—1203).—One hundred grams of the fat are mixed thoroughly with 25 c.c. of a 20% sodium carbonate solution, and the mixture is melted on a water-bath. After cooling, the aqueous layer is separated, treated with an excess of 10% barium chloride solution, the barium precipitate is collected on a filter, and the excess of barium is removed from the filtrate by the addition of sulphuric acid. The benzoic acid is then extracted from the acid solution with ether, and the residue obtained on evaporating the ethereal solution is tested for benzoic acid, preferably by heating the residue with alcohol and sulphuric acid; any benzoic acid present is thus converted into ethyl benzoate, which may be identified by its odour.

W. P. S.

Kobert's Reagent as a Test for Salicylic Acid. JOHN McCRAE (*Analyst*, 1911, **36**, 540—541).—Kobert's morphine reagent (sulphuric acid containing one drop of formaldehyde solution per c.c.) gives a characteristic rose colour with salicylic acid or salicylates. The reaction is most clearly seen when about 1/50 mg. is dissolved in two drops of sulphuric acid and a drop of the reagent then added. The test also works with *o*-acetoxybenzoic acid (aspirin) and salol.

Salicin gives a red colour with sulphuric acid alone, but if to the solution is added a drop of the reagent in such a way that mixing does not occur, a much deeper and richer red is developed.

Kobert's reagent also gives characteristic colorations with the following substances: Phenol, reddish-violet; catechol, violet (redder than the colour obtained with morphine); resorcinol, deep orange-brown; quinol, dirty greenish-brown; pyrogallol, brown; α-naphthol, dirty green; β-naphthol, dirty brown; cinnamic acid, brown; mandelic acid, yellow. L. DE K.

The Purification and Analytical Control of Potassium Ferrocyanide. KARL SCHRODER (*Zeitsch. anorg. Chem.*, 1911, **72**, 89—99. Compare Müller and Diefenthäler, Abstr., 1910, ii, 910).—Potassium ferrocyanide has the composition $K_4Fe(CN)_6,3H_2O$ even when crystallised from boiling solution, but in drying it is necessary to expose as small a surface as possible, or oxidation and loss of water take place.

Iron is best estimated in potassium ferricyanide by heating with concentrated sulphuric acid, finally raising the temperature to the boiling-point of the acid, dissolving in water and hydrochloric acid, and precipitating with cupferron (ammonium nitrosophenylhydroxylamine), igniting in a quartz crucible. The precipitate is free from alkali.

For the standardisation of permanganate solutions, the solution of potassium ferrocyanide (2 grams) is added to 100 c.c. of a cold saturated solution of mercuric chloride, and the precipitate obtained is then dissolved in 200 c.c. of the same solution, acidified with hydrochloric acid, and heated to boiling. After cooling, 30 c.c. of a solution prepared from 100 grams of manganous sulphate, 200 c.c. of concentrated sulphuric acid, and 200 c.c. of phosphoric acid, D 1·7, to the litre, are added. The values obtained on titrating with permanganate are slightly high, averaging 100·12%. C. H. D.

Apparatus for the Estimation of Amino-groups. DAVID KLEIN (*J. Biol. Chem.*, 1911, **10**, 287—289).—An apparatus is described for use in the estimation of aliphatic amino-groups by the process proposed by van Slyke (this vol., ii, 944). W. P. S.

Estimation of Nicotine in Tobacco Extracts. W. KOENIG (*Chem. Zeit.*, 1911, **35**, 1047—1048).—A reply to Tóth (this vol., ii, 943), who complains that the solutions of nicotine in toluene obtained in the author's extraction process cannot be examined polarimetrically on account of their dark colour. The author states he has never experienced any trouble in that respect with the various polariscopes.

Xylene is also a very good solvent for nicotine. The specific rotation of nicotine in a dilute xylene solution is +173°. Other

objections to the process are also overruled, but it must be understood that the method applies to extracts only and not to tobaccos.
L. DE K.

Estimation of Codeine in Opium. ALBERT E. ANDREWS (*Analyst*, 1911, **36**, 489—490).—In the process described, the opium is extracted thoroughly with cold water, and the solution is treated with lead acetate to remove colouring matters, etc., and narcotine. Sodium salicylate is then added in order to precipitate thebaine and any remaining resinous substances, and the filtered liquid is concentrated and shaken with ether to remove substances which are soluble in this solvent. The morphine is then "fixed" by the addition of a large excess of sodium hydroxide, and the codeine is extracted with ether. The ethereal solution of the alkaloid is evaporated at a low temperature, the residue is dried under reduced pressure, and weighed. The dry alkaloid may also be titrated with $N/10$-acid, using litmus as the indicator. W. P. S.

A Reaction of Sparteine. ARMAND JORRISEN (*J. Pharm. Chim.*, 1911, [vii], **4**, 251—252).—A reaction which distinguishes sparteine from other alkaloids consists in adding a small quantity of sulphur to an ethereal solution of the alkaloid, and treating the mixture with hydrogen sulphide. A bright red, bulky, precipitate in formed, which disappears on the addition of water. The precipitate is readily distinguished from those given by coniine and atropine under similar conditions; the former yields an orange-coloured precipitate and the latter a yellow precipitate. W. P. S.

A Modification of Nakajama's Reaction for Bile Pigment in Urine. A. A. VON MASLOFF (*Zeitsch. physiol. Chem.*, 1911, **74**. 297—298).—The reaction is intensified by the addition of a few drops of hydrogen peroxide. W. D. H.

Estimations of Globulin by means of Ammonium Sulphate, and the Preparation of Pure Globulins. HUGO WIENER (*Zeitsch. physiol. Chem.*, 1911, **74**, 29—66).—The usual methods of fractionating serum proteins by ammonium sulphate are regarded as valueless, and give the amount of globulin too high. If the total protein is increased, the rise appears to fall on the globulin for this reason; hence clinical investigations of this nature need entire revision. The error is greatly minimised by diluting the serum first. W. D. H.

Effect of Heat on the Peroxydase in Cow's Milk. J. J. VAN ECK (*Chem. Weekblad*, 1911, **8**, 691—702; *Zeitsch. Nahr. Genussm*, 1911, **22**, 393—400).—The author describes an apparatus adapted to determining the diminution in the proportion of active peroxydase in milk caused by heating at different temperatures.
A. J. W.